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ORIGINAL PAPER

Comparative study of photoelectric properties of regiosymmetrical poly(3,4-dialkoxythiophene)s

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Abstract A series of regiosymmetrical poly(3,4-dialkoxythiophene)s: poly(3,4-diamyloxythiophene), poly(3,4-dioctyloxythiophene), poly(3,4-di(2-ethyl-1-hexyl-oxy)thiophene), and poly(3,4-didodecyloxythiophene) were synthesized by the $FeCl_3$-oxidative approach. All these polymers were evaluated with NMR, FT-IR, gel permeation chromatography (GPC), thermo-gravimetric analysis (TGA), UV–Vis spectroscopy, and photoluminescence (PL). The polymers have excellent solubility in common organic solvents, and TGA studies show that the polymers lost 5% of their weights on heating to 250 °C above. Investigations of the UV–Vis spectroscopy show that the absorption maxima of the polymer thin films are similar to those in solutions, and the optical band gaps of the polymer thin films are ranging from 2.27 to 2.69 eV. In PL spectra, maxima emission peaks of the polymer thin films lie at 527 to 589 nm, embodying colors from green to yellow, and the quantum yields of the polymers are in the range of 22–28%. All the data indicate that the polymers have good solubility, outstanding thermal stabilities, low band gaps, and high PL quantum yields, and they might be excellent polymeric materials for applications in organic light-emitting diodes (OLEDs), light-emitting electrochemical cells, polymer solar cells, and so on.

Keywords Thiophene · Thin film · Regiosymmetrical · Band gap · OLED

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Introduction

Conjugated polymers have been developed into useful materials for a variety of applications in electronic and electrochemical devices [1], such as organic field-effect transistors (OFETs) [2], organic light-emitting diodes (OLEDs) [3–5], and sensors [6]. Among these polymers, polythiophenes (PTs) represent a class of easily processible, environmentally stable, π-conjugated polymers, which are one of the most extensively studied materials for use in OLEDs [7, 8]. In order to get efficient electronic devices, it is necessary to tune their properties, such as band gap, molecular energy level, solubility, luminescence, absorbance, and so on [9, 10]. It has been shown that the optical and transport properties of PTs can be changed by attaching different side chains [11]. Band gaps of PTs can be tailored by selecting a proper pendants. One of important example of PTs is regioregular poly((3-substituted) thiophene)s (rr-P3Ts), such as poly(3-alkylthiophene)s (P3ATs), poly(3-alkyloxythiophene)s (P3AOTs), which are being used as the hole transport layer in OLEDs. Alkoxy-substituted analogues of P3Ts exhibit even more desirable properties, such as reduced band gaps, low oxidation potentials, and a highly stable conducting state [12, 13].

The early studies on unsymmetrical thiophene units substituted in the 3-position have clearly shown that the properties of P3Ts greatly depended on the degree of regioregularity, which could be defined as the percentage of head-to-tail (HT) couplings [14–16]. Regioirregular P3Ts greatly limited the possibilities of these materials to study their properties in films and to be used in electrical applications [17]. The discovery of the symmetrical poly(3,4-ethylenedioxythiophene) (PEDOT) [18, 19] as a new modified polythiophene with high chemical stability, high electrical conductivity, and low band gap [20, 21] launched numerous investigations on the basis of new regiosymmetrical thiophene-based polymer systems [21, 22]. Literature survey reveals that introduction of long alkoxy pendants at 3- and 4-positions of the thiophene ring improves the solvent processibility and hole carrying ability [23, 24]. Due to the electron donating nature of the alkoxy moiety, polymers show facile dopability and lower band gap.

In this study, a series of regioregular poly(3,4-dialkoxythiophene)s: poly(3,4-diamyloxythiophene), poly(3,4-dioctyloxythiophene), poly(3,4-di(2-ethyl-1-hexyloxy)thiophene), and poly(3,4-didodecyloxythiophene) were synthesized successfully through the $FeCl_3$-oxidative approach.

Experimental

Materials

All reagents were purchased from Aldrich Chemical Co., Acros Organics, Merck, Fluka, and Avocado. Reagent grade solvents were dried when necessary and were purified by distillation.

