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The synthesis, electrochemical and fluorescent properties of monomers and polymers containing 2,5-diphenyl-1,3,4-thiadiazole

Yongxin Tao [a,b], Qingfeng Xu [a], Jianmei Lu [a,*], Xuebo Yang [a,b]

[a] *Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, 199 Renai Road, Suzhou 215123, China*
[b] *Key Laboratory of Fine Chemical Engineering of Jiangsu Province, Jiangsu Polytechnic University, Changzhou 213164, China*

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ABSTRACT

Three, 2,5-diphenyl-1,3,4-thiadiazole-containing vinyl monomers and their polymers were synthesized and the HOMO and LUMO energies of the compounds, as estimated from cyclic voltammetry data, were −6.35 to −6.14 eV and −3.02 to −2.84 eV, respectively. The optical band gaps (E_g) were similar to those determined from cyclic voltammograms. The fluorescent emission spectra of all monomers and polymers displayed either blue or green light emission.

1. Introduction

Five-membered, hetero-aromatic compounds containing imine (–C=N–) groups, such as imidazole [1,2], thiazole [3–5], triazole [6,7], oxadiazole [8,9], and thiadiazole [10–16] have long been of interest as luminophores for optical application, owing to their electron accepting nature. For example, a series of 1,3,4-oxadiazoles derivatives are used for electron accepting materials in organic light-emitting diodes (OLEDs) [17,18]. Monomers containing oxadiazole have been synthesized, such as 2-[4-(4-vinylbenzyloxy)phenyl]-5-phenyl-1,3,4-oxadiazole and 1-(4-vinylbenzyloxy)-3,5-bis[5-(phenyl)-2-oxadiazolyl]benzene [19,20], whilst polymers containing oxadiazole, either in the main- or side-chain have been reported [21–23]; attention has been paid to 1,3,4-thiadiazole-containing polymers [24,25]. Jansson et al. employed density functional theory in a study of a thiadiazole system as electron transportation materials [26]. Thus far, the synthesis of vinyl monomers and their polymers containing 2,5-dipheny-l,3,4-thiadiazole has not been investigated. This paper concerns three, novel monomers and their polymers and their electrochemical and fluorescent properties.

2. Experimental

2.1. Characterizations

^{1}H NMR spectra were measured with a Bruker ARX 300 MHz and INOVA 400 MHz NMR spectrometer, $CDCl_3$ or DMSO-d_6 as solution, TMS as standard. The IR spectra were recorded on an AVATAR 380 FTIR spectrometer (KBr pellet, 4000–400 cm^{-1}). Element analyses were obtained with Perkin-Elmer 2400II instrument. Mass spectra were obtained with Mass spectrum Finnigan HP5890. Molecular weight and the polydispersity relative to polystyrene were measured using a Waters1515 GPC with THF or DMF as eluent and a column temperature of 30°C. UV–visible spectra were recorded on a Perkin-Elmer λ-17 UV–vis instrument. Room temperature emission and excitation spectra were carried out using Edinburgh-920 fluorescence spectra photometer.

2.2. Synthesis of 2-(4-methylphenyl)-5-phenyl-1,3,4-thiadiazole (MPPT) and 2-(4-methoxyphenyl)-5-phenyl-1,3,4-thiadiazole (MOPPT)

All reagents and chemicals were purchased from Sinopharm and were used without further purification. MPPT and MOPPT were synthesized according to Scheme 1.

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* Corresponding author. Tel.: +86 512 65880367; fax: +86 512 65882875.
E-mail address: lujm@suda.edu.cn (J. Lu).

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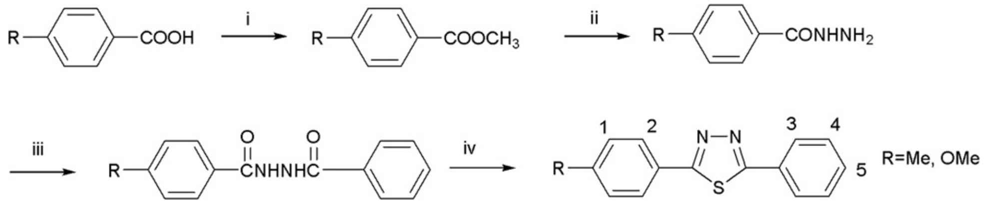


Scheme 1. Synthesis of 2-(4-methylphenyl)-5-phenyl-1, 3, 4-thiadiazole (MPPT) and 5-(4-methoxylphenyl)-2-phenyl-1,3,4-thiadiazole (MOPPT): (i) CH_3OH, H_2SO_4, reflux; (ii) excess hydrazine hydrate, reflux; (iii) benzoyl chloride, pyridine, 0 °C; (iv) Lawesson's reagent, dioxane, 80 °C.

