

# Synthesis, Spectroscopy, and Electrochemical Investigation of New Conjugated Polymers Containing Thiophene and 1,3,4-Thiadiazole in the Main Chain

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**ABSTRACT:** Novel photoluminescent donor–acceptor poly(*p*-phenylenevinylene)-type conjugated polymers containing thiophene and 1,3,4-thiadiazole units in the main chain were synthesized from 2,5-bis(5-bromomethyl-2-thienyl)-1,3,4-thiadiazole and 1,3/1,4-benzenedialdehyde by Wittig–Horner reaction. The synthesized polymers were characterized by the use of thermal analysis and spectroscopic (infrared, UV-visible absorption, and photoluminescence) measurement. The resultant material exhibited bluish green, green, and orange fluorescence in their

solution and thin film and solid forms, respectively. The redox property of the polymers has also been studied by cyclic voltammetry. The optical and electrochemical studies reveal that these novel polymers are new promising materials for the development of efficient polymer light-emitting diodes. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1882–1889, 2012

**Key words:** conjugated polymers; thiophene and thiadiazole-containing polymer; photoluminescence

## INTRODUCTION

Conjugated polymers have attracted increasing attention in the past 20 years on account of their unique electrical and optical properties.<sup>1,2</sup> Their application as light-emitting materials has resulted in a new kind of electroluminescent (EL) devices—polymer light-emitting diodes (PLEDs),<sup>3,4</sup> which have shown many advantages over molecule-based EL devices. These PLEDs are quite promising for the development of low-cost, multicolored, large-area active flat panel display. Polyphenylene vinylene (PPV),<sup>5</sup> polythiophene (PT),<sup>6,7</sup> poly(*p*-phenylene) (PPP),<sup>8</sup> and polyfluorene<sup>9,10</sup> are widely used conjugated polymers in PLEDs. These are *p*-type, hole-transporting, semiconductor materials. There have been attempts to increase efficiency, color tenability, and stability of the EL devices by synthesizing new molecules.

To modify the above-mentioned polymers, conjugated polymers constituted of *p*-phenylene units and

heterocyclic compounds such as 1,3,4-oxadiazoles, carbazoles, and/or thiophenes,<sup>11–16</sup> revealing electron- or hole-transporting properties, have been synthesized by various reactions.<sup>17–21</sup> It was found that the introduction of rings into the polymer backbone effectively improves the electronic structure and charge-transporting properties of the conjugated polymers to give photoluminescent (PL) and EL polymers with suitable levels of bandgap energies.

Some oxadiazole, triazines, and triazole-containing polymers have been synthesized as electron transporting or hole-blocking materials in the organic LEDs.<sup>22–25</sup> For most of the polymers used so far in LED devices, the charge carrier injection is not balanced, and mobility of the holes and electrons is significantly different. This charge imbalance is one of the key factors to increase the EL quantum efficiency of PLEDs. The thiadiazole ring has been incorporated into the backbone of a number of polymers with desirable chemical and thermal stability. The thiadiazoles have been broadly applied in the areas of pharmaceutical, agricultural, industrial, and polymer chemistry. Thiadiazole polyamides, polyesters, polyethers, and polyhydrazides are useful as packaging materials, fibers, electrical insulators, and membranes for reverse osmosis.<sup>26,27</sup> The molecular and electronic structure of monocyclic thiadiazoles is of considerable interest, because they are isoelectronic with thiophenes, thiazoles, pyrazines, and

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related five- and six-membered heterocycles.<sup>28</sup> These are systems of growing interest in materials science in view of the potential technological applications in fields such as electronic, nonlinear optics, sensors, or corrosion protection.<sup>29,30</sup> For full-color applications, it is necessary to have a set of red, green, and blue emitters with sufficiently high-luminous efficiency and proper chromaticity. However, to date, the corresponding development of organic materials for red electroluminescence lags significantly behind the other two primary colors. Some researchers<sup>31</sup> have found that the introduction of thiophene could cause large red shifts in the absorption spectra.

To the best of our knowledge, a light-emitting, vinylene linkage-based polymer-containing thiophene and 1,3,4-thiadiazole moieties have not been reported so far. In this work, we report the synthesis, characterization, spectroscopic, and electrochemical studies of conjugated polymers containing thiophene 1,3,4-thiadiazole and vinylene linkage in the main chain.

## EXPERIMENTAL

### Materials

5-Methyl-2-thiophenecarboxylic acid (Aldrich), triethyl phosphite (Lancaster), 1,3/1,4-benzenedialdehyde (Aldrich), Lawesson's reagent (LR; Merck India), *N*-bromosuccinimide, 4-methyl benzoic acid, hydrazine hydrate (99%), sodium methoxide, benzoyl peroxide, thionyl chloride, tetrahydrofuran (THF), *N,N*-dimethyl acetamide (AR), triethylamine (TEA; AR), and silica gel (60–120; SD Fine Chemicals, India) were used as received.