Instrumental measurements

^{1}H and ^{13}C nuclear magnetic resonance (NMR) measurements were carried out with a Bruker Avance 300 MHz using TMS/solvent signal as internal reference. FT-IR spectra of the synthesized polymers were recorded on a Nicolet 700 FT-IR spectrometer. Gel permeation chromatography (GPC) was performed with a Perkin Elmer series 200 apparatus (a mixed 10-μPS column with a length of 750 mm, refractive index detector). Tetrahydrofuran was acted as an eluant at a flow rate of 1.0 mL min^{-1} at 40 °C. Polymer solution was filtered through a 0.45 μm filter (Gelman Acro-disc PTFE) prior to injecting into the column. Calibration was conducted with polystyrene standards. Thermo-gravimetric analysis (TGA) was performed on a DuPont 9900 analyzer with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. UV–Vis spectra of the polymers were recorded on a UV-2201 (Japan) in a laboratory atmosphere at room temperature. Photoluminescence spectra were recorded on a Spex FL-2T2 (USA). The polymers were dissolved in $CHCl_3$ at a concentrations of 10^{-5} M, and the polymer solutions were de-oxygenated with high, pre-purified nitrogen prior to being injected into absorption, and fluorescence measurements. The solutions above were filtered through a 0.45 μm filter and were spin-cast on glass (for absorption and fluorescence measurements) to form thin films. The polymer thin films were dried under vacuum at room temperature and in the dark.

Preparation of monomers

*General procedure for the synthesis of 3,4-dimethoxythiophene (**1**)*

To a mixture of N-methyl-2-pyrrolidone (NMP, 130 mL) and methanol (50 mL) was added small pieces of Sodium (15.0 g, 650.0 mmol) and stirred. After the sodium disappeared, 3,4-dibromothiophene (24.2 g, 100.0 mmol) and CuI (4.8 g, 25.0 mmol) were added and the reaction solution was heated slowly to 115 °C for 3.5 h. After cooling and filtered, the filtrate was poured into 500 mL saturated NaCl solution and the sloution was extracted by diethyl ether (100 mL) for three times. The organic phase was dried over anhydrous $MgSO_4$ and evaporated. The product was purified by vacuum distillation to give **1** (9.5 g, 66.0 mmol) as a colorless oil in 66% yield, b.p. 100–102 °C (10–11 mmHg). ^{1}H-NMR ($CDCl_3$), δ (ppm): 3.85 (s, 6H), 6.18 (s, 2H). IR (KBr), ν (cm^{-1}): 3118, 3000, 2957, 2826, 1567, 1504, 1447, 1412, 1135. Elem. Anal. Calcd for $C_6H_8O_2S$: C, 50.00; H, 5.56; S, 22.22. Found: C, 50.12; H, 5.43; S, 22.15.

*General procedure for the synthesis of 3,4-dialkoxythiophene (**2a**–**2d**) [17]*

3,4-Diamyloxythiophene (**2a**): Under a nitrogen atmosphere, a solution of **1** (7.2 g, 50.0 mmol), amyl alcohol (17.6 g, 200.0 mmol), and $NaHSO_4$ (0.6 g, 5.0 mmol) in dry toluene (25 mL) was heated to 112 °C and stirred for 5 h. After the reaction, the catalyst was filtered off and the organic layer was washed with a saturated $NaHCO_3$ solution until neutral and dried over anhydrous $MgSO_4$. The crude product was purified by column chromatography (silicagel; eluent: petroleum ether/ethyl acetate (99:1 v/v)) to give **2a** (11.1 g, 32.5 mmol) as a colorless oil in 65% yield. ^{1}H-NMR (CDCl$_3$), δ (ppm): 0.91 (t, 6H, $J = 7.5$ Hz), 1.30–1.86 (m, 12H), 3.97 (t, 4H, $J = 6$ Hz), and 6.18 (s, 2H). IR (KBr), v (cm^{-1}): 3118, 2959, 2929, 2862, 1572, 1500, 1467, 1375, 1158. Elem. Anal. Calcd for $C_{14}H_{24}O_2S$: C, 65.63; H, 9.38; S, 12.50. Found: C, 65.78; H, 9.49; S, 12.34.