MPPT from 4-toluic acid as white crystals (69%): m.p. 140–141 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ_H, ppm), 2.43(s, 3H, $-CH_3$), 7.29(d, 2H, $J = 8.0$ Hz, Ar–H 1-H), 7.49–7.51(m, 3H, Ar-H 4-H & 5-H), 7.88(d, 2H, $J = 8.1$ Hz, Ar–H 2-H), 7.99–8.02(m, 2H, Ar–H 3-H); MS (m/z, %), 252.0 (M^+, 100); FTIR (KBr, cm^{-1}), 1442 (1,3,4-thiodiazole).

MOPPT from 4-methoxybenzoic acid as white crystals (65%): m.p. 132–134 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ_H, ppm), 3.89(s, 3H, $-OCH_3$), 6.99(d, 2H, $J = 8.6$ Hz, Ar–H 1-H), 7.49–7.51 (m, 3H, Ar–H 4-H & 5-H), δ7.94–8.00 (m, 4H, Ar–H 2-H & 3-H); MS(m/z, %), 268.0 (M^+, 100); FTIR (KBr, cm^{-1}), 1441(1,3,4-thiodiazole).

2.3. Syntheses of the monomers and their model compounds

The synthetic route of the monomers and their saturated model compounds are shown in Scheme 2.

2.3.1. 2-(4-bromomethyl phenyl)-5-phenyl-1,3,4-thiadiazole (BMPPT)

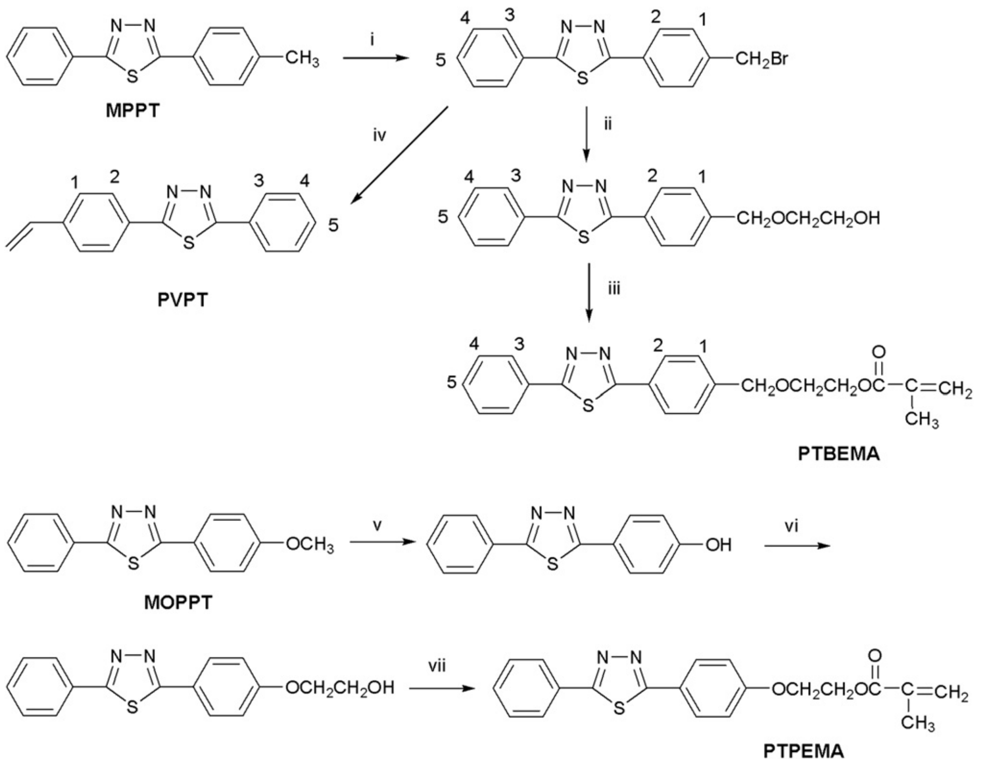
A mixture of MPPT (5.04 g, 0.02 mol), *N*-bromosuccinimide (3.56 g, 0.02 mol) and benzoyl peroxide in 120 mL benzene was stirred at 80 °C for 6 h, being irradiated by incandescent lamp. The crude product was isolated by evaporating the solvent, washed by ethanol and purified by recrystallization from cyclohexanone to yellowy crystals (6.30 g, 95%): m.p.193–195 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ_H, ppm), 4.54(s, 2H, CH_2Br), 7.50–7.54(m, 5H, Ar–H 1-H & 4-H & 5-H), 7.99–8.03(m, 4H, Ar–H 2-H & 3-H); FTIR (KBr, cm^{-1}),1440(1,3,4-thiodiazole).