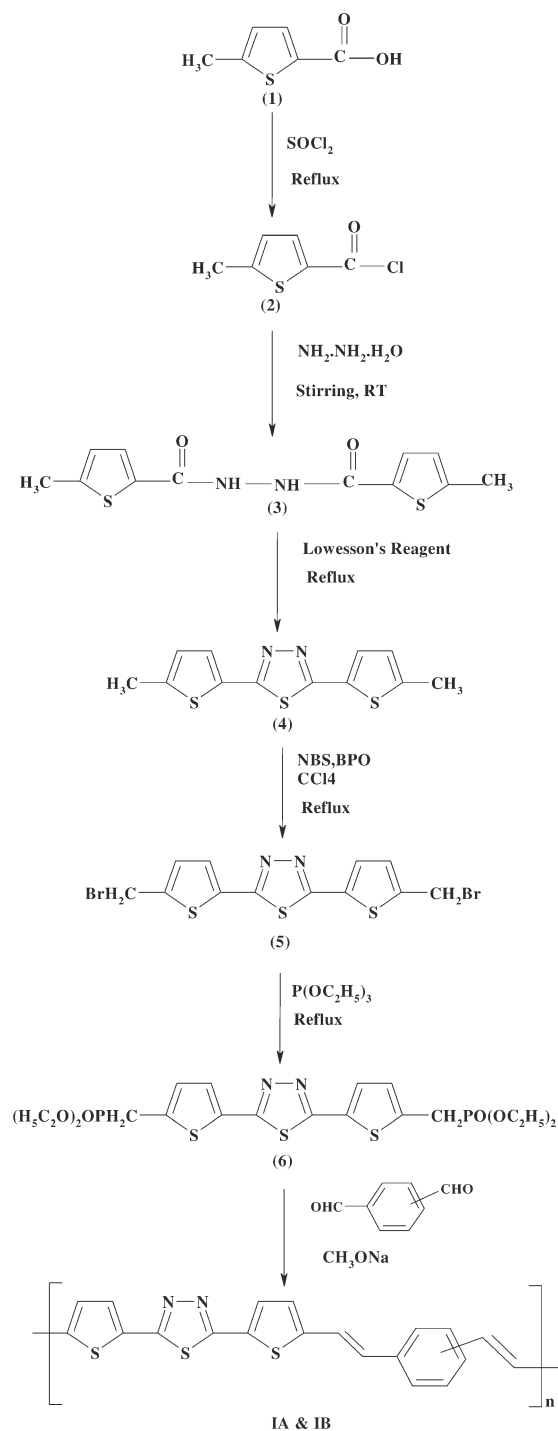
### Measurements

IR spectra were recorded on Perkin-Elmer 1600 FTIR spectrometer using KBr pellet technique. <sup>1</sup>H and <sup>13</sup>C-NMR spectra were recorded in deuterated chloroform and dimethylsulfoxide on VRX-300, Bruker 500 MHz spectrophotometer. The mass spectra were recorded on AI MS 30 double-beam mass spectrometer. The thermogravimetric (TG) analyses were made with NETZSCH 409 thermal analyzer under N<sub>2</sub> atmosphere at a heating rate of 10°C/min. The polymer determined in THF by Maldi-Tof (Micromass Tof Spec 2E, matrix used was  $\alpha$ -cyano-4-hydroxy cinnamic acid).

The UV-vis absorption and steady-state fluorescence experiments were recorded using Shimadzu UV2100 spectrophotometer and Spex fluorimeter (Fluorolog 1681), respectively. A stock solution was prepared separately for polymers by dissolving the required amount of the compound in THF (~ 2 mg/10 mL). Aliquots (3 mL) of these solutions were added to quartz cuvettes

thermostated at 25°C. The absorbance was adjusted to 0.04 at  $\lambda_{\text{max}}$  of the respective compound. The same solution was then used for the fluorescence measurement. For quantum yield measurement, a solution of Alq<sub>3</sub> was prepared in DCM and diluted to have an absorbance of 0.04 at 383 nm. Quantum yield was corrected for the refractive index of the solvents.<sup>32</sup> Alq<sub>3</sub> was used as the reference compound because of the similarity of emission spectra of Alq<sub>3</sub> and the new compounds.

Electrochemical study by cyclic voltammetry (CV) gives the location of the HOMO and LUMO levels with respect to the free electron level in vacuum.<sup>33</sup> This is important for organic electronics. The fundamental processes in organic light-emitting diodes, charge creation, migration, and recombination are decisively determined by charged states in the active, organic layer.<sup>34</sup> Despite the model character of the MO concept, information on the relative positions of both HOMOs and LUMOs is helpful with regard to the manufacture of devices and can be approximately derived from the oxidation and reduction potentials. Oxidation and reduction of polymers were performed by cyclic voltammetry in THF. For cyclic voltammetry, only soluble portion of the polymer in THF was used, and cyclic voltammograms were recorded. Cyclic voltammetry experiments were carried out at 20°C using software-controlled potentiostat/galvanostat (EG&G PAR, Model 273A). The electrochemical experiments were carried out using a conventional three-electrode standard 2 cm<sup>3</sup> cell in which a glassy carbon disk electrode (area: 0.06 cm<sup>2</sup>) and Pt gauze were used as the working and counter electrodes, respectively. Silver wire was used as quasi-reference electrode. The working solution (0.1M tetrabutylammonium perchlorate, TBAP in THF) was degassed by bubbling dry argon gas through it for about 10–15 min before each experiment. Also, during the experiment, bubbling was on well above the surface of the solution to prevent the entry of oxygen in the solution. Before each experiment, the working electrode was carefully washed and polished with 0.05  $\mu\text{m}$  alumina mixed with water. The potential was swept from 0 to -2.0 V and back to 0 V, and, in the next cycle, it was swept from 0 to +2.0 V and back to 0 V with the sweep rate of 100 mV/s to record the current-voltage curve. Cyclic voltammograms were also recorded at different scan rates. As the quasi-reference electrode was used, ferrocene was used as internal reference. So, after recording cyclic voltammograms at different scan rate, ferrocene was added to the solution, and cyclic voltammograms were recorded. Peak potentials were referred w.r.t. Fc/Fc<sup>+</sup> couple. After each experiment, the glassy carbon electrode was washed with water and polished as mentioned earlier.



