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Enhanced Infrared Properties of Regioregular Poly(3-alkylthiophenes)

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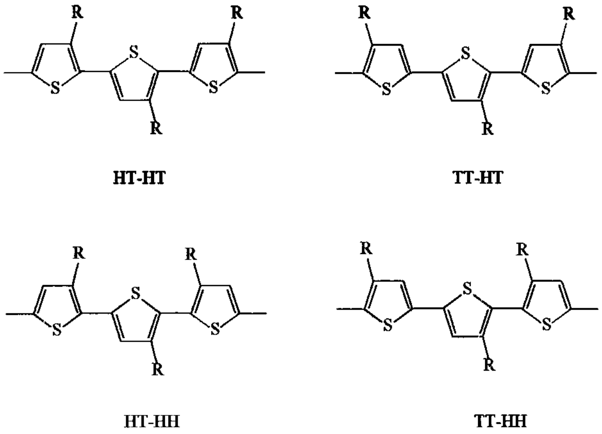
ABSTRACT: Regiorandom and regioregular head to tail coupled poly(3-butylthiophenes), poly(3-octylthiophenes) and poly(3-dodecylthiophenes) have been synthesized by direct oxidation of 3-*n*-alkylthiophenes using $FeCl_3$ as oxidant and by regiospecific dehalogenation of 2-bromo-3-*n*-alkylthiophenes. NMR characterizations indicated 70% of head to tail couplings in the polymers synthesized by $FeCl_3$ route, and more than 99% for regioselective polymerizations. The results of both the solution and the solid state UV−vis spectroscopic studies showed that all the regioregular poly(3-alkylthiophenes) had a lower $\pi-\pi^*$ transition energy, characteristic of a longer conjugation length. A series of visible−near-IR spectra of chloroform solution of $FeCl_3$-doped regioregular P3ATs is reported and shows an increase of the maximum absorption energy of doped P3ATs as a function of alkyl side chain; i.e., longer conjugation lengths are observed in the P3AT possessing the longer alkyl side chain. Moreover, the effect of solvent on electronic spectra is dramatic. The spectrum in a polar solvent, nitrobenzene, is significantly shifted toward low energy compared with spectra measured in relatively non polar solvent, such as dichloromethane, chloroform or toluene. Even after complete removal of the solvent, the more expended coil conformation persists in the cast film since infrared reflectance feature is more metal like. This study allows us to generalize the concept of secondary dopant to poly(3-alkylthiophene)/$FeCl_3$/nitrobenzene systems. Finally, reflectance spectra of regiorandom and regioregular P3ATs are compared. They are the largest values ever published for P3ATs and are comparable to highly conductive polyaniline or polypyrrole reflectances.

Introduction

Since the discovery of insoluble polythiophene and the determination of its electroconductivity in 1980,[1] many studies have been completed to improve the synthetic route and observe the chemical and physical properties of this conjugated polymer. A milestone step in the development of polythiophene occurred in 1985,[2,3] when poly(3-alkylthiophene) (P3AT) was achieved by introducing an alkyl group into the β-position of the thiophene ring. Among the many conjugated polymers, poly(3-alkylthiophenes) have been found to be an unusual class of polymers with good solubility, processability, environmental stability, electroconductivity, and other interesting properties.[4] Three general synthetic methods for polymer synthesis were developed. These included electrochemical polymerization,[5,6] oxidative polymerization of 3-alkylthiophene using an oxidant such as $FeCl_3$,[7,8] and polymerization by catalyzed dedihalogenation of 2,5-dihalo-3-alkylthiophene.[2] For P3ATs, the 3-alkyl substituent in the thiophene ring can be incorporated into a polymer chain with two different regioregularities: head to tail (HT) and head to head (HH). Furthermore this results in four triad regioisomers in the polymer chain: HT−HT, HT−HH, TT−HT, and TT−HH triads (Scheme 1). Due to the random coupling at the 2,5 position on the thiophene ring, the standard synthetic routes for PATs generate a large number of defects and materials with poor electronic properties. An important challenge was the development of a method leading to regioregular P3ATs.

Two authors have recently developed new synthetic routes that allow for complete regiochemical control. For the first time, regiochemically well-defined poly(3-alkylthiophenes) that contain almost exclusively head to tail couplings have been produced.[9,10] These types of structurally homogeneous HT arrangements were found to improve the electronic and optical properties of materials.

Scheme 1



Herein we report the detailed results of the regiorandom and regiospecific syntheses of P3ATs and their characterizations, their solution and solid state electronic spectra in the neutral and doped state, and, finally, their reflectance studies in the infrared range.

The effect of alkyl side chain length has been extensively studied on neutral P3ATs in term of fusibility, thermochromism, X-ray conformation, and electronic band gap.[11,12] In the doped state, various studies report stability data as a function of alkyl side chain length.[13,14] Herein we describe electronic conformation variations for poly(3-butylthiophene), poly(3-octylthiophene), and poly(3-dodecylthiophene), insisting on the important role of solvent/polymer interactions on the doped polymer conformation. Recently, the concept of secondary doping for polyaniline/CSA/*m*-cresol was introduced by Mc Diarmid.[15] Secondary doping is very similar in many respect to primary doping. The treatment of a polymer, already doped by a primary dopant, with an apparently