2.3.2. 2-[4-(5-phenyl-1,3,4-thiadiazole-2-yl)-benzyloxy] ethanol (PTBE)

A mixture of BMPPT (3.31 g, 0.01 mol), sodium hydroxide (0.40 g, 0.01 mol) and 20 mL glycol was stirred at 120 °C for 30 min. The mixture was poured into 100 mL ice water and the resultant yellowy precipitate was filtered off. The crude product was purified by recrystallization from acetone to white crystals (2.93 g, 94%): m.p.94–95 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ_H, ppm), 2.05(s, 1H, OH), 3.64(t, 2H, $J = 4.5$ Hz, $HOC\mathbf{H}_2$), 3.81(t, 2H, $J = 4.5$ Hz, $C\mathbf{H}_2CH_2OH$), 4.64(s, 2H, Ar–CH_2), 7.47–7.52(m, 5H, Ar–H 1-H & 4-H & 5-H), 8.00–8.03 (m, 4H, Ar–H 2-H & 3-H).

2.3.3. 4-(5-phenyl-1,3,4-thiadiazole-2-yl) phenol (PTP)

MOPPT (3.00 g, 0.011 mol) was stirred in 100 mL 50% hydrobromic acid (caution: incompatible with strong bases, strong oxidizing agents, ammonia, ozone, fluorine, water, metals; both air



Scheme 2. Synthesis of 2-[4-(5-phenyl-1,3,4-thiadiazole-2-yl)-benzyloxy] ethyl methacrylate (PTBEMA), 2-phenyl-5-(4-vinylphenyl)-1,3,4-thiadiazole (PVPT) and 2-[4-(5-phenyl-1,3,4-thiadiazole-2-yl)-phenoxy]ethyl methacrylate (PTPEMA): (i) N-bromosuccinimide, benzene, 80 °C; (ii) excess glycol, sodium hydrate, 130 °C (iii) methylacryloyl chloride, triethylamine, THF, 0 °C; (iv) (1) triphenylphosphine; (2) formaldehyde, 20% sodium hydrate solution, 0 °C; (v) 50% hydrobromic acid , 100°C; (vi) chlorethyl alcohol, sodium hydrate solution (vii) methylacryloyl chloride, triethylamine, THF, 0 °C.

and light sensitive) at 100 °C for 20 h. The precipitate was filtered off and washed by deionized water. The crude product was dissolved in NaOH solution and the insoluble residue removed by filtration. 36% Hydrochloric acid was added to the filtrate and the precipitate was filtered off, washed with deionized water and dried under vacuum to give the product as a white powder (2.93 g, 93%): ^{1}H NMR (400 MHz, DMSO-d_6, δ_H, ppm), 6.98 (d, 2H, $J = 8.8$ Hz, Ar–H 1-H), 7.62–7.64 (m, 3H, Ar–H 4-H & 5-H), 7.98 (d, 2H, $J = 8.8$ Hz, Ar–H 2-H), 8.10–8.12 (m, 2H, Ar–H 3-H), 10.38(s, 1H, OH).

2.3.4. 2-[4-(5-phenyl-1,3,4-thiadiazole-2-yl)-phenoxy] ethanol (PTPE)

A mixture of PTP (2.65 g, 0.0104 mol), sodium hydroxide (0.42 g, 0.0105 mol), 0.7 mL 2-chloroethanol (caution: toxic; incompatible with oxidizing agents) and 50 mL H_2O was stirred at 100 °C for 100 min. The precipitate was filtered off, washed with deionized water and dried under vacuum to give the product as a white powder (2.34 g, 75%): ^{1}H NMR (400 MHz, $CDCl_3$, δ_H, ppm): 2.10(s, 1H, OH), 4.00(t, 2H, $J = 4.2$ Hz, HOC**H**$_2$), 4.15(t, 2H, $J = 4.2$ Hz, C**H**$_2$CH$_2$OH), 7.02(d, 2H, $J = 8.4$ Hz, Ar–H 1-H), 7.49(br, 3H, Ar–H 4-H & 5-H), 7.95 (d, 2H, $J = 8.4$ Hz, Ar–H 2-H), 8.00(Br, 3H, Ar–H 3-H).

