# Synthesis and Characterization of New Conjugated Soluble Polythiophenes with Excellent Reversible Electrochemical Properties

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**ABSTRACT:** A series of five new conjugated polythiophene (PT) derivatives containing piperidinyl groups as a side chain were synthesized by ferric trichloride oxidization. All of the polymers were soluble in common organic solvents, and their high regioregularity were confirmed by ^{1}H-NMR. The weight-average molar masses ranged from 5931 to 22,955 g/mol with a low polydispersity index ranging from 1.18 to 1.79. The fluorescence emission maximum of poly[3-($N$-methyl propionate–4′-piperidine)methylene–thiophene] in the films was 725 nm in the yellow–red region, higher than that of the other PT derivatives. All five polymers exhibited reversible $p$-doping/dedoping (oxidation/reneutralization) processes; this indicated that these polymers could be applied in electrical equipment in the doping state. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

## INTRODUCTION

Intensive research activity on polythiophenes (PTs) has been stimulated by their applications in solution-processed polymer solar cells,[1] organic field-effect transistors,[2,3] and the fabrication of light-emitting diodes[4] since their discovery in the 1970s. Some chemically modified, alkyl-substituted PTs, such as poly(3-hexylthiophene) and poly(3-octylthiophene), have been applied in polymer solar cells[5–12] with improved solubility. To be in good accordance with the more stringent requirement of applications, conjugated PTs with improved properties have been reported by Takakazu, Hideki and Plieth et al.[13–18] In comparison with other conjugated polymers, conjugated PTs have a relatively higher charge carrier mobility, longer wavelength absorption, and lower band energy.[19–21]

However, few researchers are interested in the synthesis of piperidyl-substituted PT derivatives. In this article, we reported the synthesis of a new series of conjugated processable PT derivatives, namely, poly[3-($N$-propyl-4′-piperidine)methylene–thiophene] (PT1), poly[3-($N$-propionile-4′-piperidine)methylene–thiophene] (PT2), poly[3-($N$-methyl propionate-4′-piperidine)-methylene–thiophene] (PT3), poly[3-($N$-phenethyl-4′-piperidine)methylene–thiophene] (PT4), and poly[3-($N$-propionyl-4′-piperidine)methylene–thiophene] (PT5). Their synthetic routes and structures are described in Scheme 1. Different substituents in the side chain bring about different effects on the solubility, photochromism, and optical and electrochemical properties

because of their diverse charge transfer abilities.[22–26] Their optical properties both in solution and in spin-coated films were investigated by ultraviolet–visible (UV–vis) spectra and photoluminescence (PL). It was important to determine that these substituents influenced not only the absorptions (optical band gap) but also the electrochemical behaviors (electrical band gap). Moreover, the different steric hindrances caused by end substituents resulted in different coplanarities in both the side chain–backbone (intramolecular) and backbone–backbone (intermolecular) and dissimilar regioregularity.

## EXPERIMENTAL

### Materials

Chloroform was purified by distillation and dried by a 4A molecular sieve, and tetrahydrofuran (THF) was dried and distilled under nitrogen from metal sodium and benzophenone. Other reagents were common commercial level and were used as received without further purification. The concentration of all polymer solutions used in the optical properties studies was $10^{-3}$ mol/L, and all of the polymer films were spin-coated on a glass substrate with 10 mg/mL polymer/chloroform solutions. 3-(Bromomethyl)thiophene (**1**) and (thiophene-3-ylmethyl)phosphonic acid diethyl ester (**2**) were prepared as reported previously.[27]

### Instruments

The ^{1}H-NMR was recorded on a Bruker AV III 400-MHz NMR spectrometer (Switzerland Bruker A. G.), and CDCl₃ was used
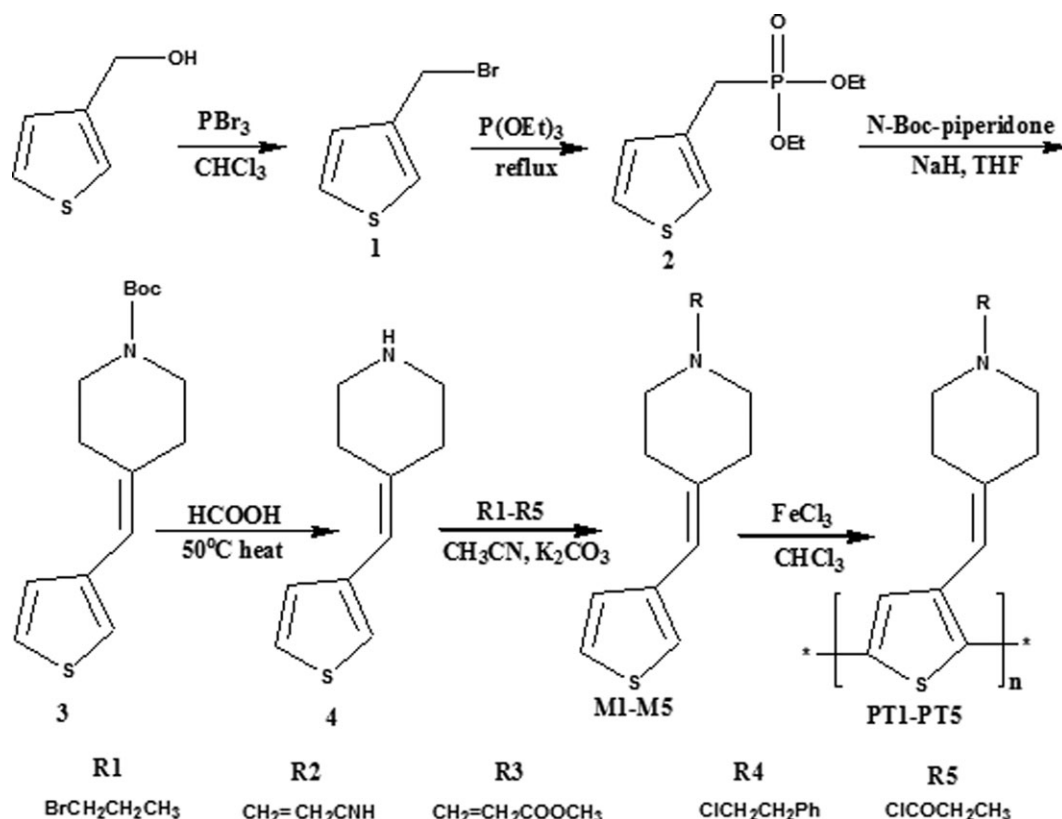
**Scheme 1.** Synthetic routes of the monomers and polymers.