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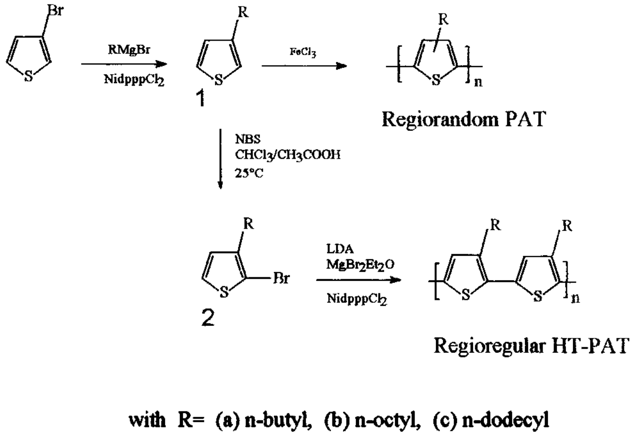
inert substance (secondary dopant) may increase the conductivity of the polymer by several orders of magnitude with concomitant changes in electronic spectra and frequently degree of crystallinity. It differs from primary doping in that the changes, depending on the primary/secondary dopant combination employed, may frequently persist, possibly to a reduced extent, upon the removal of the secondary dopant. Herein, we describe effect of solvent on vis–near-IR spectra of doped solutions of P3ATs, and link it to reflectance measurements of films cast from these solutions. This study allows us to generalize the concept of secondary dopant to the poly(3-alkylthiophenes)/FeCl$_3$/nitrobenzene system. Finally, reflectance spectra of regiorandom and regioregular P3ATs are described, showing, as expected, an important increase of the reflectance for very well-defined regioregular P3ATs with long alkyl side chains.

Experimental Section

The basic reactions used for the synthesis of the regiorandom and regioregular poly(3-alkylthiophenes) are shown in Scheme 2.

Scheme 2



Preparation of 3-*n*-alkylthiophenes. 1a-1b-1c. All 3-*n*-alkylthiophenes were prepared by the literature procedure of Kumada[16] by coupling the Grignard reagent of 1-bromoalkane with 3-bromothiophene in dry ether using [1,3-bis(diphenylphosphino)propane]nickel (II) chloride (Ni(dppp)Cl$_2$) as catalyst. The products were prepurified through a silica gel column using heptane as eluent and finally purified by fractional distillation under reduced pressure. The purity was checked by HPLC, and the structure was characterized by ^{1}H NMR and GC-MS.

3-*n*-Butylthiophene, 1a. After purification (50% yield) a colorless liquid was obtained. Bp: 65 °C/15 mbar. ^{1}H NMR (CDCl$_3$): δ 7.25 (d, 1H), 6.96 (m, 2H), 2.65 (t, 2H), 1.65 (m, 2H), 1.42 (m, 2H), 0.96 (t, 3H). Purity was found to be 100% by HPLC.

3-*n*-Octylthiophene, 1b. After purification (60% yield), a colorless liquid was obtained. Bp: 70 °C/0.8 mbar. ^{1}H NMR (CDCl$_3$): δ 7.25 (d, 1H), 6.94 (m, 2H), 2.64 (t, 2H), 1.62 (m, 2H), 1.3 (m, 10H), 0.92 (t, 3H). Purity was found to be 100% by HPLC.

3-*n*-Dodecylthiophene, 1c. After purification (80% yield) a colorless liquid was obtained. Bp: 110 °C/0.6 mbar. ^{1}H NMR (CDCl$_3$): 7.25 (d, 1H), 6.94 (m, 2H), 2.66 (t, 2H), 1.58 (m, 2H), 1.2 (m, 18H), 0.8 (t, 3H). Purity was found to be 100% by HPLC.

Preparation of 2-Bromo-3-*n*-alkylthiophenes. 2a–c. We first attempted to prepare 2-bromo-3-*n*-alkylthiophenes by the procedure of Gronowitz,[17] but the bromination was not regioselective. For example, bromination of 3-*n*-octylthiophene yielded a mixture of 3-*n*-octylthiophene (11%), 2-bromo-3-*n*-octylthiophene (74%), 5-bromo-3-*n*-octylthiophene (5%), and 2,5-dibromo-3-*n*-octylthiophene (10%). In fact, it was very difficult to extract 2-bromo-3-*n*-octylthiophene with good purity and yield. So, regioselective bromination of all 3-*n*-alkylthiophenes was performed using *N*-bromosuccinimide in CHCl$_3$/AcOH 1/1. This procedure gives almost no 5-bromo-3-*n*-alkylthiophene, and therefore purification is greatly simplified. Purity was checked by HPLC, and the structure was characterized by ^{1}H NMR and GC/MS.

Monobromination of 3-Butylthiophene, 2a. First, 4.92 g (27.6 mmol) of *N*-bromosuccinimide was gradually added to 3.66 g (26 mmol) of 3-butylthiophene in 50 mL of CHCl$_3$/AcOH 1/1. After complete addition the mixture was stirred for an half an hour at room temperature and then poured into 250 mL of distilled water. The organic phase was neutralized twice with KOH 10%, washed with distilled water, and dried over magnesium sulfate and the solvent removed by rotary evaporation.

The crude product contained 0.5% of 3-*n*-butylthiophene, 98% of 2-bromo-3-*n*-butylthiophene, and 1% of 2,5-dibromo-3-*n*-butylthiophene (determined by HPLC). The mixture was twice distilled to afford 4.45 g (80% yield) of colorless 2-bromo-3-*n*-butylthiophene. Bp: 40 °C/0.4 mbar. ^{1}H NMR (CDCl$_3$): δ 7.2 (d, 1H), 6.8 (d, 1H), 2.6 (t, 2H), 1.65 (m, 2H), 1.42 (m, 2H), 0.96 (t, 3H). Purity was determined to be 100% by HPLC.

Monobromination of 3-Octylthiophene, 2b. Compound **2b** was prepared in an identical fashion as **2a**. The crude product was obtained from a reaction starting with 4 g (20.4 mmol) of **1b**. After complete reaction the mixture contained 0.5% of 3-*n*-octylthiophene, 90% of 2-bromo-3-*n*-octylthiophene, 0.3% of 5-bromo-3-*n*-octylthiophene, and 9.2% of 2,5-dibromo-3-*n*-octylthiophene (determined by HPLC). The mixture was twice distilled to afford 4.75 g (85% yield) of colorless 2-bromo-3-*n*-octylthiophene. Bp: 82 °C/0.35 mbar. ^{1}H NMR (CDCl$_3$): δ 7.19 (d, 1H), 6.8 (d, 1H), 2.59 (t, 2H), 1.6 (m, 2H), 1.3 (m, 10H), 0.9 (t, 3H). Purity was determined to be 99.85% by HPLC. The 5-bromo-3-*n*-butylthiophene (0.15%) was not observed in the ^{1}H NMR but was clearly identified by GC/MS.