2.4. Monomers

2.4.1. 2-[4-(5-phenyl-1, 3, 4-thiadiazole-2-yl)-benzyloxy] ethyl methacrylate (PTBEMA)

Methylacryloyl chloride (0.52 g, 5 mmol) in 5 mL dichloromethane was slowly added dropwise into a solution of PTBE (1.56 g, 5 mmol) and triethylamine (0.51 g, 5 mmol) in 10 mL dichloromethane at 0–5 °C; the ensuing solution was stirred for 12 h. The crude product was isolated by evaporating the solvent, and purified using gel chromatography (silica gel, mineral ether/ethyl acetate = 2:1) to yield a white powder, (1.68 g, 88%): m.p.80–82 °C; ^{1}H NMR (300 Hz, $CDCl_3$, δ_H, ppm), 1.98(s, 3H, CH_3), 3.78(t, 2H, $J = 4.7$ Hz, ArCH$_2$OC**H**$_2$), 4.37(t, 2H, $J = 4.7$ Hz, ArCH$_2$OCH$_2$C**H**$_2$), 4.65(s, 2H, Ar–C**H**$_2$), 5.61 (s, 1H, = CH$_2$, cis), 6.16(s, 1H, = CH$_2$, trans), 7.47–7.52(m, 5H, Ar–H 4-H & 5-H), 7.99–8.03(m, 4H, Ar–H 2-H & 3-H); FTIR (KBr, cm^{-1}), 1713 (C=O), 1450 (1,3,4-thiodiazole); Anal. Calcd. for $C_{21}H_{20}N_2O_3S$ (380.4): C 66.31; H 5.26; N 7.37; S 8.42. Found: C 66.37; H 5.31; N 7.33; S 8.39.

2.4.2. 2-phenyl-5-(4-vinylphenyl)-1, 3, 4-thiadiazole (PVPT)

A mixture of BMPPT (3.31 g, 10 mmol) and triphenylphosphine (caution: toxic; incompatible with oxidizing agents, acids) (2.63 g, 10 mmol) in 50 mL chloroform was stirred at 70 °C for 5 h and cooled to room temperature. 37% Formaldehyde solution (20 mL) was poured into the solution and stirred. Subsequently, 30 mL 20% sodium hydroxide solution was slowly added dropwise into the solution and the mixture unceasingly stirred at room temperature for 12 h. The chloroform solution was separated from water solution, washed by water, dried by anhydrous magnesium sulfate. The crude product was isolated by evaporating chloroform, and purified by recrystallization from absolute alcohol to yield white lamellar crystals (2.24 g, 85%): m.p.157–159 °C; ^{1}H NMR(300 Hz, $CDCl_3$, δ_H, ppm), 5.38(d, 1H, $J = 10.9$ Hz, CH$_2$=, cis), 5.88(d, 1H, $J = 17.6$ Hz, CH$_2$=, trans), 6.72(dd, 1H, $J_1 = 17.6$ Hz, $J_2 = 10.9$ Hz, CH$_2$=C**H**), 7.50–7.55(m, 5H, Ar–H 1H & 4-H & 5-H), δ7.97–8.04(m, 4H, Ar–H 2-H & 3-H); FTIR(KBr, cm^{-1}): 1689 (C=C), 1442(1,3,4-thiodiazole); Anal. Calcd. for $C_{16}H_{12}N_2S$(264.2.4): C 72.72; H 4.54; N 10.60; S 12.12. Found: C 72.93; H 4.75; N 10.45; S 11.93.

2.4.3. 2-[4-(5-phenyl-1, 3, 4-thiadiazole-2-yl)-phenoxy] ethyl methacrylate (PTPEMA)

Methylacryloyl chloride (0.52 g, 5 mmol) in 5 mL dichloromethane was slowly added dropwise into the solution of PTPE (1.49 g, 5 mmol) and triethylamine (0.51 g, 5 mmol) in 10 mL dichloromethane at 0–5 °C. The solution was unceasingly stirred for 12 h. The crude product was isolated by evaporating the solvent, and purified by gel chromatography (silica gel, mineral ether/ethyl acetate = 1:1) to yield white powder (1.66 g, 91%): m.p.93–94 °C; ^{1}H NMR (300 Hz, $CDCl_3$, δ_H, ppm), 1.97(s, 3H, CH_3), 4.31(t, 2H, $J = 4.5$ Hz, ArOC**H**$_2$), 4.54(t, 2H, $J = 4.5$ Hz, ArOCH$_2$C**H**$_2$), 5.61(s,1H,=CH$_2$, cis), 6.16(s,1H,=CH$_2$, trans), 6.95–7.04(m, 2H, Ar–H 1-H), 7.40(Br, 3H, Ar–H 4-H & 5-H), 7.90–7.98 (m, 4H, Ar–H 2-H & 3-H); FTIR (KBr, cm^{-1}), 1725 (C=O), 1442(1, 3, 4-thiodiazole); Anal. Calcd. for $C_{21}H_{20}N_2O_3S$ (366.1): C 65.55; H 4.95; N 7.64; S 8.75. Found: C 65.51; H 4.98; N 7.63; S 8.72.