**Scheme 1** IA: Thia-PTmPV (m-linkage); IB: Thia-PTpPV (p-linkage).

### Monomer Synthesis

#### Synthesis of bis(5-methyl-2-thienyl) hydrazide (3)

A mixture of 5.68 g (40 mmol) of 5-methyl-2-thiophene carboxylic acid (**1**) and an excess of thionyl chloride (10 mL) was dissolved in dry benzene (30 mL), then the mixture was refluxed for 4 h, and the excess thionyl chloride and benzene were distilled out. To the residue, 30 mL dry benzene was added

and distilled. This procedure was repeated thrice to ensure the complete removal of thionyl chloride. Then the mixture of resulting acid chloride and TEA (2 mL) in *N,N*-dimethylacetamide (30 mL) was cooled to 0°C, and hydrazine hydrate (1 mL and 20 mmol) was slowly added into it. After the addition, the reaction mixture was allowed to attain the room temperature and then it was stirred for next 3 h. Resulting solution was poured into the ice-cold water, and corresponding hydrazide was precipitated out. The precipitate was filtered and washed with water and cold methanol, and white solid product was obtained.

Yield: 4.82 g (87%). M. P.: 290°C.

IR (KBr): 3200 (N—H stretching), 1640 (C=O stretching), 1596, and 1450  $\text{cm}^{-1}$  (C=C stretching).  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  2.51 (s, 6H, Ar—CH<sub>3</sub>),  $\delta$  6.92 (d, 2H, Ar—H),  $\delta$  7.68 (d, 2H, Ar—H), and 10.34 (s, 2H, NH).  $^{13}\text{C-NMR}$ : 15.45, 127.07, 129.67, 135.04, 146.01, and 161.23 ppm. Mass (m/z): 280.

#### Synthesis of 2,5-bis (5-methyl-2-thienyl)-1,3,4-thiadiazole (4)

A mixture of bis(5-methyl-2-thienyl)hydrazide (**3**) (4.20 g and 15 mmol) and LR (12.12 g and 30 mmol) was stirred in refluxing 1,4-dioxane for 24 h, a light brown product precipitated during the reaction. After the reaction, precipitate was collected by filtration and washed with 1N NaOH to remove excess of LR and then with water. The crude product was crystallized by petroleum ether to yield needle shape crystal.

Yield: 3.68 gm (88%) M. P.: 105°C

IR (KBr): 1588, 1450 (C=C stretching), 1566 (C=N stretching), 1411, and 1245  $\text{cm}^{-1}$  (C—S—C linkage).  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.59 (s, 6H, Ar—CH<sub>3</sub>), 6.83 (d, 2H, Ar—H), and 7.38 (d, 2H, Ar—H).  $^{13}\text{C-NMR}$ : 15.52, 126.28, 129.53, 129.82, 144.58, and 160.68 ppm. Mass (m/z): 278.

#### Synthesis of 2,5-bis (5-bromomethyl-2-thienyl)-1,3,4-thiadiazole (5)

A mixture of 2,5-bis (5-methyl-2-thienyl)-1,3,4-thiadiazole (**4**) (2.78 g and 10 mmol) and *N*-bromosuccinimide (3.89 g and 22 mmol) was dissolved in  $\text{CCl}_4$ ,

**TABLE I**  
Thermal Behavior Data of Polymers

Polymer	$E^{\text{ox}}$	$E^{\text{red}}$	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$
	V versus Fc/Fc <sup>+</sup>		eV	
Thia-PTmPV	0.69	-1.57	-5.74	-3.48
Thia-PTpPV	0.70	-1.62	-5.75	-3.43