Monobromination of 3-Dodecylthiophene, 2c. Compound **2c** was prepared as an identical fashion as **2a** except for purification. The crude product was obtained from a reaction starting with 4 g (15.9 mmol) of **1c**. After complete reaction, the mixture contained 0.5% 3-*n*-dodecylthiophene, 95% 2-bromo-3-*n*-dodecylthiophene 0.5% 5-bromo-3-*n*-dodecylthiophene, and 4% 2,5-dibromo-3-*n*-dodecylthiophene (determined by HPLC). The mixture was twice purified by chromatography using heptane as eluent to afford 4.26 g (81% yield) of colorless 2-bromo-3-*n*-dodecylthiophene. ^{1}H NMR (CDCl$_3$): δ 7.19 (d, 1H), 6.8 (d, 1H), 2.6 (t, 2H), 1.58 (m, 2H), 1.21 (m, 18H), 0.79 (t, 3H). Purity was determined to be 99.75% by HPLC. The 5-bromo-3-*n*-butylthiophene (0.25%) was not observed in the ^{1}H NMR but was clearly identified by GC-MS.

General Synthesis for Regiorandom Poly(3-*n*-alkylthiophenes). A simple and inexpensive method to produce P3AT is by direct oxidation of 3-*n*-alkylthiophenes using FeCl$_3$ as the oxidant/catalyst according to Sugimoto et al.[7]

A suspension of dry FeCl$_3$ (0.1 mmol) in 500 mL of dry distilled CHCl$_3$ was stirred for approximately 15 min. A dark green solution with some residual FeCl$_3$ was obtained. To this solution, 3-alkylthiophene (0.025 mmol) dissolved in 150 mL of dry distilled CHCl$_3$ was added dropwise over a period of 30 min. The mixture turned black immediately. The reaction mixture was stirred overnight at room temperature. The reaction was then stopped at this point by addition of methanol. The mixture was filtered and carefully washed with methanol and water. The solid was then dissolved in THF, precipitated again using methanol, and dried under vacuum.

Regiorandom Poly(3-*n*-Butylthiophene), RPBT. Yield: 65%. $M_n = 13\,000$; $M_w = 40\,000$; IP = 3. ^{1}H NMR (CDCl$_3$): δ 7 (1H), 2.8 (1.45H), 2.6 (0.55H), 1.7–1.45 (4H), 0.95 (3H); Anal. Calcd: C, 69.6; H, 7.25; S, 23.2; Fe, 0. Found: C, 69.4; H, 7.24; S, 23.4; Fe, 0.01.

Regiorandom Poly(3-*n*-Octylthiophene), RPOT. Yield: 60%. $M_n = 16\,100$; $M_w = 57\,000$; IP = 3.5. ^{1}H NMR (CDCl$_3$): δ 7 (1H), 2.8 (1.4H), 2.6 (0.6H), 1.6–1.25 (12H), 0.87

(3H). Anal. Calcd: C, 74.2; H, 9.3; S, 16.5; Fe, 0. Found: C, 74; H, 9.2; S, 16.3; Fe, 0.019.

Regiorandom Poly(3-*n*-dodecylthiophene), RPDDT. Yield: 70%. $M_n = 9400$; $M_w = 29\,500$; IP = 3.1. ^{1}H NMR ($CDCl_3$): δ 7 (1H), 2.8 (1.5H), 2.6 (0.5H), 1.7−1.45 (20H), 0.95 (3H). Anal. Calcd: C, 76.8; H, 10.4; S, 12.8; Fe, 0. Found: C, 76.5; H, 10.5; S, 12.7; Fe, 0.05.

General Synthesis for Regioregular Poly(3-alkylthiophenes). All regioregular poly(3-alkylthiophenes) were prepared according to Mc Cullough et al.[18] All operations were carried out under inert atmosphere conditions using pure nitrogen and solvents dried and distilled according to well-established procedures.[19]

To the mixture of dry diisopropylamine (1.8 mL, 12.7 mmol) in 65 mL of THF was added 5.08 mL (12.7 mmol) of 2.5 M *n*-butyllithium at room temperature. The mixture was then cooled to −40 °C and stirred for 40 min. The *n*-butyllithium reacted with diisopropylamine to produce LDA. The mixture was then cooled to −80 °C and 12.7 mmol of 2-bromo-3-alkylthiophene was added. The mixture, stirred at −40 °C for 15 min, turned from pale yellow to pink. The mixture was then cooled to −60 °C, (12.7 mmol) $MgBr_2Et_2O$ was added, and the reaction was stirred for 20 min. At these temperatures, $MgBr_2Et_2O$ was not soluble. The reaction was then allowed to slowly warm to 0 °C. At that time, all of the $MgBr_2Et_2O$ was soluble and had reacted, and the solution was clear and yellow.

At 0 °C, 0.5 mol % of Ni(dppp)Cl_2 was added. The mixture was allowed to warm to room temperature overnight. The solution gradually turned to red whereas viscosity increased. The polymer was then precipitated with ethanol containing a small portion of concentrated HCl. The resulting red precipitate was then filtered, washed with methanol, water, and methanol again, and dried under vacuum. The polymer was then dissolved in THF and precipitated again to remove oligomers and impurities.

Regioregular Poly(3-*n*-butylthiophene), HTPBT. Yield: 75%. $M_n = 3600$; $M_w = 4600$; IP = 1.3. ^{1}H NMR ($CDCl_3$): δ 6.99 (1H), 2.8 (2H), 1.6−1.28 (4H), 0.87 (3H). Anal. Calcd: C, 69.6; H, 7.25; S, 23.2. Found: C, 69.3; H, 7.1; S, 23.5.