3,4-Dioctyloxythiophene (**2b**): **2b** was obtained as a colorless oil from **1** and octyl alcohol with a procedure similar to that described for **2a**. Yield: 62%. ^{1}H NMR (CDCl$_3$), δ (ppm): 0.91 (t, 6H, $J = 7.5$ Hz), 1.29–1.87 (m, 24H), 3.98 (t, 4H, $J = 6$ Hz) and 6.18 (s, 2H). IR (KBr), v (cm^{-1}): 3115, 2954, 2929, 2862, 1560, 1498, 1460, 1375, 1155. Elem. Anal. Calcd for $C_{20}H_{36}O_2S$: C, 70.59; H, 10.59; S, 9.41. Found: C, 70.73; H, 10.67; S, 9.56.

3,4-Di(2-ethyl-1-hexyloxy)thiophene (**2c**): **2c** was obtained as a colorless oil from **1** and 2-ethylhexyl alcohol with a procedure similar to that described for **2a**. Yield: 59%. ^{1}H NMR (CDCl$_3$), δ (ppm): 0.91 (t, 12H, $J = 7.5$ Hz), 1.30–1.82 (m, 24H), 3.88 (t, 4H, $J = 6$ Hz) and 6.18 (s, 2H). IR (KBr), v (cm^{-1}): 3113, 2971, 2929, 2853, 1561, 1498, 1466, 1367, 1146. Elem. Anal. Calcd for $C_{20}H_{36}O_2S$: C, 70.59; H, 10.59; S, 9.41. Found: C, 70.73; H, 10.67; S, 9.56.

3,4-Didodecyloxythiophene (**2d**): **2d** was obtained as a white solid from **1** and dodecyl alcohol with a procedure similar to that described for **2a**. Yield: 54%, m.p. 39–40 °C. ^{1}H-NMR (CDCl$_3$), δ (ppm): 0.91 (t, 6H, $J = 7.5$ Hz), 1.29–1.86 (m, 40H), 3.97 (t, 4H, $J = 6$ Hz) and 6.17 (s, 2H). IR (KBr), v (cm^{-1}): 3115, 2956, 2925, 2852, 1566, 1500, 1462, 1375, 1157. Elem. Anal. Calcd for $C_{28}H_{52}O_2S$: C, 74.34; H, 11.50; S, 7.08. Found: C, 74.54; H, 11.67; S, 6.95.

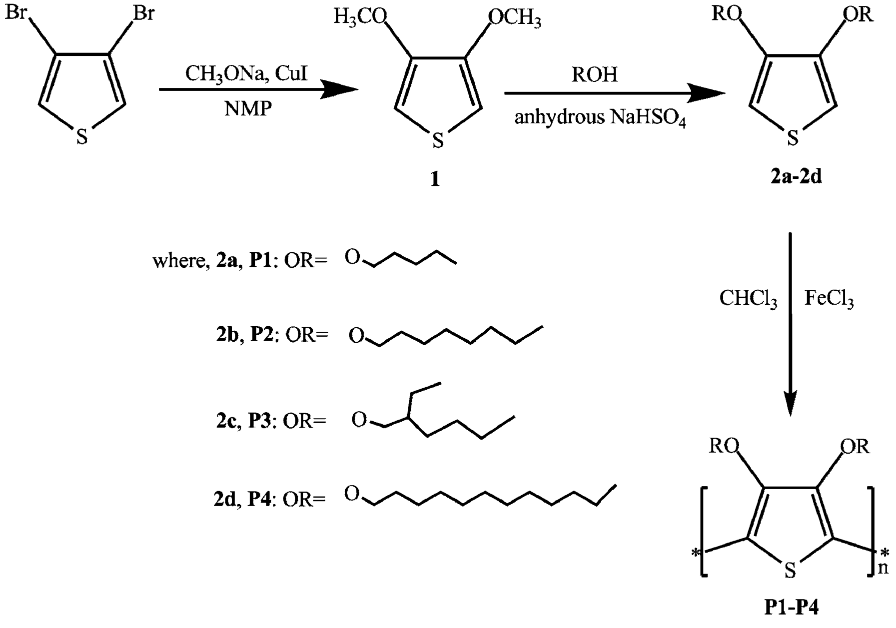
Preparation of polymers

*General procedure for the synthesis of ploy(3,4-dialkoxythiophene) (**P1–P4**)*

The polymers were synthesized by FeCl$_3$ oxidation in chloroform solvent according to a procedure similar to that described in the literature [25, 26], as shown in Scheme 1.