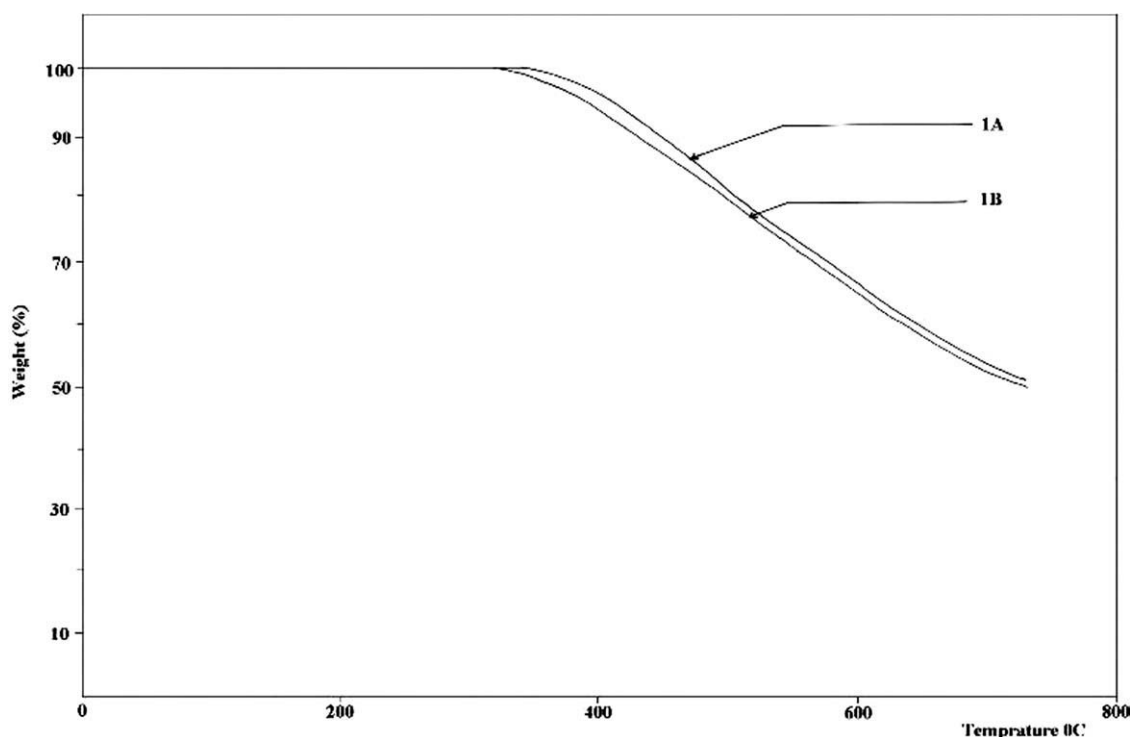


Figure 1 TG curve for polymer IA and IB.

catalytic amount of benzoyl peroxide was added, and the reaction mixture was stirred at reflux temperature for 5 h. The resulting solution was filtered and washed with chloroform. The filtrate was evaporated under reduced pressure to give crude product. The product was purified by washing with water and methanol to get pale yellow solid.

Yield: 3.96 g (91%), M.P: 254°C

IR (KBr)-1588, 1450 (C=C stretching), 1566 (C=N stretching), 1404, 1250  $\text{cm}^{-1}$  (C—S—C linkage), and 1202  $\text{cm}^{-1}$  (CH<sub>2</sub>—Br wagging). <sup>1</sup>H-NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  4.74 (s, 4H, —CH<sub>2</sub>Br), 7.15 (d, 2H, Ar—H), and 7.40 (d, 2H, Ar—H). Mass (m/z): 436.

## Polymer synthesis

### Synthesis of Thia-PTmPV (IA)

A mixture of 2,5-bis(5-bromomethyl-2-thienyl)-1,3,4-thiadiazole (0.872 g and 2 mmol) and excess of triethylphosphite (4 mL) was refluxed for 4 h. After 4 h,

the isolation of the intermediate was done by cooling the reaction mixture followed by the addition of hexane. The intermediate compound was washed several times with hexane to remove excess of triethylphosphite, and then the solvent was removed under reduced pressure. After cooling the reaction mixture to 0–5°C, the intermediate bis-phosphonate was dissolved in dry methanol, sodium methoxide (2.5 g) was added in one portion, and reaction mixture was allowed to attain room temperature. To this reaction mixture, 1,3-benzenedialdehyde (0.272 g and 2 mmol) was added dropwise. The reaction mixture was stirred for 3 h at 60°C. After completion of the

TABLE II  
Optical Data of the Polymers in Solution and on Film

Polymer	IDT <sup>a</sup> (°C)	Temperature (°C) at various weight loss (%)		
		10	20	40
Thia-PTmPV	350	458	512	648
Thia-PTpPV	325	437	500	635

<sup>a</sup> Initial decomposition temperature.

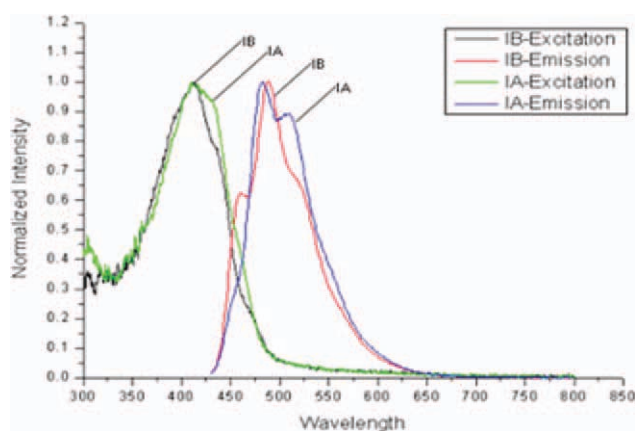
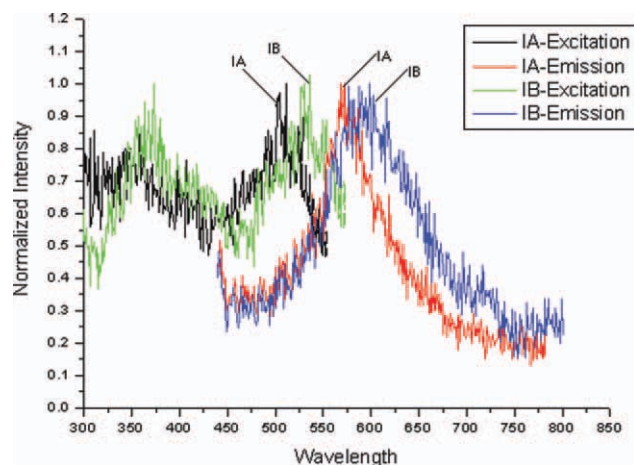


Figure 2 Excitation and emission spectra of IA and IB in THF. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 3** Excitation and emission spectra of IA and IB on film. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

reaction, the excess of methanol was evaporated, and then it was dumped in ice-cold water. The precipitated polymer was then collected by filtration. Polymer was washed with water and then purified by extraction with methanol in Soxhlet extractor for 10 h.

IR (KBr): 944 (vinylene linkage bonds trans configuration), 1414, 1209, 1045 (C—S—C linkage) 1688, and 2720 (aldehyde). Maldi-Tof showed molecular mass of 2650 for soluble portion.