as solvent. The gel permeation chromatography measurements were performed on a PerkinElmer model 200 high performance liquid chromatography (HPLC) system with a tandem column of PIgel 5-$\mu$m MIXED-C (300 $\times$ 7.5 mm$^2$) with THF (HPLC grade) as the eluent by a flow rate of 0.5 mL/min. The concentration of the polymer was 1 mg/mL, and the solution was filtered through a 45-$\mu$m filter. The molecular weight and the molecular weight distribution were calculated on the basis of monodispersed polystyrene standards. The UV–vis spectra were recorded on a Shimadzu 3100 spectrometer. Fluorescence measurements were carried out on an Edinburgh Instruments, Ltd., FLS920 fluorescence spectrophotometer. Cyclic voltammetry measurements were carried out with a BAS 100 electrochemical analyzer (Ark Technology Co.Ltd; china) at a potential scan rate of 0.1 V/s. Thermogravimetric analysis (TGA) of polymer powders was conducted on a thermal analyzer of a PerkinElmer Diamond thermogravimetry/differential thermal analyzer. A heating rate of 10°C/min with a nitrogen flow of 75 cm$^3$/min was used, with the runs being conducted from room temperature to 800°C. Scanning electron microscopy measurements were carried out with a cold-field emission scanning electron microscope PEG 250. The films were prepared on a glass substrate with a TA280 spin coater (800 rpm for 5 s and then 2500 rpm for 30 s).

**Synthesis of 3-(N-Boc-4′-piperidine)methylene–thiophene (3)**
To a mixture of sodium hydride (0.60 g, 25.00 mmol) dissolved in 10 mL of THF, a mixture of **2** (2.34 g, 10.00 mmol) and THF (10 mL) was added dropwise. The mixture was stirred

continuously and cooled by an ice bath with the protection of a nitrogen atmosphere. Then, N-Boc-piperidone (1.97 g, 10.00 mmol) was added to the mixture, and the reaction mixture was kept in an ice bath for 1 h and then at room temperature for overnight. After the reaction was accomplished, THF was removed by a rotary evaporator. The residue was poured into distilled water, and the organic phase was obtained by extraction with chloroform. The solvent was evaporated to give the crude product and was further purified by thin-layer chromatography (TLC) on silica (n-hexane/ethyl acetate = 6 : 1, retention factor ($R_f$) = 0.6) to finally afford product **3** (1.97 g) as a yellowish oil.

Yield = 80.41%. $^1$H-NMR (CDCl$_3$, ppm, $\delta$): 7.49 (1H, s, thiophene-2-H), 7.43 (d, thiophene-4-H), 7.34–7.35 (1H, d, thiophene-5-H), 6.19 (1H, s, thiophene-C—H), 3.56–3.60 (4H, m, piperidine-2.6-H), 2.16–2.21 (4H, m, piperidine-3,5-H), 1.45 (9H, s, Boc-H).

**Synthesis of 3-(4′-Piperidine)methylene–thiophene (4)**
A mixture of compound **3** (1.50 g, 6.00 mmol) and anhydrous formic acid (15 mL) was continuously stirred for 24 h at 50°C (water bath). The organic solvent was evaporated, and then, the residue was dissolved in chloroform to carry out TLC on silica (ethyl acetate/methanol/triethylamine = 4 : 1 : 1, $R_f$ = 0.5) to afford compound **4** (0.80 g) as a yellowish oil.

Yield = 83.00%. $^1$H-NMR (CDCl$_3$, ppm, $\delta$): 7.39–7.40 (1H, d, thiophene-5-H), 7.38 (1H, s, thiophene-2-H), 7.05–7.06 (1H, d, thiophene-4-H), 6.05 (1H, s, thiophene-C—H), 2.69–2.72 (4H,

m, piperidine-2,6-H), 2.44–2.45 (1H, m, piperidine-1-H), 2.34–2.40 (4H, m, piperidine-3,5-H).

### Synthesis of 3-(*N*-Propyl-4′-piperidine)methylene–thiophene (M1)

To a solution of **4** (0.40 g, 2.20 mmol) in 15 mL of acetonitrile was added propyl bromide (0.41 g, 3.30 mmol) and sodium bicarbonate (0.55 g, 6.60 mmol). The mixture was stirred well and the reaction was accomplished by refluxing for 4 h. Then, the solvent was removed, and the organic phase was extracted from mixture by chloroform. After drying, filtration, and evaporation, the crude product was subjected to TLC on silica (*n*-hexane/acetate/methanol/triethylamine = 30 : 5 : 1 : 1) to yield M1 (0.37 g) as yellowish oil.