A solution of anhydrous FeCl$_3$ (3.9 g, weighed under a nitrogen atmosphere, 24.0 mmol) and dry chloroform (30 mL) was stirred at room temperature under a nitrogen atmosphere until its color became dark green; then, a solution of **2a**–**2d** (6.0 mmol) in dry chloroform (20 mL) was added dropwise. The mixture was stirred overnight at room temperature and the crude polymer was precipitated in methanol, and filtered. The polymer was added into a solution of chloroform (50 mL) and saturated aqueous hydrazine (100 mL), which was stirred and refluxed for 2 h. The organic layer was separated and washed with a NaHCO$_3$ solution and dried over anhydrous MgSO$_4$. Then the polymer solution was concentrated and the polymer was precipitated in methanol and filtered into a Soxhlet thimble. Soxhlet extractions were performed with methanol (to remove monomer), hexanes (to remove oligomers), and chloroform. Finally, the chloroform fraction was reduced and dried in vacuo to give **P1**–**P4** as a violet film in 45–55% yield.

P1: 53% yield. ^{1}H-NMR (CDCl$_3$), δ (ppm): 0.86 (t, 6H, $J = 6.9$ Hz), 1.27–1.81 (m, 12H,), 4.12 (s, (br), 4H). ^{13}C NMR (CDCl$_3$), δ (ppm): 146.21, 115.23, 70.14,



Scheme 1 Synthetic procedure of monomers and polymers

29.92, 28.17, 22.64, 14.08. IR (KBr), *v* (cm^{-1}): 2960, 2929, 2859, 1607, 1381, 1109. Elem. Anal. Calcd: C, 65.63; H, 9.38; S, 12.50. Found: C, 65.74; H, 9.16; S, 12.29.

P2: 55% yield. ^{1}H NMR ($CDCl_3$), δ (ppm): 0.86 (t, 6H, $J = 6.9$ Hz), 1.26–1.82 (m, 24H), 4.12 (s, (br), 4H). ^{13}C NMR ($CDCl_3$), δ (ppm): 146.34, 115.41, 70.35, 31.92, 30.29, 29.69, 29.46, 26.12, 22.70, 14.09. IR (KBr), *v* (cm^{-1}): 2955, 2923, 2858, 1601, 1386, 1105. Elem. Anal. Calcd: C, 70.59; H, 10.59; S, 9.41. Found: C, 70.72; H, 10.43; S, 9.38.

P3: 45% yield. ^{1}H NMR ($CDCl_3$), δ (ppm): 0.88 (t, 12H, $J = 6.8$ Hz), 1.23–1.62 (m, 24H), 3.92 (s, (br), 4H). ^{13}C NMR ($CDCl_3$), δ (ppm): 146.99, 115.90, 72.09, 40.02, 30.13, 28.94, 23.39, 23.01, 13.97, 10.87. IR (KBr), *v* (cm^{-1}): 2967, 2929, 2860, 1666, 1380, 1069. Elem. Anal. Calcd: C, 70.59; H, 10.59; S, 9.41. Found: C, 70.64; H, 10.39; S, 9.29.

P4: 48% yield. ^{1}H NMR ($CDCl_3$), δ (ppm): 0.86 (t, 6H, $J = 6.9$ Hz), 1.27–1.80 (m, 40H), 4.13 (s, (br), 4H). ^{13}C NMR ($CDCl_3$), δ (ppm): 146.54, 115.54, 70.44, 31.96, 29.60, 29.57, 29.54, 29.52, 29.35, 29.31, 29.00, 25.84, 22.66, 14.06. IR (KBr), *v* (cm^{-1}): 2960, 2925, 2853, 1610, 1381, 1107. Elem. Anal. Calcd: C, 74.34; H, 11.50; S, 7.08. Found: C, 74.54; H, 11.34; S, 6.93.