#### Synthesis of Thia-PTpPV (IB)

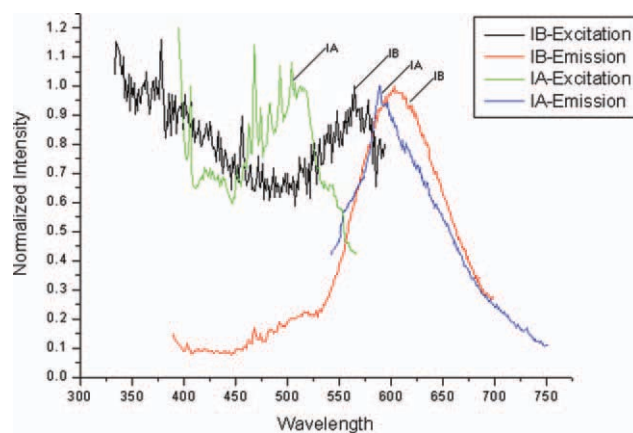
Thia-PTpPV (IB) was synthesized according to the procedure used for the synthesis of Thia-PTmPV (IA), using 1,4-benzenedialdehyde instead of 1,3-benzenedialdehyde.

IR (KBr): 945 (vinylene linkage bonds trans configuration), 1045, 1209, 1414 (C—S—C linkage), 1685, and 2725 (aldehyde)  $\text{cm}^{-1}$ . Maldi-Tof showed molecular mass of 2800 for soluble portion.

## RESULTS AND DISCUSSION

### Synthesis and characterization

The synthetic route for the polymers, Thia-PTmPV (IA) and Thia-PTpPV (IB), is outlined in Scheme 1.



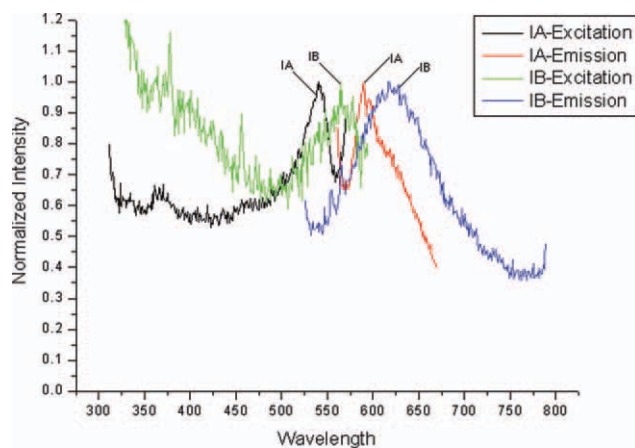
**Figure 4** Excitation and emission spectra of soluble portion of IA and IB in solid state. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The monomer bis(5-methyl-2-thienyl) hydrazide (**3**) was synthesized from 5-methyl-2-thiophenecarboxylic acid (**1**) as the starting material. 5-Methyl-2-thiophenecarboxylic acid was first treated with thionyl chloride to yield 5-methyl-2-thiophenecarboxyl chloride (**2**); the resultant acid chloride was reacted with hydrazine hydrate in TEA to yield (**3**) in 87% yield. The ring closure reaction of bis(5-methyl-2-thienyl) hydrazide (**3**) with LR at the reflux temperature was carried out to yield 2,5-bis(5-methyl-2-thienyl)1,3,4-thiadiazole (**4**), and it was brominated with *N*-bromosuccinimide to give 2,5-bis(5-bromomethyl-2-thienyl)-1,3,4-thiadiazole (**5**) and then converted into the corresponding 2,5-bis{5-[(diethoxyphosphinyl)methyl]-2-thienyl}-1,3,4-thiadiazole (**6**) by the reaction of (**5**) with excess triethylphosphite. The polymerization between monomer (**5**) and 1,3/1,4-benzenedialdehyde was carried out through Wittig-Horner reaction in the presence of sodium methoxide in a methanol at 60°C. The polymers were obtained as a solid, which were extracted with methanol in Soxhlet extraction. IR spectrum of compound (**6**) exhibits bands at 1250  $\text{cm}^{-1}$  (phosphate ester), 1020  $\text{cm}^{-1}$  (P—O—C linkage), and 1568  $\text{cm}^{-1}$  (C=N stretching).  $^1\text{H-NMR}$  (500 MHz and  $\text{CDCl}_3$ ) spectrum of bisphosphonate (**6**) showed signals at  $\delta$  1.31 (t, 12H,  $\text{CH}_2\text{—CH}_3$ ), 3.38 (d, 4H,  $\text{CH}_2\text{—P}$ ), 4.09–4.15 (m, 8H,  $\text{CH}_2\text{—CH}_3$ ), 7.02–7.03 (t, 2H, Ar—H), and

**TABLE III**  
Optical Data of the Polymers in Solid State

Polymer	$\lambda_{\text{max}}$ (nm)		$\lambda_{\text{em}}$ (nm)		Quantum yield <sup>a</sup> ( $\Phi$ )	Optical bandgap (eV)
	Solution	Film	Solution	Film		
Thia-PTmPV	412	373, 513	483, 510	573	0.47	2.67
Thia-PTpPV	412	379, 531	460, 489, 517	598	0.46	2.75

<sup>a</sup> The quantum yield is w.r.t.  $\text{Alq}_3$ . Quantum yield of  $\text{Alq}_3$  in DCM is 0.22.<sup>36</sup>



**Figure 5** Excitation and emission spectra of insoluble portion of IA and IB in solid state. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

7.40 (d, 2H, Ar-H). Mass spectrum shows molecular ion peak at  $m/z$  550.