Yield = 75.70%. $^1$H-NMR(CDCl$_3$, ppm, $\delta$): 7.29–7.30 (1H, d, thiophene-5-H), 7.28 (1H, s, thiophene-2-H), 7.03–7.05 (1H, d, thiophene-4-H), 6.24 (1H, s, thiophene-C—H), 2.45–2.51 (4H, m, piperidine-H), 2.28–2.43 (6H, m, piperidine-1-H, piperidine-C—H), 1.49–1.51 (2H, m, piperidine-C—C—H), 0.87–0.93 (3H, t, piperidine-C—C—C—H).

### Synthesis of 3-(*N*-Propionitrile-4′-piperidine) methylene–thiophene (M2)

The preparation process was the same as that for compound M1, except that acrylonitrile (0.17 g, 3.30 mmol) instead of propyl bromide was used.

Yield = 0.43 g, 84.30%. $^1$H-NMR (CDCl$_3$, ppm, $\delta$): 7.38 (2H, t, thiophene-2,5-H), 6.99–7.10 (1H, d, thiophene-4-H). 6.21 (1H, s, thiophene-C—H), 2.71–2.75 (2H, t, piperidine-C—C—H), 2.53–2.76 (4H, m, piperidine-2,6-H), 2.27–2.44 (4H, m, piperidine-3,5-H), 2.47–2.48 (2H, t, piperidine-C—H).

### Synthesis of 3-(*N*-Methyl propionate-4′-piperidine) methylene–thiophene (M3)

The preparation process was the same as that for compound M1, except that methylacrylate (0.28 g, 3.30 mmol) instead of propyl bromide was used.

Yield = 0.47 g, 81.00%. $^1$H-NMR (CDCl$_3$, ppm, $\delta$): 7.24 (1H, s, thiophene-2-H), 6.96–7.08 (2H, m, thiophene-4,5-H), 6.18 (1H, s, thiophene-C—H), 3.68 (3H, s, piperidine-C—C—COO—C—H), 2.71–2.76 (2H, t, piperidine-C—H), 2.51–2.58 (4H, m, piperidine-2,6-H), 2.47–2.49 (2H, t, piperidine-C—C—H), 2.32–2.35 (4H, m, piperidine-3,5-H).

### Synthesis of 3-(*N*-Phenethyl-4′-piperidine) methylene–thiophene (M4)

The preparation process was the same as that for compound M1, except that (2-chloroethyl)benzene (0.46 g, 3.30 mmol) instead of propyl bromide was used.

Yield = 0.48 g, 77.40%. $^1$H-NMR (CDCl$_3$, ppm, $\delta$): 7.38 (1H, s, thiophene-2-H), 7.28–7.30 (2H, m, thiophene-4,5-H), 7.15–7.18 (5H, m, Ph-H) 6.17 (1H, s, thiophene-C—H), 2.86–2.88 (2H, t, piperidine-C—H), 2.62–2.67 (4H, m, piperidine-2,6-H), 2.44–2.48 (2H, t, piperidine-C—C—H), 2.47–2.49 (2H, t, piperidine-C—C—H), 2.09–2.28 (4H, m, piperidine-3,5-H).

### Synthesis of 3-(*N*-Propionyl-4′-piperidine) methylene–thiophene (M5)

The preparation process was the same as that for compound M1, except that propionyl chloride (0.31 g, 3.3 mmol) instead of propyl bromide was used.

Yield = 0.37 g, 71.20%. $^1$H-NMR (CDCl$_3$, ppm, $\delta$): 7.38 (1H, s, thiophene-2-H), 7.24–7.26 (2H, m, thiophene-4,5-H), 6.25 (1H, s, thiophene-C—H), 3.76–3.80 (4H, m, piperidine-2,6-H), 3.27–3.43 (2H, m, piperidine-CO—C—C—H), 2.44–2.48 (2H, t, piperidine-C—C—H), 2.25–2.43 (4H, m, piperidine-3,5-H), 1.09–1.15 (3H, t, piperidine-CO—C—C—H).

### Synthesis of the Polymers (PT1–PT5)

A solution of monomer in 10 mL of chloroform was added to a mixture of ferric trichloride and 10 mL of chloroform. The reaction needed to be kept in an ice bath and under a nitrogen atmosphere for 24 h. The reaction mixture was poured into methanol, and the red precipitate was collected by suction filtration. The solid was dissolved in 35 mL of chloroform, and 60 mL of concentrated aqueous ammonia solution was added. The mixture was stirred for 2 days, and then the organic phase was separated, dried with anhydrous sodium sulfate, filtered, and evaporated to obtain dedoped polymer. The final solid material was purified by a Soxhlet extractor with methanol and chloroform, respectively. Then, a claret-colored solid was yielded by the evaporation of chloroform.

### PT1

Starting with M2 (0.37 g, 1.67 mmol) in 20 mL of anhydrous chloroform, the polymer PT1 (0.22 g) was isolated as a dark red solid.

Yield = 58.20%. Number-average molecular weight ($M_n$) = 8480 g/mol, weight-average molecular weight ($M_w$) = 9582 g/mol, and polydispersity index (PDI) = 1.13.

### PT2

Starting with M2 (0.43 g, 1.85 mmol) in 20 mL of anhydrous chloroform, we isolated polymer PT2 (0.22 g) as a dark red solid.

Yield = 51.61%. $M_n$ (g/mol) = 5027, $M_w$ (g/mol) = 5931, PDI = 1.18.

### PT3

Starting with M3 (0.47 g, 1.77 mmol) in 20 mL of anhydrous chloroform, we isolated polymer PT3 (0.28 g) as a dark red solid.