Results and discussion

Characterization of polymers

The chemical structures of the polymers were confirmed by NMR spectra and FT-IR. The singlet peak around δ 6.18, due to =C–H protons on thiophene ring, is not found in the ^{1}H-NMR spectra of **P1**–**P4**, which reflects the high degree of polymerization of the corresponding polymer. A broad peak around δ 4.1 belongs to $-OCH_2-$ protons of the alkoxy group appending on thiophene ring. In addition, multiple peaks were obtained in the range of δ 1.27–1.81, due to $-(CH_2)_n-$ protons of the alkoxy groups, and a triplet peak around δ 0.86 belongs to $-CH_3$ protons of the alkoxy groups. The ^{13}C-NMR spectra of **P1**–**P4** showed characteristic peaks at δ 146.21–146.99 (C-3 and C-4 of 3,4-dialkoxythiophene unit), 115.23–115.90 (C-2 and C-5 of 3,4-dialkoxythiophene unit), 70.14–72.09 ($-OCH_2$ of the alkoxy group), 10.87–40.02 (alkyl carbons, $-(CH_2)_nCH_3$ of alkoxy groups). IR spectroscopy is a useful technique for characterizing the structures of polymers. Take **P2** for instance, The thiophene =C–H stretching is reflected by peaks centered at 3,115 cm^{-1} for **2b**, while it disappears in the IR spectra of **P2**, which means the successful polymerization of the corresponding polymer. The absorption bands at 2,955 cm^{-1} corresponds to the $-CH_3$ asymmetric stretching vibration, and the absorption bands at 2,923 and 2,858 cm^{-1} correspond to the $-CH_2-$ stretching vibration. The thiophene ring (C=C) stretching is observed at 1,601 cm^{-1}. The bands centered around 1,386 cm^{-1} are attributable to the deformation vibration mode of $-CH_2-$ and $-CH_3$. The characteristic stretching vibrations of the C–O–C group can be observed at 1,105 cm^{-1} in the spectra. The elemental analysis results for the polymers are in agreement with their expected empirical formula. All the polymers show excellent solubility, and they can be soluble in many common organic solvents, such as $CHCl_3$, THF, DMF, and so on. Polymers were measured by means of gel permeation chromatography (GPC) using THF as eluant against polystyrene standards. The average molecular weights of the polymers were measured as Mw = 9,743 (PD = 1.80) for **P1**, 11,528 (PD = 1.83) for **P2**, 4,238 (PD = 2.02) for **P3** and 7,529 (PD = 1.91) for **P4** (Table 1). Mw of **P3** is less than the others and this might attribute to its steric hindrance in side substituted group.

Thermal analysis

Thermal characterization of **P1**–**P4** was accomplished by TGA. Figure 1 depicts the TGA traces of polymers. The temperature (T_d) which corresponding to a 5% weight lossing for **P1**–**P4** is summarized in Table 1, under a nitrogen atmosphere. In

Table 1 The molecular weight and decomposition temperature of the polymers

Polymer	Mw[a]	Mn[b]	PD[c]	T_d(°C)[d]
P1	9,743	5,413	1.80	311
P2	11,528	6,299	1.83	302
P3	4,238	2,098	2.02	252
P4	7,529	3,942	1.91	265

[a] Mw is the weight-average molecular weight

[b] Mn is the number-average molecular weight

[c] PD is the index of polydispersity

[d] T_d is the temperature resulting in 5% weight loss based on initial weight

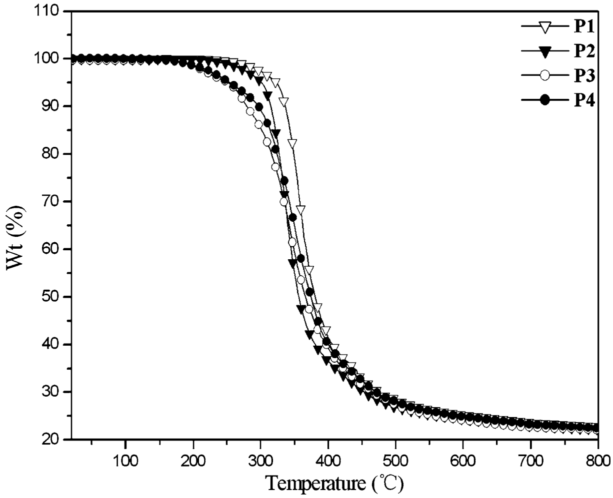


Fig. 1 TGA curves of **P1–P4**

Table 2 The optical data of the polymers in chloroform (1 × 10^{-5} M) solutions and in thin films

Polymer	In chloroform solution				In thin film			
	λ^{abs}max[a] (nm)	λ^{ex}max[b] (nm)	λ^{em}max[c] (nm)	Φ_f^d (%)	λ^{abs}max (nm)	λ^{ex}max (nm)	λ^{em}max (nm)	E_g^e (eV)
P1	489	492	561	25	491	496	570	2.30
P2	510	529	578	28	512	531	589	2.27
P3	414	435	517	22	414	442	527	2.69
P4	473	464	549	24	473	480	555	2.39