IR spectrum of polymer (IA), which shows the absorption band at  $944\text{ cm}^{-1}$ , indicates that the vinylene bonds are in trans configuration. A strong absorption band is observed at  $1688$  and  $2720\text{ cm}^{-1}$  due to aldehyde,  $1414$ ,  $1209$ , and  $1045\text{ cm}^{-1}$  due to (C-S-C linkage). IR spectrum of polymer (IB) exhibits bands at  $945$ ,  $1045$ ,  $1209$ ,  $1414$ ,  $1457$ ,  $1535$ ,  $1591$ ,  $1685$ , and  $2725\text{ cm}^{-1}$ . The polymers (Thia-PTmPV and Thia-PTpPV) are sparingly soluble in  $\text{CHCl}_3$ , THF, and DMSO. Because of poor solubility, polymers were subjected to extraction in THF by Soxhlet apparatus for about 100 h. The soluble portions of the polymers were obtained by evaporating THF. The polymer determined in THF by Maldi-Tof (Micromass Tof Spec 2E, matrix used was  $\alpha$ -cyano-4-hydroxy cinnamic acid) is proved to be low-molecular weight. Maldi-Tof showed molecular mass of 2650 and 2800 for soluble portion of (IA) and (IB), respectively.

### Thermogravimetric analysis

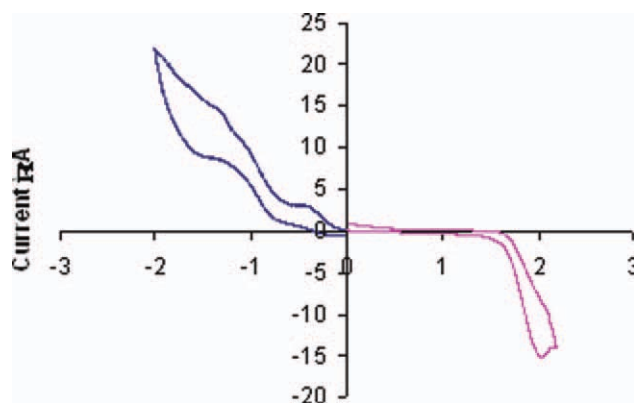
Thermal stability of polymers is important for the lifetime of the device. Thermal stability of the polymers was determined by thermogravimetric (TG) analysis under nitrogen at a heating rate of  $10^\circ\text{C}/\text{min}$ . TG

**TABLE IV**  
Electrochemical Data of Polymers

Polymer	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm)
s-Thia-PTmPV <sup>a</sup>	513	590
i-Thia-PTmPV <sup>b</sup>	536	594
s-Thia-PTpPV <sup>a</sup>	541	603
i-Thia-PTpPV <sup>b</sup>	565	618

<sup>a</sup> s-soluble.

<sup>b</sup> i-insoluble.



**Figure 6** Cyclic voltammogram of IA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

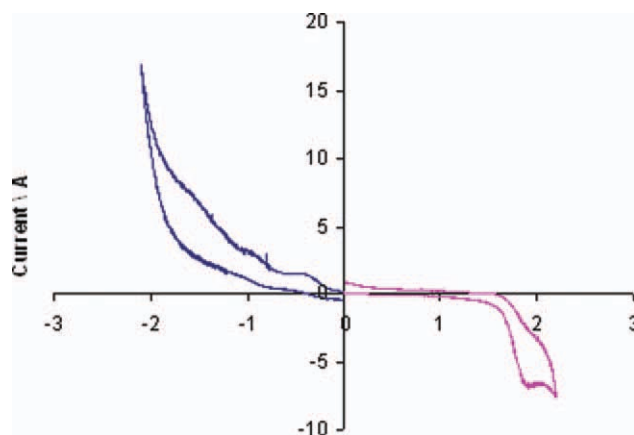
analysis reveals that the polymers are stable in nitrogen up to  $325^\circ\text{C}$ . The results indicated that the introduction of the thiadiazole moiety increased the rigidity in the structure. The decomposition temperatures of polymers are relatively high due to the rigid structure. The temperature characteristics, such as initial decomposition temperature, temperature for 10% weight loss ( $T_{10}$ ), temperature for 20% weight loss ( $T_{20}$ ), and temperature for 40% weight loss ( $T_{40}$ ) of the polymers are summarized in Table I. TG curves of polymers IA and IB are shown in Figure 1.

### Optical Properties

Studies for UV-vis absorption and steady-state fluorescence experiments were carried out with both the portions (soluble and insoluble) of the polymers.

### UV-vis and PL study of soluble portion in solution and on thin film

The solutions were prepared by dissolving the polymers in THF, and its film on the glass was used for



**Figure 7** Cyclic voltammogram of IB. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

TABLE V  
HOMO (IP) and LUMO (EA) Energy Levels Data of Polymers

Compound	$E_{pc1}$	$E_{pc2}$	$E_{pa1}$	eV	eV
	V versus Fc/Fc <sup>+</sup>			Bandgap ( $E_g^a$ )	Optical bandgap solution
Thia-PTmPV	-2.11	-2.52	+0.94	3.05	2.67
Thia-PTpPV	-1.98	-2.52	+0.83	2.81	2.75

UV-vis absorbance and fluorescence measurement. The absorption and photoluminescence spectra of the polymers in solution and in thin film were measured at room temperature. The data is given in Table II.