2.5. Polymerizations

The polymerization of the 2,5-diphenyl-1,3,4-thiadiazole-containing vinyl monomers was carried out in toluene with 2,2′-azobisisobutyronitrile (AIBN) as initiator. A mixture of the monomer (1 mmol), AIBN (0.01 mmol) and 2 mL cyclohexanone was placed in a round flask. The flask was sealed and cycled between vacuum and N_2 for four times, and immersed in an oil bath at 65 °C for 6 h. After polymerization, the products were dissolved in THF and precipitated into a large amount of methanol. The precipitate was filtered, washed by methanol and dried under vacuum. The crude polymers were purified by Soxhlet extractor with ethanol to remove of starting monomers.

Poly(PTBEMA) a white powder, yield: 0.351 g, 92.0%. ^{1}H NMR (300 Hz, $CDCl_3$, δ_H, ppm): 1.00–1.11 (Br, CH_3), 1.98 (Br, CH_2), 3.57 (Br, ArCH$_2$OCH$_2$), 4.09 (Br, ArCH$_2$OCH$_2$CH$_2$), 4.40 (Br, ArC**H**$_2$), (m, 2H, Ar–H), 7.36 (Br, Ar–H 1-H & 4-H & 5-H), 7.82 (Br, Ar–H 2-H & 3-H); FTIR (KBr, cm^{-1}): 1729 (C=O), 1442 (1,3,4-thiodiazole); GPC data (THF as eluent): Mn = 19,600, PDI = 1.90.

Poly(PVPT) a white powder, yield: 0.235 g, 89.1%. ^{1}H NMR (300 Hz, $CDCl_3$, δ_H, ppm): 1.3–1.9(Br, CH_2), 1.9–2.6(Br, CH), 7.3(Br, Ar–H), 7.50(Br, Ar–H), 7.68–7.73(Br, Ar–H), 7.94–7.97 (Br, Ar–H), 8.01–8.03(Br, Ar–H); FTIR (KBr, cm^{-1}): 2924 (–C–H–), 1443(1,3,4-thiodiazole); GPC data (DMF as eluent): Mn = 20,800, PDI = 1.52.

Poly(PTPEMA) a white powder, yield: 0.344 g, 94.0%. ^{1}H NMR (400 Hz, $CDCl_3$, δ_H, ppm): 0.93 1.10, 1.25 (Br, CH_3), 1.92 (Br, CH_2), 4.07 (Br, ArOCH$_2$CH$_2$), 6.77(Br, Ar–H), 7.30 (Br, Ar–H), 7.65(Br, Ar–H), 7.75 (Br, Ar–H); FTIR (KBr, cm^{-1}): 1728 (C=O), 1443 (1,3,4-thiodiazole); no GPC data due to poor solubility.

3. Results and discussion

3.1. Synthesis and polymerization of the monomers

To prepare the 2,5-diphenyl-1,3,4-thiadiazole-containing monomers, two inter-mediate compounds, MPPT and MOPPT were synthesized from 4-toluic acid and 4-methoxybenzoic acid via esterification, ammonolysis with hydrazine hydrate, amidation with benzoyl chloride, annelation with Lawesson's reagent and white crystal formation in excess 65% overall yield. Because the hydrogen of methyl group in the benzene ring could be easily substituted by *N*-bromosuccinimide, BMPPT was synthesized from MPPT via bromation. To improve on solubility, the reactive benzyl bromine group could react via chain-extended reaction. PTBE was synthesized from BMPPT via etherification with excessive glycol in the presence of sodium hydroxide. It was a near quantitative reaction. On the other hand, the vinyl monomer, PVPT could be prepared from BMPPT via Wittig reaction with triphenylphosphine and formaldehyde [27,28]. The methoxy group in the benzene ring could be translated to phenolic hydroxyl group via demethylation. PTP was synthesized from MOPPT with hydrobromic acid. PTPE was synthesized from PTP via etherification with chloroethanol due to

Table 1
UV–vis and fluorescent parameters of the monomers and polymers containing 2,5-diphenyl-1,3,4-thiadiazole.

sample	λ_{max} (nm) UV–vis	λ_{max} (nm) excitation	λ_{max} (nm) emission	Φ_f	λ_{max} (nm) excitation	λ_{max} (nm) emission
	In DMF				In solid state	
PTBEMA	311	354	390	0.047	388	450
PTPEMA	321	365	398	0.049	350	412
PVPT	323	368	390	0.054	392	425
poly (PTBEMA)	308	358	410	0.049	389	450
poly (PTPEMA)	321	328	405	0.050	367	414
poly (PVPT)	315	384	448	0.352	430	515

the improvement of solubility. The two methacrylate-type monomers, PTBEMA and PTPEMA could be prepared from two model compounds containing hydroxyl group via esterification by methacrylic chlorine. The three monomers can be polymerized via the initiation of AIBN. All monomers exhibit good solubility in common organic solvent such as chloroform, THF and DMF, while the polymers can be dissolved by chloroform, poly(PTBEMA) is easily soluble in THF and DMF, and poly(PVPT) is slight soluble in THF and DMF, but poly(PTPEMA) has very poor solubility in THF or DMF. Thin films of poly(PTBEMA), poly(PVPT) and poly(PTPEMA) can be prepared by spin coating from their solution in chloroform.