[a] λ^{abs}max is the absorption maxima of UV–Vis

[b] λ^{ex}max is the excitation maxima of photoluminescence

[c] λ^{em}max is the emissive maxima of photoluminescence

[d] Φ_f is the quantum yield

[e] E_g is the optical band gap of polymer thin film

general, T_d of all the polymers were above 250 °C, displayed satisfactory thermal stability. **P3** showed the lowest T_d due to its lowest molecular weight, while **P1** showed the highest T_d. It showed that the losing weight of polymer is increased with the length of pendant chain. This trend is similarly to that of poly((3-substituted) thiophene)s [27].

UV–Vis spectroscopy

The UV–Vis spectra of the polymers were recorded both in solution and in thin film, and the corresponding spectral data are summarized in Table 2. As shown in the Fig. 2a, the absorption maxima of the polymers in chloroform solutions are 489 nm

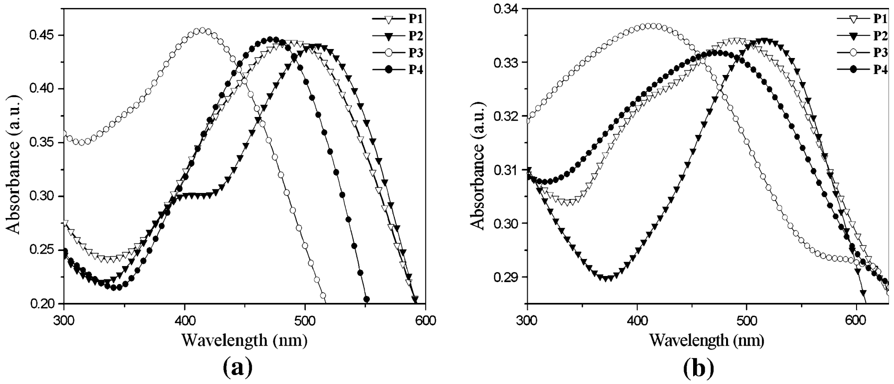


Fig. 2 UV–vis absorption spectra of **P1**–**P4** in chloroform solutions (10^{-5} M) and in thin films: **a** in chloroform solutions, **b** in thin films

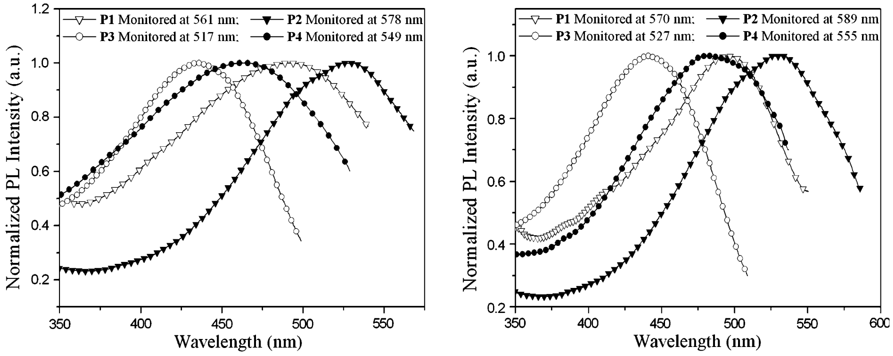
for **P1**, 510 nm for **P2**, 414 nm for **P3** and 473 nm for **P4**. The difference among absorption maxima of polymers might assume that the polymers are able to form microaggregate and their effective conjugation length is varied according to corresponding polymer. The maximum wavelength of **P3** is less than others because of its largest steric hindrance effect. The absorption maxima of the polymer thin films (Fig. 2b) are similar to those in solutions, indicating that the effective conjugation lengths both in solid film and in $CHCl_3$ solution are close-by.