In solution, the polymers emit strong bluish green fluorescence in the visible range. The polymers show absorption maxima at 412 nm for both the polymers, Thia-PTmPV and Thia-PTpPV. Broad bands were obtained indicating the noncoplanarity and rotational freedom of the individual rings. The emission spectra exhibit peaks at 483 nm with a shoulder at 510 nm for Thia-PTmPV and 489 nm with a shoulder at 460 and 517 nm for Thia-PTpPV. The excitation emission spectra of soluble portion of the polymers, IA and IB, in THF and on film are shown in Figures 2 and 3, respectively. The 0-0 transition was determined from the intersection of the absorption and emission spectra, which corresponds to bandgap of 2.67 eV for Thia-PTmPV and 2.75 eV for Thia-PTpPV. The bandgap value is less compared to those of poly(phenylene-1,3,4-oxadiazole)s (3.22–3.02 eV)<sup>24,35</sup> and a series of 1,3,4-oxadiazole- and triphenylamine-containing molecules (2.98–2.83eV).<sup>22</sup> This can be attributed to the strong electron-donating nature of the thiophene ring and the highly conjugated structure of the polymer. The polymers are sparingly soluble in THF, and the fluorescence quantum yield of the polymers in THF was estimated with respect to Alq<sub>3</sub>.<sup>36</sup> The relative quantum yield for both the polymers is around 47%. The absorption spectra of the films of the polymer Thia-PTmPV showed absorption at 373 and 513 nm, whereas Thia-PTpPV showed at 379 and 531 nm. The PL of solid film was weak. The PL spectra of the film samples show emission at 573 nm for Thia-PTmPV, whereas, for Thia-PTpPV, emission was observed at 598 nm corresponding to the yellow green emission. Emission maxima are red shifted compared to the solution.

#### PL study of the soluble and insoluble portion of the polymers in solid state

PL measurements of the solid portions of the polymer (dry powder) were carried out by taking the respective solid compounds in glass tube at room temperature. It was found that polymers emit orange fluorescence in solid state. The data is given in Table III. From the table, it was seen that the emis-

sion maximum of PL of insoluble part of the polymer is red shifted to its corresponding soluble portion. It indicates that the soluble portion contributes to low-molecular weight, while insoluble portion consists of high-molecular weight polymers. The PL properties of the film prepared from the THF solution and the solid portion of the polymer (dry powder) were compared. The PL study revealed that the polymers emit fluorescence at higher wavelength in solid state when compared with solution and film. The excitation emission spectra of the polymers, IA and IB, in solid state are shown in Figures 4 and 5.

#### Electrochemical study

The CV in the oxidation region exhibits one irreversible wave with  $E_{p,a} = +1.23$  V versus SCE. It is due to the formation of the radical cation. Two adjacent nitrogen atoms in a heterocyclic unit seem to favor follow-up reactions and decomposition of the cation radical.<sup>37</sup> The irreversibility of the oxidation of conjugated systems containing 1,3,4-oxadiazole units was mentioned before in several publications.<sup>38–44</sup> Reduction and oxidation potentials as well as the electrochemically determined energy gaps are listed in Table IV. The cyclic voltammograms of Thia-PTmPV and Thia-PTpPV are shown in Figures 6 and 7. The oxidation to the cation radical is fully irreversible for both the compounds. Two adjacent nitrogen atoms in a heterocyclic unit seem to favor follow-up reactions and decomposition of the cation radical. Both polymers show quasi-reversible two reduction peaks that indicate the formation of mono- and dianions. All peak potentials given in Table IV are comparable to other reported oligoheterocycles<sup>37</sup> containing thiophene and thiadiazole reported earlier.

The potential of oxidation and reduction processes obtained in CV can be used to estimate the HOMO and LUMO energy levels of the molecules.<sup>45</sup>

$$E_{\text{HOMO}} = -qE^{\text{ox}} - 4.5\text{eV}$$

$$E_{\text{LUMO}} = -qE^{\text{red}} - 4.5\text{eV}$$

In the above equations,  $E^{\text{ox}}$  and  $E^{\text{red}}$  are determined with respect to NHE. It is to be noted that the redox potential of ferrocene/ferrocenium couple is +0.55 V versus NHE. Thus, Table V shows the



values of  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  for the two molecules, Thia-PTmpPV and Thia-PTpPV. More recently, D'Andrade et al.<sup>33</sup> have verified the correlation between cyclic voltammetric potential and  $E_{\text{HOMO}}$  determined by direct method. The following relation was satisfied by a large number of molecules:

$$E_{\text{HOMO}} = -(1.4 \pm 0.1)qE^{\text{ox}} - (4.6 \pm 0.08)\text{eV},$$

where  $E^{\text{ox}}$  is the cyclic voltammetric oxidation potential determined with respect to ferrocene/ferrocenium couple in polar organic liquids. The  $E_{\text{HOMO}}$  calculated using this equation is in good agreement with the values given in Table V.

### CONCLUSION

In conclusion, novel PPV-based polymers containing thiophene and 1,3,4-thiadiazole heterocyclic moieties in the main chain were successfully designed and synthesized by Wittig–Horner reaction. Polymers have found to be thermally stable and exhibited photoluminescence in solution, as well as in the form of film, and, in solid state, these polymers exhibit bluish green, green, and orange fluorescence, respectively. The optical measurement showed the bandgap for these polymers in the range of 2.67–2.75 eV. CV experiments showed that these polymers have LUMO energy levels ranging from –3.43 to –3.48 eV and HOMO energy levels ranging from –5.74 to –5.75 eV w.r.t ferrocene/ferrocenium couple in polar organic solvents.