Yield = 60.33%. $M_n$ = 4763 g/mol, $M_w$ = 6430 g/mol, PDI = 1.35.

### Poly[3-(*N*-propionyl-4′-piperidine)methylene–thiophene] (PT5)

Starting with M4 (0.48 g, 1.70 mmol) in 20 mL of anhydrous chloroform, we isolated polymer PT4 (0.27 g) as a dark red solid.

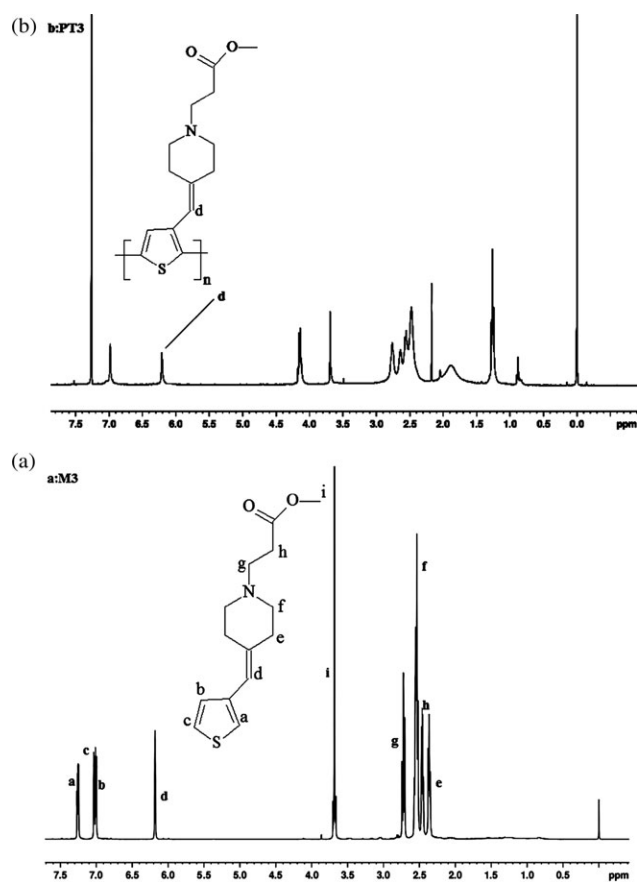Yield = 65.90%. $M_n$ = 4838 g/mol, $M_w$ = 6628 g/mol, PDI = 1.37.

**Figure 1.** $^1$H-NMR spectra of (a) M3 and (b) PT3 in CDCl$_3$ at room temperature.

**Poly[3-(N-phenethyl-4′-piperidine)methylene–thiophene] (PT5)**

Starting with M5 (0.37 g, 1.57 mmol) in 20 mL of anhydrous chloroform, we isolated polymer PT5 (0.24 g) as a dark red solid.

Yield = 65.90. $M_n$ = 12,866 g/mol, $M_w$ = 22,995 g/mol, PDI = 1.79.

## RESULTS AND DISCUSSION

### Synthesis and Structure Characterization

The molecular structures and synthetic routes of the monomers and polymers are depicted in Scheme 1. 3-Thienylmethanol was brominated with phosphorus tribromide to afford **1,** and then, **1** was reacted with equimolar triethyl phosphite to obtain the Wittig–Horner–Emmons[28–30] reagent **2**. Compound **3** was prepared by a Wittig–Horner–Emmons reaction. The *Boc* group of compound **3** was removed to yield **4** in the presence of anhydrous formic acid. The monomers (**M1–M5**) were obtained by alkylation with R1–R5 (Scheme 1), then to polymerize with ferric trichloride in anhydrous chloroform to afford the polymers as a red power. The polymers were soluble in chloroform and THF, and the solvatochromism phenomenon was performed in different organic solutions. The color was much darker in chloroform than in THF with the same concentration.

From the gel permeation chromatography results, it could be seen that $M_n$ and $M_w$ of polymers ranged from 4763 (PT3) to 12,866 (PT5) and 5931 (PT2) to 22,995 (PT5), respectively. All five polymers exhibited low PDI values; this was attributed to the perfect elimination of low molecular weight in the purification state.

The monomers and polymers were identified by $^1$H-NMR spectroscopy in CDCl$_3$. As an example, the identified $^1$H-NMR spectroscopy of M3 and PT3 measured in CDCl$_3$ are shown in Figure 1, and the regioregularity of the resulting polymers were predetermined qualitatively by the regioregularity of PT3. In PT3, a d singlet assigned to the thiophene-C—H at 6.18 ppm was clearly observed. This proton was near the thiophene ring, assigned to the head–tail unit; this indicated a high regioregularity.[31–34] In other cases (head–head, tail–tail), two peaks of thiophene-C—H would be observed; this was attributed to the effects of diverse conformations of the thiophene ring. Another typical signal at 6.98 ppm ascribed to thiophene-ring proton showed a singlet with a weak shoulder at 7.0 ppm; this indicated the presence of a low fraction of the head–head sequences.

### Optical Properties

The optical properties of PT1–PT5 were investigated by UV–vis absorption and PL spectroscopy. The normalized absorption and emission spectra in chloroform solution are shown in Figure 2. The polymers PT1–PT5 exhibited absorption and emission maxima at 505, 474, 477, 486, and 458 and 598, 592, 595, 592, and 588 nm, respectively. The different absorptions were caused by the unique steric hindrance of substituted groups in the side chain with diverse abilities of electron withdrawing and electron donating, and diverse coplanarity between the side chain and backbone. In Figure 2(B), one shoulder peak at 635–685 nm was observed in all five polymers; this was attributed to the increased interactions between the polymer chains with emitted light.