Regioregular Poly(3-*n*-octylthiophene), HTPOT. Yield: 45%. $M_n = 19\,400$; $M_w = 49\,000$; IP = 2.5. ^{1}H NMR ($CDCl_3$): δ 6.99 (1H), 2.8 (2H), 1.6−1.2 (12H), 0.87 (3H). Anal. Calcd: C, 74.2; H, 9.3; S, 16.5. Found: C, 74.1; H, 9.2; S, 16.4.

Regioregular Poly(3-*n*-dodecylthiophene), HTPDDT. Yield: 70%. $M_n = 12\,000$; $M_w = 25\,000$; IP = 3.1. ^{1}H NMR ($CDCl_3$): δ 6.99 (1H), 2.8 (2H), 1.7−1.4 (20H), 0.95 (3H). Anal. Calcd: C, 76.8; H, 10.4; S, 12.8. Found: C, 76.7; H, 10.5; S, 12.6.

Film Formation and Doping. High quality films of PATs in the neutral form were cast from chloroform solution using spin coating.

Doped solutions were obtained by addition of $FeCl_3$ in solution in nitromethane to the polymer in solution in different solvents (toluene, xylene, dichloromethane, nitrobenzene). Vis−near-IR spectra were recorded from diluted solution. Films were slowly cast from concentrated suspensions of doped polymer.

Instrumentation. Proton NMR spectra were recorded at 200 MHz on a Bruker AC2000, in $CDCl_3$ at room temperature. Proton chemical shifts (δ) are reported in ppm down field from tetramethylsilane (TMS). HPLC was performed using Merck RP 18 endcapped column, at 25 °C. Compounds were eluted with acetonitrile/methanol 90/10 and detected by a UV spectrophotodetector at 254 nm. GC−MS analyses were performed on a Varian 3400 coupled with a TSQ Finnigan MAT. Molecular weight distribution curves of polymers were determined by Gel Permeation Chromatography (GPC) using 10^5, 10^4, and 10^3 Å μ-Styragel columns at 35 °C. Polymers were eluted with tetrahydrofuran and detected using a refractive detector (Waters, Model R4000). Polystyrene standards of molecular weight ranging from 233 000 to 750 were used for calibrating GPC columns for hydrodynamic volume vs elution volume. Elemental analysis were performed by standard methods.

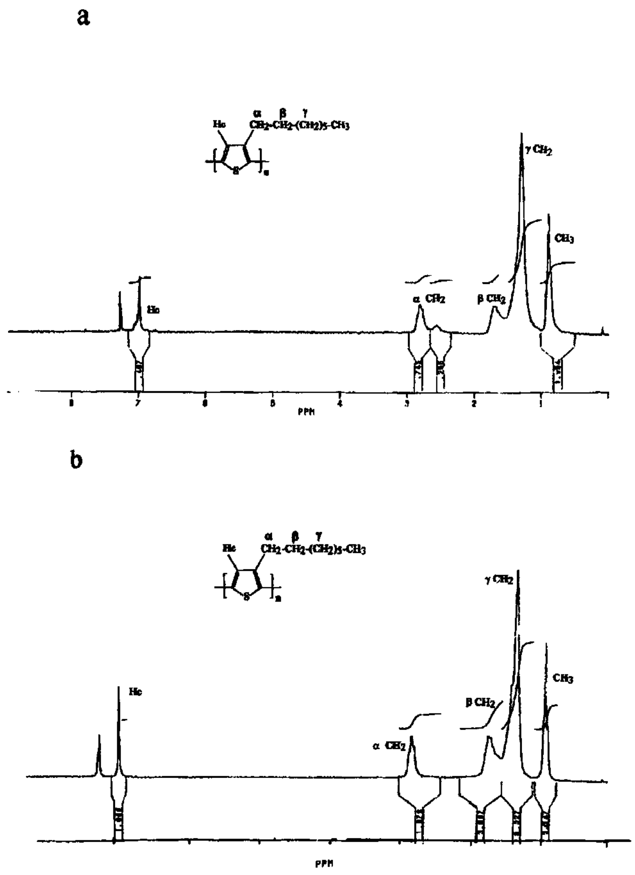


Figure 1. 200-MHz ^{1}H NMR spectrum at 25 °C in chloroform-*d*: (a) a regiorandom poly(3-octylthiophene); (b) a regioregular poly(3-octylthiophene).

Reflectance and transmittance measurements were performed using a Shimadzu UV−vis 1205 sperctrophotometer or a Bruker IFS88 spectrometer. This last one was equipped with a variety of light sources, beamsplitters, and detectors for two of the IR portions and the visible region: mid-IR (6000−550 cm^{-1}), near-IR (10000−1800 cm^{-1}), and the visible region (25000−9000 cm^{-1}). In the mid-IR a KBr beamsplitter divided the light and a DTGS detector measured the signal. In the near-IR a CaF2 beamsplitter and an InSb detector were used. In the visible region a quartz beamsplitter and a Si diode detector were used. The tungsten light source covered the range from the visible to the near-IR whereas the Globar source covered the mid-IR range. The overlap between spectral regions obtained with different instruments was very good. For the absolute values of reflectance, a gold mirror was used as a reference for the IR and an aluminum mirror for the visible range.

Film thicknesses were determined using a Dektak ST surface profiler.

Cyclic voltametry was performed on thin films cast from $CHCl_3$ solutions, immersed in 0.1 M $BuNPF_6$ in CH_3CN. The reference electrode was SCE and the scan rate was 50 mV/s. It was then possible to measure the change in UV−vis absorption of thin films cast onto an indium−tin oxide (ITO) coated glass electrode as a function of applied potential.