3.2. *Characterization of the polymers, monomers and model compounds*

1,3,4-Thiadiazole is the electron-accepting five-membered hetero-aromatic unit containing two imine –C=N– groups. Because of the electron-withdrawing ability of the imine –C=N– group, the ^{1}H NMR data of 2,5-diphenyl-1,3,4-thiadiazaole derivatives show the chemical shift of Ar–H (2-H, 3-H) (Scheme 2) at around 8.0 ppm and the chemical shift of Ar–H (4-H, 5-H) at around 7.5 ppm. The chemical shift of Ar–H (1-H) is under the influence of ortho substituent. The FTIR data exhibit absorption peak at around 1440 cm^{-1} is assigned to 1,3,4-thiadiazole.

3.3. *Absorption spectra*

The absorption spectra of the three monomers and their polymers in DMF exhibit a broad band in the UV region. The bands are ascribed to 2,5-diphenyl-1,3,4-thiadiazole group absorption. The optical band gaps (E_g) are taken as the absorption onset of the UV–vis spectra from the intersection of two tangents drawn at the declining current and background current. The absorption maxima and the onset are shown in Tables 1 and 2 respectively.

3.4. *Fluorescence properties*

The excitation and emission spectra of the monomers and polymers were investigated in DMF as well as in the solid state. Fig. 1 shows the excitation maxima of PTBEMA and poly(PTBEMA) in DMF are 354 nm and 358 nm respectively, while their emission maxima are 390 nm and 410 nm. The emission maximum of poly(PTBEMA) compared to PTBEMA is 20 nm red-shifted, because the chromophore of the monomer is completely dispersed in the dilute solution whereas the chromophores within the polymer exist intramolecular associating interactions. In solid state, the emission spectra of PTBEMA and poly(PTBEMA) were obtained by excitation at 400 nm. As shown in Fig. 2, both peaks are identical at around 450 nm, pure blue light corresponds to coordinates ($x = 0.15$, $y = 0.13$) of the1931 Commission Internationale De L'Eclairage chromaticity diagram. In contrast within the solid state and in DMF solution, the red-shift of the emission peak clearly indicates chromophores π–π stacking interactions in the solid state. In Fig. 3, we display the emission spectra of the PTPEMA and poly(PTPEMA), and similar result is also found. In DMF solution (see Fig. 4), the emission maxima of PVPT and poly(PVPT) are 390 nm and 448 nm respectively. The emission peak of poly(PVPT) compared to PVPT shows 58 nm red-shifted, because PVPT has no flexible chain between the chromophore and C=C double bond, and the chromophores within poly(PVPT) leads to more intense intramolecular interactions. In solid state (see Fig. 5), The emission maximum of poly(PVPT) is 515 nm, green light corresponds to coordinates ($x = 0.29$, $y = 0.51$), whereas emission maximum of PVPT is 425 nm. Circa 90 nm red-shifted may be due to both intramolecular and intermolecular interactions. To better understand the fluorescent properties of the polymers and monomers, the optical parameters are presented in Table 1. In solution, the excitation maxima of PTBEMA, poly(PTBEMA), PVPT, poly(PVPT) and PTPEMA are red-shifted by ca. 40–70 nm in comparison with their absorption maxima, respectively. It points the formation of static excimer. But poly(PTPEMA) is an exception, its excitation maximum is only 7 nm red-shifted to its absorption maximum. We conjecture that poly(PTPEMA) in dilute DMF trend to the formation of dynamic excimer rather than static excimer.