In Figure 3, the normalized absorption and emission spectra of PT1–PT5 in the films spin-coated onto the quartz substrate were investigated. The polymers exhibited absorption and
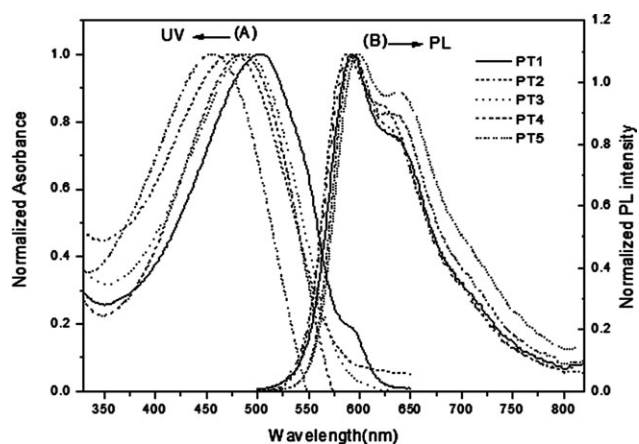


**Figure 2.** (A) Normalized UV–vis absorption spectra of the polymer solutions in chloroform. (B) Normalized PL spectra of the five polymers in chloroform (excited at 450 nm).
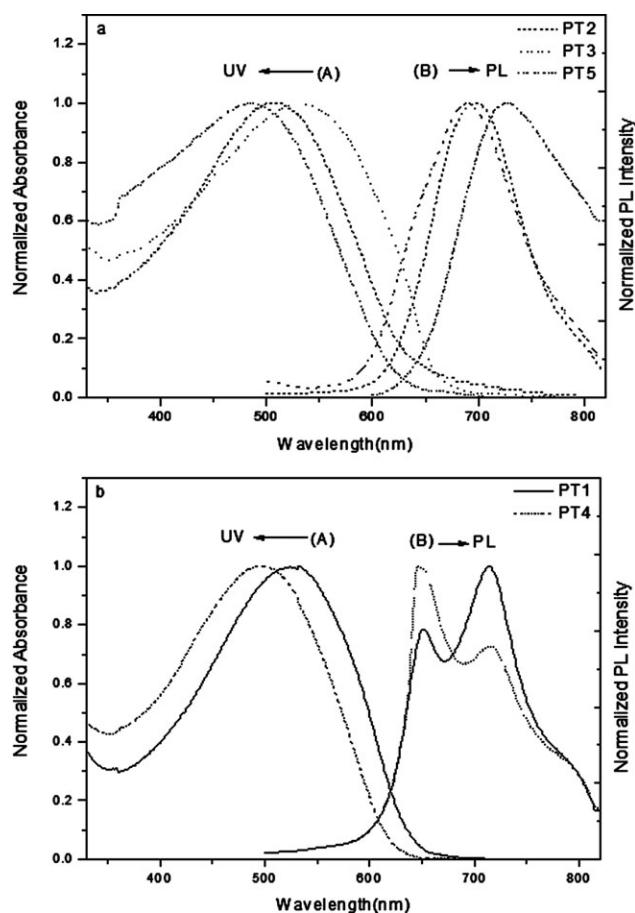
**Figure 3.** (a) Normalized UV–vis absorption spectra of the polymers in the film. (b) Normalized PL spectra of the five polymers in the film (excited at 450 nm). All of the films were spin-coated from 10 mg/mL polymer/chloroform solutions.

emission maxima at 532, 509, 533, 499, and 483 and 650, 689, 725, 714, and 699 nm, respectively, and led to a redshift in the solid state. Furthermore, the optical energy gap ($E_g^{opt}$) of each polymer was estimated by the following equation: $E_g^{opt} = 1240/\lambda_{edge}$ (where $\lambda_{edge}$ is the onset wavelength of the absorption spectrum in the long-wave direction, as determined by the tangent method),[35] which varied from 1.67 to 1.96 eV (Table I). The PT3 film exhibited a lowest $E_g^{opt}$ (1.67 eV) and could be loosely defined as a good, low-band-gap material.[36] It was interesting to find that PT2, PT3, and PT5 had only one peak but

PT1 and PT4 had two peaks in the PL spectra [Figure 3(b)]. The previous one indicated that PT2, PT3, and PT5 had a higher regioregularity in the solid state than in solution, and the latter one, along with the redshift, were caused by increased interactions between the polymer chains in the solid state or a lager overlap of $\pi$ orbitals on the thiophene backbone due to an increased coplanarity of thiophene rings in the solid state induced by alignment of the alkyl chains.

To investigate a solvatochromism effect, we measured the UV–vis spectroscopy of PT1–PT5 in different solvents, and the results are presented in Table I. All of the polymers were soluble in common good solvents ($CHCl_3$, $CHCl_3$–MeOH, and THF) and were partially soluble in poor solvents (MeOH and toluene). In general, the UV–vis spectra of PT1, PT2, PT4, and PT5 measured in good solvents displayed a redshift from those measured in poor solvents; this was attributable to polymer folding and the formation of an intramolecular aggregate. However, in contrast to the generality, the spectra of PT3 measured in good solvents exhibited blueshifts from those measured in poor solvents because of its aggregation. Moreover, as an example for PT2 shown in Figure 4, all of the polymer films had no evident change in the temperature range 12–70°C; this indicated that these polymers had stable optical absorbances in different temperature situations, which was attributed to the stable structures and aggregations in solutions with diverse temperatures.