Results and Discussion

NMR Spectroscopy. Recent 2D NMR spectroscopic work by Sato and Morii has shown that the four singlets in the aromatic region can be clearly attributed to the four protons with each peak representing the different types of trimeric sequences of HT−HT (δ 6.98), HT−HH (δ 7), TT−HT (δ 7.02), and TT−HH (δ 7.05) linked thiophene ring.[20]

Figure 1 shows the NMR spectra of a POT synthesized by the regiospecific method and by the standard

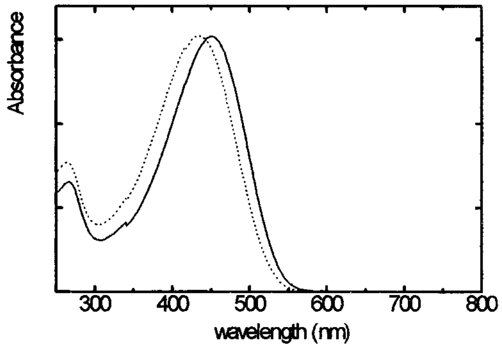


Figure 2. Electronic absorption spectra of polymer solutions of a (—) regioregular poly(3-butylthiophene) (···) regiorandom poly(3-butylthiophene)

Table 1. UV−Vis Data for Different P3ATs

	λ_{max} solution (nm) (in chloroform)		λ_{max} solid state (nm)	
	RPATs	HTPATs	RPATs	HTPATs
PBT	431	452	450	532 565 609
POT	433	450	500	531 560 605
PDDT	431	451	507	530 560 603

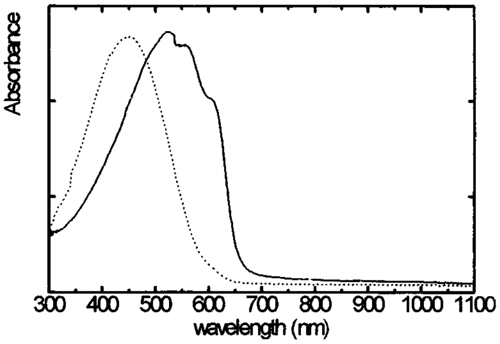


Figure 3. Electronic absorption spectra of polymer film cast from chloroform solutions: (—) regioregular poly(3-butylthiophene); (···) regiorandom poly(3-butylthiophene).

$FeCl_3$ polymerization method. The observed data are consistent with a random mixture of the four triads for the regiorandom POT and with an unique structure, the HT−HT linkage, for the polymer obtained from the regioregular polymerization.

Moreover, previous reports showed that the α-methylene protons of the alkyl group could be resolved by two different diads: HT (δ 2.8) and HH (δ 2.6).[20,21] Spectra of RPOT shows that the polymer has a regiorandom chain structure with a distribution of HT and HH linkages of 70/30. In contrast, only one sharp band for the thiophene proton, which denotes the HT−HT structure, is observed in the ^1H NMR spectra of HTPOT. The spectrum does not indicate the presence of other irregular linkage as observable within the resolution in this region. The extended ^1H NMR spectrum in the α-methylene proton region is indicative of >99% for the HT linkage. A similar analysis indicates 70% of the desired regiochemistry in the PBT and PDDT synthesized by $FeCl_3$ method, but more than 99% for regioselective polymerization.

UV−Vis Spectroscopy. In conjugated polymers, the extent of conjugation directly affects the observed energy of the $\pi-\pi^*$ transition, which appears as the maximum absorption. The results of both solution and solid state UV−vis analysis are shown in Table 1. Examples of spectra are shown in Figures 2 and 3. On dissolution, a major blue shift of the $\pi-\pi^*$ absorption band is observed, analogous to that observed in a number of soluble poly(diacetylenes).[22] The conformation of PATs in solution would be that of a coil with a small effective conjugation length, and that of the solid state phase would be a more extended structure with more extensive electronic delocalization. Hotta et al. suggested that P3ATs in solution are in a disordered conformation whereas casting into film restores a more ordered backbone with an associated more extensive delocalization of the π electron wave functions.[23] In solution, the regioregular polymers have a maximum absorption wavelength at 450 nm, which is 20 nm longer than the regiorandom polymers. This suggests that regioregular polymer chain has a more rodlike conformation with a longer conjugation length. The λ_{max} data for UV−vis spectra of solid state P3ATs show that all the regioregular PATs had a lower $\pi-\pi^*$ transition energy than that of the regiorandom PATs. The regiorandom polymers have maximum absorption wavelengths at 450, 500, and 507 nm for RPBT, RPOT, and RPDDT, respectively, whereas regioregular polymers have a maximum at 530 nm with other intense lower energy peaks at 560 and 605 nm, whatever the alkyl side chain length is.

The effect of a microstructural irregularity is to create a sterically driven twist of the thiophene rings out of coplanarity with a decrease in conjugation. It is therefore absolutely critical to have structurally homogeneous conducting polymers in order to allow for a maximum intramolecular orbital overlap. So, it is clear that regioregular polymers have a well-defined structure with no irregularity, which is consistent with the structure determined by NMR. These regioregular P3ATs have a absorption maximum more redshifted than the others P3ATs[23−24] and even that of other regioregular P3ATs.[25]

Changes of absorption spectrum of polythiophene derivatives upon electrochemical doping have been investigated by several groups.[26,27] As the doping proceeds, the intensity of the interband absorption decreases continuously and its absorption maximum shifts hypsochromically. Concurrently, two new absorption features appear in the subgap region at ≈0.5 and 1.5 eV. These absorption bands have been attributed to electronic transition between the valence band and two bipolaron levels symmetric with respect to the gap center.[26] At the highest doping level, the spectrum presents the characteristics of the free carrier absorption of the metallic state.[26]

Figure 4 shows the absorption spectra of HTPOT at various applied potentials. The comparison of the evolution of spectra of all P3ATs synthesized (not shown here) shows that, up to a potential of 0.8−0.9 V, the same general behavior is observed, namely a decrease of the interband absorption and a simultaneous increase of the absorbance at 800 nm (1.5 eV) which correspond to the upper bipolaron level.[24] At the highest doping level a residual interband absorption is still apparent while the absorbance decreases in the whole spectral range except for low energy. At these potentials (1 V), the spectroscopic characteristics are consistent with the appearance of a quasi-metallic behavior. This evolution of the spectroscopic properties of the polymers upon doping is in good agreement with results of Hotta et al. on poly(3-methylthiophene).[28]