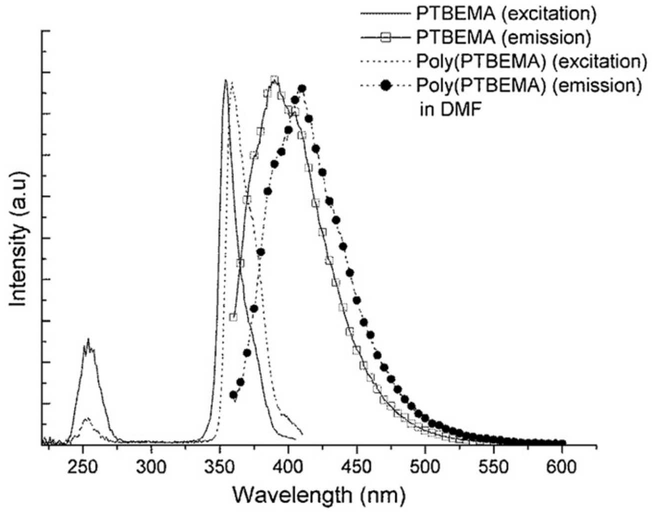


Fig. 1. Excitation and emission spectra of PTBEMA and poly(PTBEMA) in DMF.

Solution fluorescence quantum yield of the samples was measured in DMF dilute solutions by using quinine bisulfate

Table 2
Electrochemical and optical parameters of the monomers and polymers containing 2,5-diphenyl-1,3,4-thiadiazole.

	E_{Ox} eV	E_{red} eV	HOMO eV	LUMO eV	E_g (CV) eV	λ_{onset} (UV) nm	E_g (UV) eV
PTBEMA	1.54	−1.90	−6.28	−2.84	3.44	355	3.49
PTPEMA	1.61	−1.90	−6.35	−2.84	3.51	367	3.38
PVPT	1.56	−1.76	−6.30	−2.98	3.32	370	3.35
poly (PTBEMA)	1.49	−1.79	−6.23	−2.95	3.28	356	3.48
poly (PTPEMA)	1.61	−1.72	−6.15	−3.02	3.33	367	3.38
poly (PVPT)	1.40	−1.83	−6.14	−2.91	3.23	366	3.39

E_g (UV) = hc/λ_{onset} (UV); E_g (CV) = $E_{Ox} - E_{red.}$

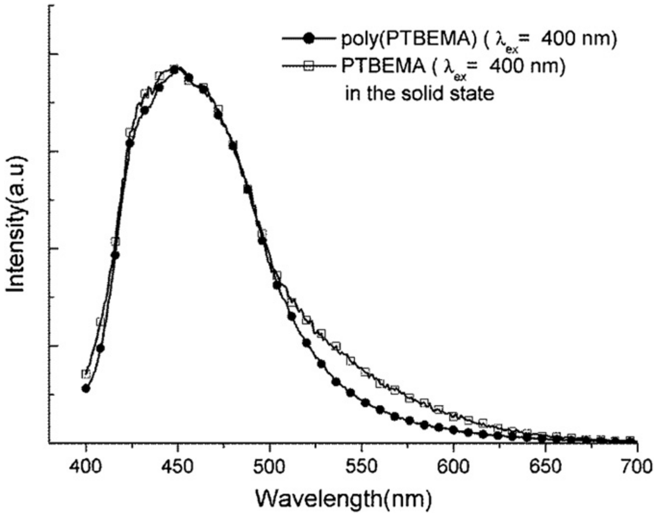


Fig. 2. Emission spectra of PTBEMA and poly(PTBEMA) with $\lambda_{ex} = 400$ nm in the solid state.

($\Phi_f = 0.546$ in 0.1 N H_2SO_4) as standards [29]. Calculations are done by Eq. (1), where Φ_{unk} is the fluorescence quantum yield of the sample, Φ_{std} the fluorescence quantum yield of the standard, I_{unk} and I_{std} the integrated emission intensities of the sample and the standard, respectively, A_{unk} and A_{std} the absorbance of the sample and the standard at the excitation wavelength, respectively, and η_{unk} and η_{std} the refractive indexes of the corresponding solution:

$$\Phi_{unk} = \Phi_{std}(I_{unk}/A_{unk})\,(A_{std}/I_{std})\,(\eta_{unk}/\eta_{std})^2 \qquad (1)$$

Table 1 also summarizes the fluorescence quantum yield of the monomers and polymers in dilute solution. We can see that the values are around 0.05, except for poly(PVPT). The main reason for higher fluorescence quantum yield of poly(PVPT) is that compact structure within the polymer restrict the rotation between benzene ring and thiadiazole.

3.5. *Electrochemical properties*

Cyclic voltammetry (CV) measurements were carried out on an electrochemical analyzer in DMF with 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte at a sweeping rate of 100 mV/s. The electrochemical experiments were made under nitrogen in a three compartment cell with a platinum working electrode, a platinum counter electrode, and a calomel reference electrode without any electrolyte. The onset potentials were estimated from the intersection of two tangents drawn at the rising current and background current of the cyclic voltammogram. The HOMO and LUMO energies of the monomers and their polymers were estimated from anodic and cathodic onset of cyclic voltammetry data to be from −6.35 to −6.14 eV, and from −3.02 to −2.84 eV respectively. The HOMO and LUMO levels are of importance to match the Fermi energy of an electrode. Our work provides a new ideal to tune parameters for the HOMO and LUMO levels. The optical band gaps (E_g) taken as the absorption onset of the UV–vis spectra were similar to the band gaps determined from the cyclic voltammogram. The electrochemical parameters are presented in Table 2.