**Electrochemical Properties**

The electrochemical behaviors of PT1–PT5 were investigated by CV in boron trifluoride ether solutions at a potential sweep rate of 0.1 V/s. As shown in Figure 5, the cyclic voltammograms of PT1–PT5 exhibited the reversible $p$-doping/dedoping (oxidation/reneutralization) process, indicating a good electrical properties under doping conditions. The electrochemical onset $p$-doping (oxidation) potentials ($E_{on}^{ox}$'s) and onset reneutralization potentials ($E_{on}^{red}$'s) of the five polymers are listed in Table II. The $E_{on}^{ox}$ values of all five polymers were observed in the range 1.25–1.43 V. Compared with PT2, $E_{on}^{ox}$ decreased 0.07 V for PT3 and PT5 and increased 0.08 and 0.11 V for PT4 and PT1,
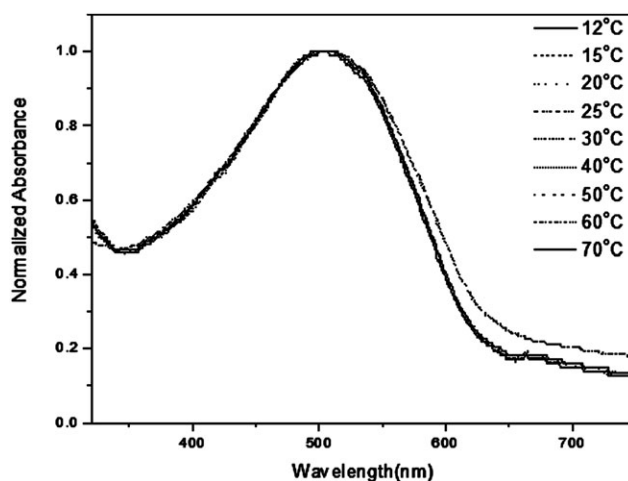
**Table I.** UV–Vis Absorption Maxima and $E_g^{opt}$ Values of the Polymers

| Polymers | UV-Vis Absorption Spectra [$\lambda_{max}$ (nm)] | | | | $E_g^{opt}$ (eV) |
| | $CHCl_3$ | $CHCl_3$/MeOH | THF | Toluene | |
|---|---|---|---|---|---|
| PT1 | 505 | 500 | 492 | 490 | 1.88 |
| PT2 | 474 | 463 | 464 | Insoluble | 1.70 |
| PT3 | 477 | 490 | 487 | 494 | 1.67 |
| PT4 | 486 | 479 | 485 | 464 | 1.96 |
| PT5 | 458 | 456 | 444 | Insoluble | 1.85 |



**Figure 4.** Temperature effect for PT2 in the film spin-coated from a 10 mg/mL PT2/chloroform solution.
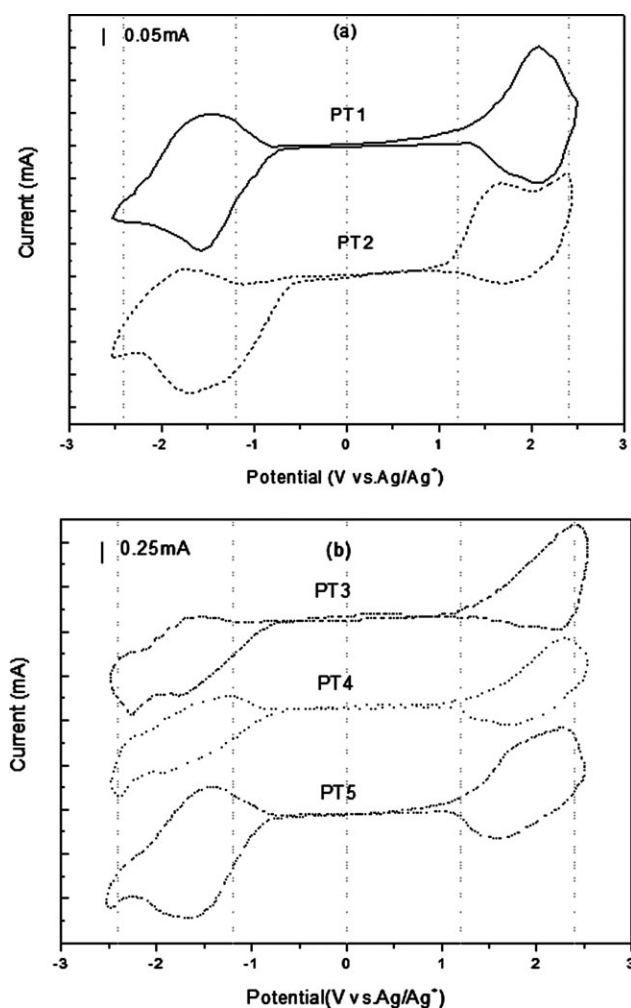
**Figure 5.** Cyclic voltammograms of the polymer films on platinum plates in a boron trifluoride ether solution at a potential sweep rate of 0.1 V/s. The current scale intervals were (a) 0.05 mA for PT1–PT2 and (b) 0.25 mA for PT3–PT5.

respectively; this was attributed to the different end groups in the side chain, although $E_{on}^{red}$ of PT2 was the highest due to the presence of propionitrile groups. Furthermore, to expediently compare the optical and electrochemical properties, we calculated the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels and the electrochemical band gaps ($E_g^{EC}$) from the oxidation and neutralization potentials according to the following equations:[37,38]

$$HOMO(eV) = -E_{on}^{ox} - 4.71$$

$$LUMO(eV) = -E_{on}^{red} - 4.71$$

$$E_g^{EC}(eV) = E_{on}^{ox} - E_{on}^{red}$$

where $E_{on}^{ox}$ and $E_{on}^{red}$ are the measured potentials relative to Ag/Ag$^+$. The electrochemical properties and the energy level parameters of the polymers are listed in Table II.