Up to an applied potential of 0.8V, these absorbance variations occur around an isobestic point at 630 nm,

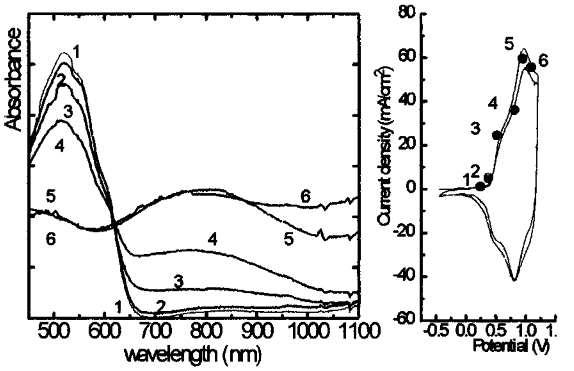


Figure 4. Left: Absorption spectra of HTPOT coated onto an ITO glass electrode at various potentials (electrolytic medium, 0.1 M $BuNPF_6$): 0.35, 0.4, 0.6, 0.8, 0.95, and 1 vs SCE. Right: Cyclic voltamogram of HTPOT recorded in 0.1 M $BuNPF_6$. (●) potential imposed for spectroelectrochemical measurements.

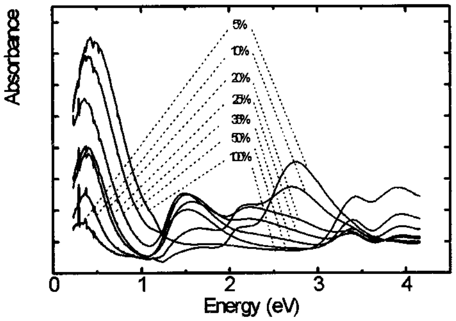


Figure 5. Absorption spectra of a 0.4 mg/mL chloroform solution of HTPOT doped by $FeCl_3$ at different doping levels which correspond to the ratios between the number of mole of dopant introduced into the polymer solution and the number of mole of thiophene units.

indicating that only two phases coexist in the doped polymer chain, i.e. a neutral region where the $\pi-\pi^*$ transition is unchanged and a localized region surrounding the charge storage configuration (bipolarons). As the doping level is increased, the subgap absorption grows at the expense of the $\pi-\pi^*$ transition.

The absorption spectra of the solution of doped HTPOT at different doping levels are compared in Figure 5 for a polymer concentration of 0.4 mg/mL. In fact, the doping level corresponds to the ratio between the number of mole of dopant introduced into the polymer solution and the number of mole of thiophene units. The spectra of HTPOT doped in solution present the same general features as the electrochemical doping ones. The two principal subgap absorption bands with maximum at $\hbar w_1 \approx 1.5$ eV and $\hbar w_2 \approx 0.4$ eV in the doped polymer are consistent with the charge storage predominantly in bipolaron. The $\pi-\pi^*$ transition energy of the polymer in solution (onset at ≈ 2.2 eV, peak at 2.7 eV) is however greater than $(\hbar w_1 + \hbar w_2) \approx 1.9$. $\hbar w_1 + \hbar w_2$ seems to be more probably equal to the $\pi-\pi^*$ transition energy of the solid state polymer (onset at ≈ 1.8 eV; peak at 2.2 eV).

The spectra show an additional intense absorption band near 2.2 eV. Patil et al. have already mentioned the presence of a little absorption near 2.15 eV at low doping level on P3HT.^{29} This additional absorption was not the result of a (third) polaron mode. Detailed examination of different spectra showed that this feature strongly decreases at high doping level whereas the magnetic data indicate a monotonic increase in the number of polaron per ring. Evolution of spectra is in good agreement with Patil's work. The absorption band at 2.15 eV appears at the first doping level, increases up to 10% doping and then disappears after 40% doping.

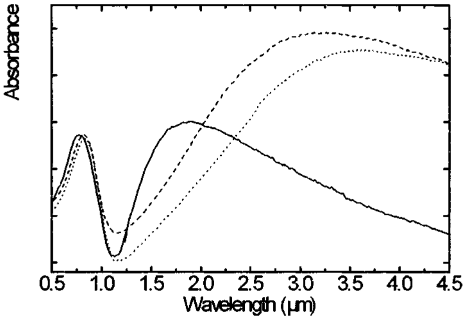


Figure 6. Absorption spectra of a $FeCl_3$ doped 0.4 mg/mL chloroform solution: of (—) HTPBT; (- -) HTPOT; (···) HTPDDT.

Moreover, in contrast to electrochemical doping, spectra do not present any isobestic point. This suggests that more than two phases coexist in the polymer chain.

Yet, it is interesting to notice that this absorption band energy corresponds to the $\pi-\pi^*$ transition of the neutral HTPOT cast film. So we suggest that addition of a little part of $FeCl_3$ to the polymer solution implies consumption of neutral polymer chain, appearance of a doped insoluble localized region (bipolaron band at 830 nm), and precipitation of some region of neutral thiophene ring near doped part of the polymer chain (band at 2.2 eV). Upon more doping, the polymer in solution is first consumed since the $\pi-\pi^*$ transition band intensity significantly decreases whereas the band at 2.15 eV remains constant between 10% and 20% doping. Then the solution and the solid state polymers are doped at the same time that nearly all the π electron oscillator strength is shifted into the two intense infrared bands. This would imply that at low doping level three phases coexist in a single chain of polymer, a soluble region for the neutral thiophene ring, distant from doped region, an insoluble region for the neutral thiophene ring, near the doped region, and the doped region.