### References

- Epstein, A. J. *MRS Bull* 1997, 16.
- Aklrud, L. *Prog Polym Sci* 2003, 28, 875.
- Yang, Y. *MRS Bull* 1997, 31.
- Greenham, N. C.; Friend, R. H. In *Solid State Physics*, Vol. 49; Ehrenreich, H., Spaepen, F., Eds. Academic Press: San Diego, CA, 1995; p 2.
- Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* 1990, 347, 539.
- Berggren, M.; Inganäs, O.; Gustafsson, G.; Rasmussen, J.; Andersson, M. R.; Hjertberg, T.; Wennerstrom, O. *Nature* 1994, 372, 444.
- Pei, J.; Yu, W.-L.; Huang, W.; Heeger, A. J. *Chem Commun* 2000, 1631.
- Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv Mater* 1992, 4, 36.
- Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn J Appl Phys* 1991, 30, L1941.
- Leclerc, M. *J Polym Sci Part A: Polym Chem* 2001, 39, 2867.
- Brown, A. R.; Bradley, D. D. C.; Burroughes, J. H.; Friend, R. H.; Greenham, N. C.; Burn, P. L.; Holmes, A. B.; Kraft, A. *Appl Phys Lett* 1992, 61, 2793.
- Chung, S.-J.; Kwon, K.-Y.; Lee, S.-W.; Jin, J.-I.; Lee, C.-H.; Lee, C.-E.; Park, Y. *Adv Mater* 1998, 10, 1112.
- Chung, S.-J.; Jin, J.-I.; Lee, C.-H.; Lee, C.-E. *Adv Mater* 1998, 10, 684.
- Huang, W.; Meng, H.; Yu, W.-L.; Gao, J.; Heeger, A. J. *Adv Mater* 1998, 10, 593.
- Huang, W.; Meng, H.; Yu, W.-L.; Pei, J.; Chen, Z.-K.; Lai, Y.-H. *Macromolecules* 1999, 32, 118.
- Peng, Z.; Bao, Z.; Galvin, M. *Adv Mater* 1998, 10, 680.
- Gilch, H. G.; Wheelwright, W. L. *J Polym Sci A* 1966, 1/4, 1337.
- Hörhold, H. H.; Opfermann, J. *Makromol Chem* 1970, 31, 105.
- Hörhold, H. H.; Helberg, M. *Makromol Chem Macromol Symp* 1987, 12, 229.
- Bao, Z.; Chen, Y.; Cai, R.; Yu, L. *Macromolecules* 1993, 26, 5281.
- Koch, F.; Heitz, W. *Macromol Chem Phys* 1997, 198, 1531.
- Tamoto, N.; Adachi, C.; Nagai, K. *Chem Mater* 1997, 9, 1077.
- Pei, Q.; Yang, Y. *Chem Mater* 1995, 7, 1568.
- Li, X. C.; Spencer, G. C. W.; Holmes, A. B.; Moratti, S. C.; Cacialli, F.; Friend, R. H. *Synth Met* 1996, 76, 153.
- Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. J. *Science* 1995, 267, 1969.
- Weinstock, L. M.; Shinkai, I. In *Comprehensive Heterocyclic Chemistry*, Vol. 6; Potts, K. T., Ed. Oxford: Pergamon, UK, 1984.
- Arán, V.; Goya, P.; Ochoa, C. *Adv Heterocycl Chem* 1988, 44, 81.
- Glossman, D. *J Mol Struct (Theochem)* 1995, 330, 385.
- Strohriegel, P.; Grazulevicius, J. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H., Ed.; Wiley/VCH: Chichester, UK, 1997.
- Mullen, K.; Wegner, G. In *Electronic Materials: The Oligomer Approach*; Wiley/VCH: Weinheim, 1998.
- Xue, C.; Luo, F.-T. *Tetrahedron* 2003, 59, 5193.
- Su, J.; Xu, T.; Chen, K.; Tian, H. *Dyes Pigm* 2000, 44, 87.
- D'Andrade, B. W.; Datta, S.; Forrest, S. R.; Djurovich, P.; Polykarpov, E.; Thompson, M. P. *Org Electron* 2005, 6, 11.
- Kraft, A.; Crimdsale, A. C.; Holmes, A. B. *Angew Chem* 1998, 110, 416.
- Janietz, S.; Schulz, B.; Torronen, M.; Sundholm, G. *Eur Polym J* 1993, 29, 545.
- Ravikishore, V. V. N.; Narasimhan, K. L.; Periasamy, N. *Phys Chem Chem Phys* 2003, 5, 1386.
- Mitschke, U.; Debaerdemaeker, T.; Bauerle, P. *Eur J Org Chem* 2000, 3, 425.
- Mitschke, U.; Osteritz, E. M.; Debaerdemaeker, T.; Sokolowski, M.; Bauerle, P. *Chem Eur J* 1998, 4, 2211.
- Bauerle, P.; Mitschke, U.; Osteritz, E. M.; Sokolowski, M.; Müller, D.; Groß, M.; Meerholz, K. *Proc SPIE Int Soc Opt Eng* 1998, 3476, 32.
- Janietz, S.; Schulz, B. *Eur Polym J* 1996, 32, 465.
- Schulz, B.; Bruma, M.; Brehmer, L. *Adv Mater* 1997, 9, 601.
- Freydank, A.; Janietz, S.; Schulz, B. *J Electroanal Chem* 1998, 456, 61.
- Yu, W.-L.; Meng, H.; Pei, J.; Huang, W. *J Am Chem Soc* 1998, 120, 11808.
- Huang, W.; Yu, W.-L.; Meng, H.; Pei, J.; Li, S. F. Y. *Chem Mater* 1998, 10, 3340.
- Mishra, A.; Nayak, P. K.; Ray, D.; Patankar, M. P.; Narasimhan, K. L.; Periasamy, N. *Tetrahedron Lett* 2006, 47, 4715.