In Table II, it can be seen that the $E_g^{EC}$ values of the polymers ranged from 2.00 eV for PT3 to 2.29 eV for PT4, and the tend-

ency was consistent with the $E_g^{opt}$ values determined from absorption ranges from 1.67 eV for PT3 to 1.96 eV for PT4 (see Table I). In this case, all of these polymers had similar $E_g^{EC}$ values and were consistent with many other PT-based polymers found in the literature, such as poly[3-(2′-pentyloxy-5′-(1‴-oxooctyl) phenyl)thiophene] (2.35 eV), and poly[3-(10-n-octyl-3-phenothiazine vinylene)thiopheneco-2,5-thiophene] (2.0 eV). The lowest $E_g^{EC}$, which is the most important considerable parameter in electron-transporting material applications, was seen in PT3. Compared with PT3, the $E_g^{EC}$ of PT4 was 0.29 eV larger; this was due to the larger steric hindrance induced by the phenethyl end groups in the side chain. As is often observed for conjugated polymers, $E_g^{EC}$ was found to be slightly higher than $E_g^{opt}$; this might have been related to structural differences in the thin film due to swelling by the solvent or the exciton binding energy for conjugated polymers.[39]

**Surface Morphology Analysis**

To characterize the surface morphology of polymers, we used scanning electron microscopy to further investigate. All of the samples were prepared in the same way. First, polymer films were spin-coated and were then fixed on a sample stage by conducting paper. The all of the solid samples were carbon-coated to improve their electrical conductivity. As shown in Figure 6, all five polymers exhibited globular particles, and some differences are also clearly shown in the figure. First, different diameter particles existed in each system, showed the different growth states, and determined the PDI with a tendency of the larger disparities for larger PDIs. Some aggregations emerged in PT2, PT3, and PT4; this was attributed to the denser samples and intramolecular involvement among molecules caused by the long side chains. Furthermore, a few particles were irregular balls (in the case of PT1); this was caused by methylene oxidation (the group linked the thiophene ring and piperidine) in the air.

**Thermal Analysis**

The polymer thermal stability was examined by TGA under nitrogen, and the curves of PT1–PT5 are shown in Figure 7. We recorded the initial decomposition temperature ($T_i$), the 5% decomposition temperature ($T_d$), and the polymer fusion temperature [melting temperature ($T_m$)]. The results are shown in Table III. All of the polymers exhibited two-step weight loss processes, except PT1, starting at 248°C and displaying a relatively appreciable thermal stability. For the one-step sample, PT1, the thermal decomposition involved the complete loss of

**Table II.** Electrochemical Properties of the Polymers

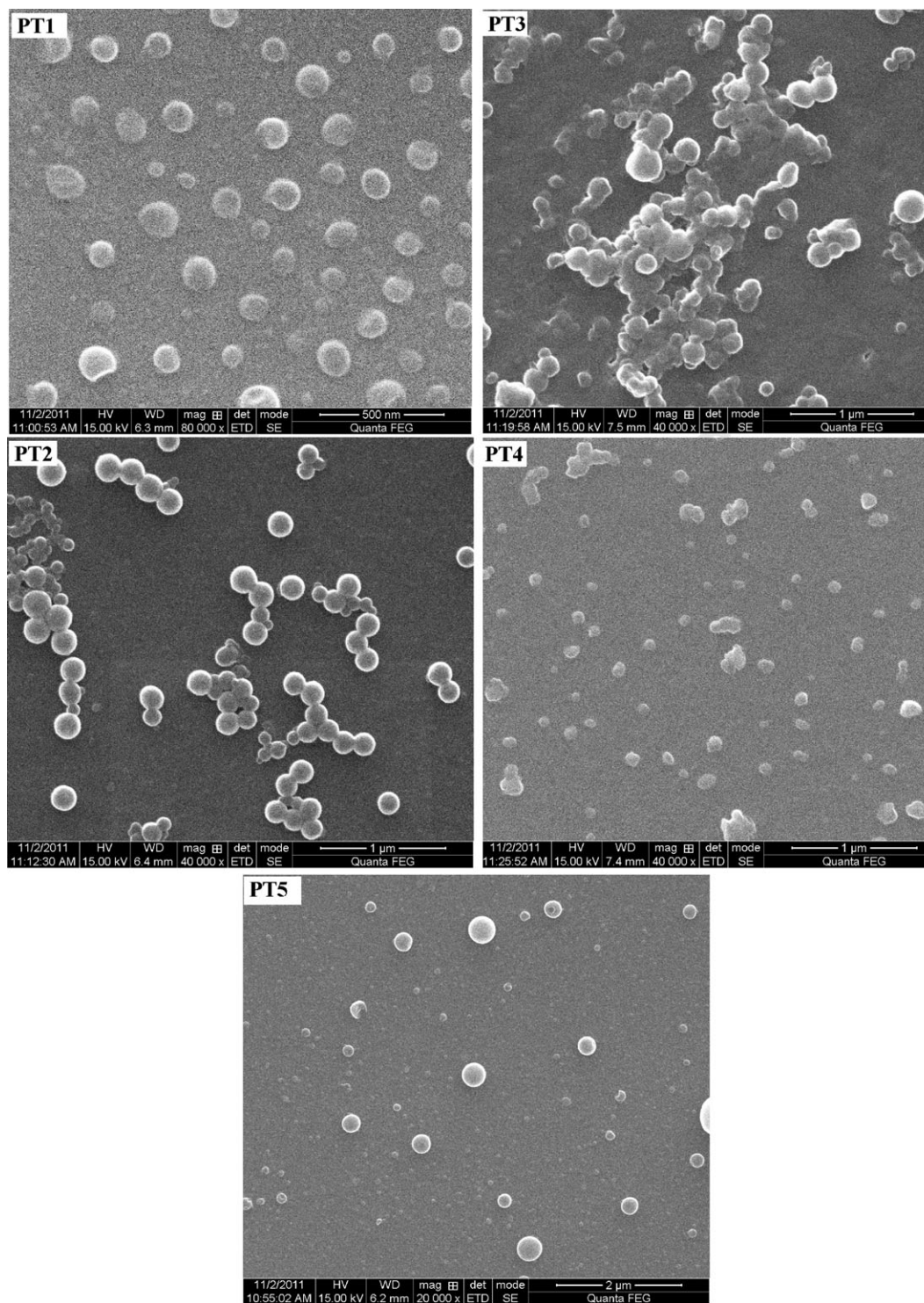| Polymer | p-Doping $E_{on}^{ox}$ (V) | HOMO (eV) | Reneutralization $E_{on}^{red}$ (V) | LUMO (eV) |
|---------|---------|---------|---------|---------|
| PT1 | 1.43 | −6.14 | −0.83 | −3.88 |
| PT2 | 1.32 | −6.03 | −0.72 | −3.99 |
| PT3 | 1.25 | −5.96 | −0.75 | −3.96 |
| PT4 | 1.40 | −6.11 | −0.89 | −3.82 |
| PT5 | 1.25 | −5.96 | −0.96 | −3.75 |