A series of visible–near-IR spectra of chloroform solution (polymer concentration of 0.4 mg/mL, doping level of 25%) of regioregular P3ATs is shown in Figure 6. All polymers present the same general features: two absorption bands in the near-IR, characteristic of the bipolaron bands. However, detailed examination emphasizes interesting trends. For spectroscopic data in solution, a change in the maximum absorption energy of doped P3ATs as a function of alkyl side chain is observed. As indicated by a lower energy of the maximum absorptions, longer conjugation lengths are obtained with P3ATs possessing the longer alkyl side chain.

The shift to lower energy of the first bipolaron band in HTPDDT is found to be 50 nm (855 vs 804 nm) relative to HTPBT and 20 nm (855 vs 836 nm) relative to HTPOT, whereas the shift to lower energy of the second bipolaron band is found to be 1.7 μm (3.75 vs 1.83 μm) relative to HTPBT and 0.56 μm (3.75 vs 3.19 μm) relative to HTPOT. We interpret this effect as an increasing steric interaction between polymer chains when alkyl side chain size decreases. In regioregular PDDT, polymer chains are kept away by long dodecyl side chains, and due to perfect regioregularity of the linkage, long alkyl side chain interpenetration is en-

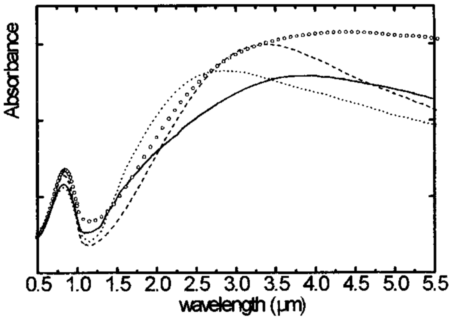


Figure 7. Visible−near-IR spectra of a $FeCl_3$-doped 0.4 mg/mL (···) toluene (- -) chloroform, (—) dichloromethane, and (○) nitobenzene solutions of HTPDDT.

Table 2. Vis−Near-IR Data for Doped HTPDDT for a Variety of Solvents

	Toluene	Chloroform	Dichloromethane	Nitrobenzene
first bipolaron band	826 nm	829 nm	833 nm	850 nm
second bipolaron band	2.8 µm	3.3 µm	3.8 µm	4.6 µm
dielectric constant of solvent	2.4	4.8	9.1	35.7

hanced and the polymer adopts a more linear conformation which extends the conjugation.

The absorption spectra of HTPDDT doped in solution in different solvents are compared in Figure 7, for a polymer concentration of 0.4 mg/mL and a doping level of 25%. Only the bipolaron range is reported. Data are detailed in Table 2.

As can be seen, the effect on electronic spectra of changing the solvent is dramatic. The spectrum in a polar solvent, nitrobenzene ($e_r = 35.7$) is significantly shifted toward low energy compared with spectra measured in a relatively nonpolar solvent, such as dichloromethane ($e_r = 9.1$), chloroform ($e_r = 4.8$) and toluene (e_r=2.4).

Previous reports have mentioned similar trends for polyacetylene or polyaniline.[30,31] It was reported a decade ago that THF vapor increases the conductivity of *n*-doped polyacetylene up to 4 orders of magnitude.[30] A similar phenomenon has been reported for free standing films of polyaniline exposed to water vapor.[31]

In the case of toluene, it is postulated that there is a weak polymer chain−solvent interaction; i.e., there is little solvatation of the positive charges on the polymer and of negative $FeCl_4^-$ ions. The positive and negative ions associated with the chain tend to form ion pairs, thus inhibiting electrostatic repulsion between the positive charges on the chain. This effect tends to favor a compact coil conformation of the polymer. As the dielectric constant of the solvent increases, the doped polymer chain−solvent interactions also increase. The solvatation of the positive and/or negative ions associated with the polymer increases, resulting in coulombic repulsion of positive charges on the polymer chain and in an expansion of the initial compact coil conformation of the poly(alkylthiophene) chain, and thus a greater conjugation length.

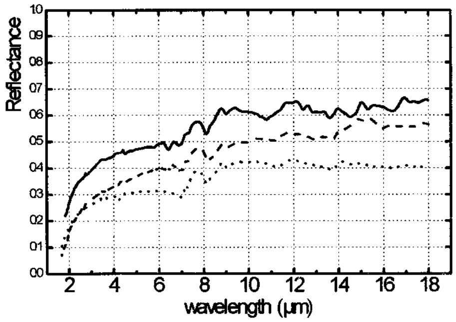


Figure 8. Near-IR−mid-IR reflectance spectra of doped $FeCl_3$ HTPDDT film cast from (—) nitrobenzene, (- -) dichloromethane, and (···) chloroform solutions.

More recently, Mc Diarmid et al. proposed the secondary doping concept for the Pani/CSA/*m*-cresol system.[15] Effect of exposure to *m*-cresol is to change the molecular conformation of the polyaniline from compact coil to expanded coil, resulting in an enhancement of the free carrier feature and a decrease of the localized polarons. So we show for the first time a similar phenomenon for the poly(3-alkylthiophene)/$FeCl_3$ system.

Mc Diarmid defines the secondary doping as an apparently “inert” substance which, when applied to a primary doped polymer, induces further changes in the above properties. It differs from a primary doping in that the newly enhanced properties may persist even upon complete removal of the secondary dopant.

Figure 8 shows the reflectance spectra of a $FeCl_3$-doped HTPDDT cast from nitrobenzene, dichloromethane, and chloroform solutions. Film thickness (~10 µm) allows measurements without glass interference. Reflectances approach 60% in the mid-IR for film cast from nitrobenzene and decrease to 50% and 40% as the dichloromethane and the chloroform, respectively, are put in place of nitrobenzene. The molecular conformation in the solid state is a major factor in determining the electronic properties such as reflectance. Consecutively, these results clearly show the dependence of molecular conformation in the solid state upon its conformation in the solution from which the film is cast. Reflectance results are consistent with vis−near-IR absorbance spectra of HTPDDT in solution in nitrobenzene, dichloromethane, and chloroform, namely, the greatest reflectances are obtained for films cast from solutions with a high dielectric constant solvent and a vis−near-IR absorbance spectrum shifted to lower energy. From this point of view, nitrobenzene can be considered as a good secondary dopant as defined previously, for HTPDDT doped with the primary dopant $FeCl_3$: in solution, a more expanded coil conformation of the polymer chain is obtained for a solvent with a high dielectric constant. Even after complete removal of the solvent, the more expanded coil conformation seems to persist in the cast film since reflectance feature is more metal like.