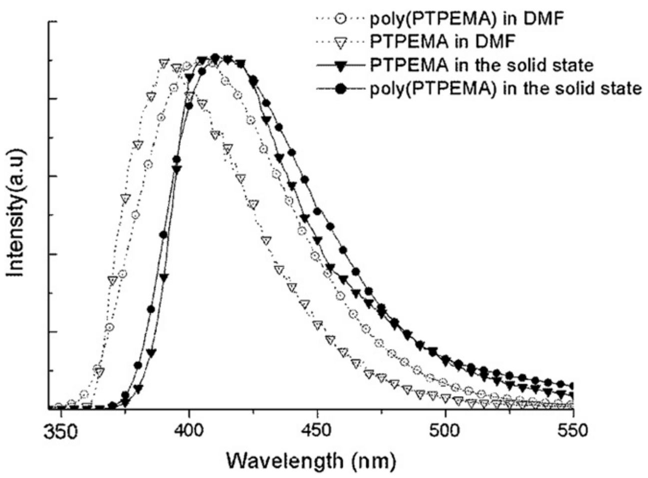


Fig. 3. Emission spectra of PTPEMA and poly(PTPEMA) in DMF and in the solid state.

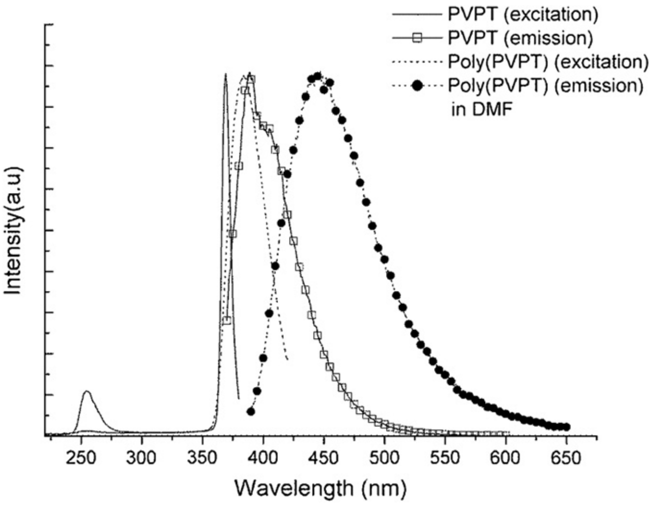


Fig. 4. Excitation and emission spectra of PVPT and poly(PVPT) in DMF solution.

4. Conclusions

Three new monomers containing 2,5-diphenyl-1,3,4-thiadiazole have been synthesized and their polymers which can emit strong blue or green fluorescence have a good solubility in $HCCl_3$ or DMF, but poly(PTPEMA) is rather poor in DMF. Poly(PTBEMA), poly(PVPT) and poly(PTPEMA) thin films can be prepared by spin

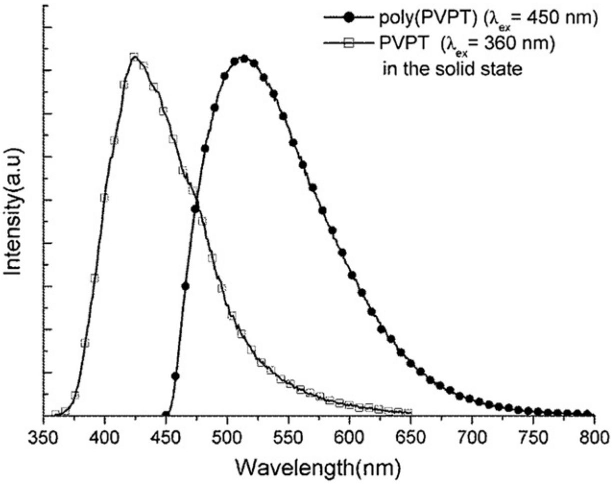


Fig. 5. Emission spectra of PVPT and poly(VPT) in the solid state.

coating from their chloroform solution. Poly(PTBEMA) in the solid emits pure blue light and poly(PVPT) emits green light as well as ploy(PTPEMA) emits indigo light. Chromophorous intramolecular and intermolecular interaction can lead to fluorescence red-shift and tune parameters for the HOMO and LUMO levels.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.dyepig.2009.07.007.

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