The optical band gaps (E_g) of the polymers are calculated according to the formula: $\alpha h\nu = B\,(h\nu - E_g)^n$ where α is the absorbance coefficient, h is the Planck constant, and n (the value is 0.5) is the transition type, respectively [8, 28]. By drawing the $(h\nu A)^2 - h\nu$ curves and extending the linearity edge of absorbance to intersect with energy axis, then the energy band gap is obtained. The optical energy band gaps were calculated from the absorption edge in the polymer thin films to be 2.27–2.69 eV (Table 2). Ban gaps of the polymers are much lower than that of poly(3-dodecyloxythiophene) (2.80 eV) prepared by our group [29].

Photoluminescence (PL) properties

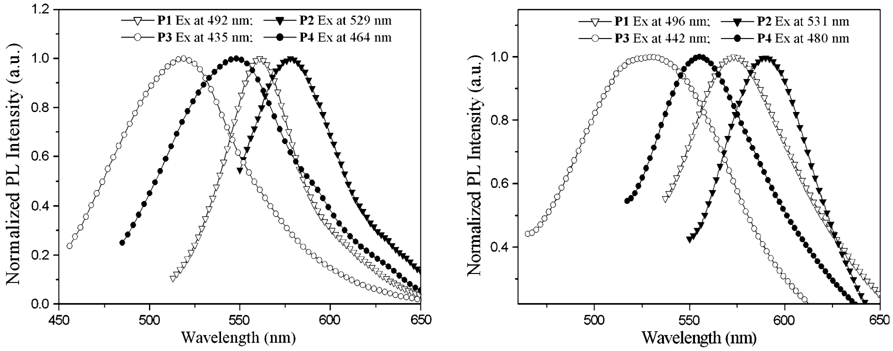
PL spectra can provide a great deal of information on the electronic structures of the conjugated polymers. The PL spectra of the polymers were recorded both in solution and in thin film, and all the excitation and emission spectral data are summarized in Table 2. Figure 3 shows the PL excitation curves of the four polymers both in chloroform solutions (Fig. 3a) and in thin films (Fig. 3b), the excitation maxima of the polymers in the two states are consistent with the absorption maxima of UV–Vis spectra.

The PL emission curves shown in Fig. 4 are obtained by excitated at excitation maxima of the polymers, respectively. As shown in Fig. 4a, the PL emissive maxima of the polymers in chloroform solutions are 561 nm for **P1**, 578 nm for **P2**, 517 nm for **P3** and 549 nm for **P4**. The PL emission spectra of these polymer thin films are shown in Fig. 4b. The polymers emit yellowish-green light with emission peaks at 570 nm for **P1**, yellow light at 589 nm for **P2**, green light at 527 nm for **P3**



(a) **(b)**

Fig. 3 Normalized PL excitation spectra of **P1**–**P4** in chloroform solutions (10^{-5} M) and in thin films: **a** in chloroform solutions, **b** in thin films



(a) **(b)**

Fig. 4 Normalized PL emission spectra of **P1**–**P4** in chloroform solutions (10^{-5} M) and in thin films: **a** in chloroform solutions, **b** in thin films

and at 555 nm for **P4**. Consequently, the PL emission spectra of the polymer thin films exhibit only a little red shift in comparison to those obtained from their solutions. This can be attributed to the interchain or intrachain mobility of the excitons and excimers generated in the polymer in the solid stated phase.

PL quantum yield is also an important feature of the optical properties of conjugated polymers. The quantum yields of the polymers in chloroform solutions were determined using quinine sulfate as a standard [30, 31] and summarized in Table 2. As depicted in Table 2, the quantum yields of the polymers are in the range of 22–28%. These results indicate that the polymers can be used as light-emitting materials in devices.

Conclusion

In this article, four regioregular poly(3,4-dialkoxythiophene)s: poly(3,4-diamyloxythiophene), poly(3,4-dioctyloxythiophene), poly[3,4-di(2-ethyl-1-hexyloxy)thiophene] and poly(3,4-didodecyloxythiophene) were synthesized successfully by the $FeCl_3$-oxidative approach. All polymers showed good solubility, outstanding thermal stabilities, low E_g values and high PL quantum yields. Their electronic and optical properties were consistent with the conjugated backbone structure. The band gaps of poly(3,4-dialkoxythiophene)s are adjusted easily by changing the steric hindrance of alkoxyl-substituted groups for a particular purpose. Moreover, we have succeeded in embodying colors from green to yellow with these polymers by changing the structure of the side chains. On the basis of these results, these conjugated polymers might be a promising material for applications in organic light-emitting diodes and other photoelectronic devices.

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