A systematic study of all P3ATs described in this article has been carried out. Figure 9 shows reflectance spectra of regiorandom and regioregular PBT, POT, and PDDT films cast from nitrobenzene solutions. For P3ATs, we observe for the first time a change in the maximum reflectance as a function of the alkyl side chain. Thus it is clear that side chains play a heavy role in controlling the local and three-dimensional structures and modify the resultant physical properties.

For regioregular P3ATs, the greatest reflectances are observed in P3ATs possessing the longer alkyl side chain, i.e., in the 10−16 µm range, reflectance increases from ≈50% to 60% and 62−63% as the octyl chain and

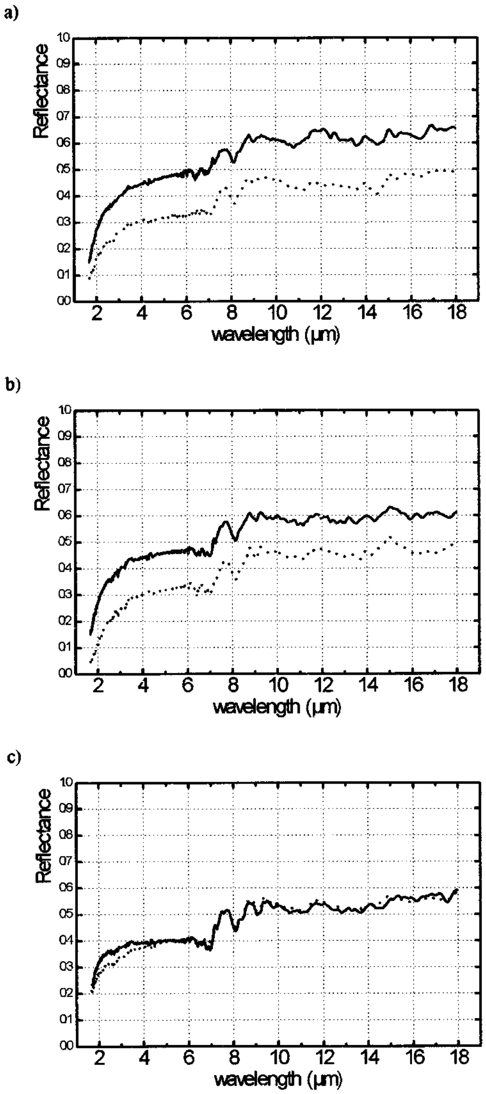


Figure 9. Near-IR−mid-IR reflectance spectra of doped $FeCl_3$ P3ATs film cast from nitrobenzene solutions: (a) (- -) RPDDT and (—) HTPDDT; (b) (- -) RPOT and (—) HTPOT; (c) (- -) RPBT and (—) HTPBT.

the dodecyl chain take the place of the butyl side chain. These results are in good agreement with vis−near-IR absorption data and confirm the best organization of the polymer chain when long alkyl side chain are grafted on the thiophene backbone. Mc Cullough et al. showed that films of neutral HTPATs were very ordered system with a virtually single stacking distance, dependent on the alkyl side chain length.[32] So, one can expect that upon doping, a partial organization could be restored. Thus polymer with long alkyl chain will be more organized since the long alkyl chain will tend to minimize steric or Coulombic interchain interaction. For regiorandom P3ATs, changes of reflectance as the alkyl chain length increases are at the opposite of HTP3ATs' one. The greatest reflectances are observed in P3ATs possessing the shorter alkyl side chain, i.e., in the 10−16 μm range, reflectance increases from ≈44% to 46% and 50% as the octyl chain and the butyl chain take the place of the dodecyl side chain. We interpret this effect as an increase of the steric intrachain interaction between a longer alkyl chain in a regiorandom polymer leading to a decrease of the conjugation length. This important phenomenon occurs essentially for any alkyl side chain greater than butyl (Figure 9). Almost exclusively head to tail linkage is found in regioregular P3ATs, resulting in an increased conjugation length and in enhanced electronic properties. This is confirmed by comparison of HTP3AT reflectance vs RP3AT reflectance, essentially in the case of PDDT. Nevertheless, the identical reflectance data for PBT suggest that the butyl side chain is not long enough to induce sufficient steric interaction in the doped state. In any case, reflectances observed in this work seem to be the greatest ever published for P3ATs and are comparable to highly conductive polyaniline or polypyrrole reflectances.[33−35]

Conclusions

A series of P3ATs with different regioregularities were obtained, among which are completely regioregular head to tail and 30% regiorandom poly(3-alkylthiophenes). The regioregular HT-PATs were characterized as a class of polymer with regiospecific head to tail conformation, significantly extended conjugation length, a self-organized structure of the polymer chain, and low bandgap. Effects on electronic properties of both alkyl side chain and dielectric constant of solvent have been demonstrated; i.e., in regioregular polymers, a long alkyl side chain allows a better organization by keeping out polymer chains which tend to reduce inter chain interactions and high dielectric constant solvents enhance intrachain conformation by extending the chain because of Coulombic repulsions of the solvated cationic charges of the polymer backbone. These effects persist, even after complete removal of the solvent, as demonstrated by reflectance spectra. In that respect, we define nitrobenzene as a secondary dopant for the P3AT/$FeCl_3$ system. High reflectances, comparable to highly conductive polyaniline or polypyrrole reflectances, have been observed but considerable work remains to be done to optimize the enhanced desirable properties and to understand and to fit the response to IR solicitations.

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