**Figure 6.** Scanning electron micrographs of the polymers. Magnifications: PT1, 80,000×; PT2, 40,000×; PT3, 40,000×; PT4, 40,000×; and PT5, 20,000×.

the side chain, whereas for the two-step samples (PT2–PT5), the decomposition started with the cracking of the functional group, followed by the loss of the methylenic chain. In all cases, the residual weight at 600°C roughly corresponded to a methylene thiophenic structure of the repeating unit. The differences

in the chemical structure of the polymers were well reflected by their $T_d$ values. The molecular weight also influenced the $T_d$ value (not the main factor), with a larger molecular weight being related to a higher starting $T_d$, as observed in the cases of PT1 and PT2.
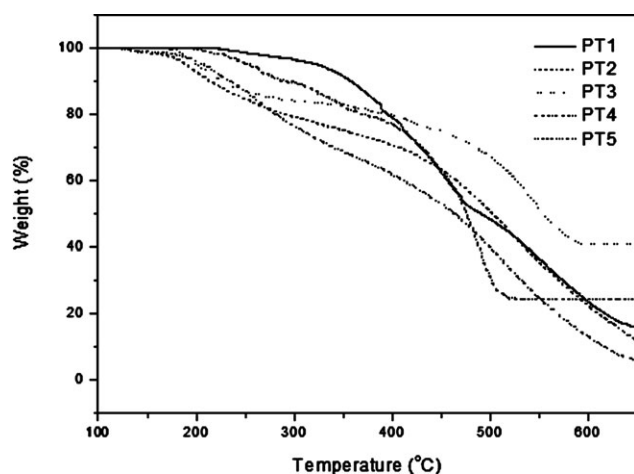
**Figure 7.** TGA curves of the polymers. A heating rate of 10°C/min with a nitrogen flow of 75 cm³/min was used with the runs being conducted from room temperature to 800°C.

**Table III.** $T_d$ and $T_m$ Values of the Polymers

| Polymer | PT1 | PT2 | PT3 | PT4 | PT5 |
|---|---|---|---|---|---|
| $T_i$ (°C) | 248 | 150 | 189 | 204 | 202 |
| $T_d$ (°C) | 325 | 233 | 237 | 248 | 250 |
| $T_m$ (°C) | 228 | 175 | 200 | 206 | 189 |

For all of the samples, the TGA thermograms showed a clear endothermic peak, which belonged to the polymer fusion. As already observed for the $T_d$'s, the $T_m$'s of the different polymers were related to the kind of functional groups introduced in the side chains and to their molecular weight. No evident endothermic flexures were found; this indicated that these polymers had stable and regular molecular conformations.

**CONCLUSIONS**

A series of new conjugated piperidinyl-substituted PTs PT1–PT5 were synthesized with the ferric trichloride oxidative polymerization method. All of the polymers were soluble in common good solvents and partially soluble in poor solvents. PT1, PT3, and PT4 showed higher solubility because of their functional groups and lower molecular weight. The high regioregularity of PT3 was confirmed by ¹H-NMR spectra and also existed in the other polymers in this series. Both in solution and solid state, the luminescence properties of PT3 was the best in this series, and its light emission was in the yellow–red region in the film (725 nm). In both the UV–vis and PL spectra, all of the polymers exhibited redshifts from the solution to the solid film; this was attributed to the high distortion of the excited state with respect to the solid state. Furthermore, the $E_g^{EC}$ values of all the polymers were slightly higher than the $E_g^{opt}$ values; this was attributed to structural differences in the thin films due to swelling by the solvent or the exciton binding energy for the conjugated polymers. From the calculated data of $T_d$ and $T_m$, we found that PT1 possessed higher $T_d$ and $T_m$ values than the

other samples. This suggested a stronger binding force between the propyl and piperidinyl groups. Strikingly, all five polymers exhibited reversible *p*-doping/dedoping (oxidation/reneutralization) processes; this indicated that these polymers had good electrical properties under doping conditions.

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