

Substituent Effects on Direct Arylation Polycondensation and Optical Properties of Alternating Fluorene-Thiophene Copolymers^{*}

Min-min Sun, Wen Wang^{**}, Lu-ying Liang, Shu-hui Yan, Ming-lu Zhou and Qi-dan Ling^{**}

Fujian Key Laboratory of Polymer Materials, College of Materials Science and Engineering, Fujian Normal University, Fuzhou 350007, China

Abstract Four thiophene derivatives were prepared by replacing the 3,4 positions of thiophene by $-\text{OCH}_3$, $-\text{CH}_3$, $-\text{COOCH}_3$ and $-\text{CN}$, respectively. The polycondensations *via* direct arylation took place between the four thiophene derivatives and 2,7-dibromo-9,9-dioctylfluorene under six various catalytic conditions to investigate the substituent effects. The substituent can affect the electron cloud density of the active C—H bond, which can be monitored by the NMR chemical shift. The experimental results show that the reactivity decreases with increasing the chemical shift of active C—H bonds in the four thiophene derivatives, and thus can promote the direct arylation polycondensation. This phenomenon is explained by the electrophilic aromatic substitution ($\text{S}_{\text{E}}\text{Ar}$) mechanism. UV-Visible absorption and photoluminescence were studied to investigate the substituent effect on optical properties of the four copolymers. The results show that these alternating fluorene-thiophene copolymers with different substituents are good fluorescent materials and promising in PLED applications.

Keywords: Direct arylation polycondensation; Alternating copolymers; Substituent effects; Chemical shift.

INTRODUCTION

Due to the strong ability to light capture, π -conjugated polymers are considered to be the most promising optoelectronic materials the application in polymer solar cells (PSCs)^[1], organic light emitting diode (OLEDs)^[2], organic field-effect transistors (OFETs)^[3], *etc.* Traditional methods of preparing π -conjugated polymers have been widely reported. Stille and Suzuki coupling polymerizations are regarded as the classics of traditional polymerization methods, which are widely applied in the preparation of π -conjugated polymers^[4, 5]. Recently, the polycondensation *via* direct arylation has been widely recognized as an atom economy and environmentally friendly method to prepare π -conjugated polymers, which draws lots of researchers' attention. Ozawa and his colleagues first used 2-bromo-3-hexylthiophene as raw materials, successfully prepared P3HT with high molecular weight and high regioregularity *via* direct arylation polycondensation^[6]. This new method has obvious advantages over the polymerization *via* traditional methods, such as fewer synthetic steps, less time, less harmful substances on human beings and the environment, *etc.*^[7]. Besides, the polycondensation *via* direct arylation is more efficient than traditional coupling polymerizations in terms of the molecular weight and photoelectric properties. For example, Lu *et al.* prepared poly[(4,4'-dinonyl-2,2'-bithiazole-5,5'-diyl)-(9,9-dioctylfluorene-2,7-

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^{**} Corresponding authors: Wen Wang (王文), E-mail: wangwen@fjnu.edu.cn

Qi-dan Ling (凌启淡), E-mail: qdling@fjnu.edu.cn

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diyl)] with higher molecular weight^[8], which is three times larger than that previously obtained *via* Suzuki reaction^[9]. Chang *et al.* not only prepared polymer poly[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene-2,6-diyl-alt-2,1,3-benzothiadiazole-4,7-diyl] with higher molecular weight, but also increased the power conversion efficiency (PCE) when the polymer was applied in polymer solar cells^[10]. However, due to more than one type of reactive C—H bond, the polycondensation *via* direct arylation is not easily controlled and can produce insoluble branched and cross-linked materials^[8]. Reaction conditions for each comonomers or set of comonomers are substrate specific and require optimization. Accordingly, if the problem of regioselectivity in polycondensation can be solved, it will become the most promising method for preparing π -conjugated polymers.

Previous researches focused on the polycondensation *via* direct arylation between the same C—H comonomer and the various C—Br comonomers^[11, 12]. 2,7-Dibromo-9,9-dioctylfluorene and 4,7-dibromo-2,1,3-benzothiadiazole were regarded as the optimal C—Br comonomers because they not only had high reactivity, but also prevented the formation of branched or cross-linked structures. In our work, we focused on the polycondensation between the various C—H comonomers and the same C—Br comonomer, and prepared four alternating fluorene-thiophene copolymers to investigate the substituent effects. Thus, four thiophene derivatives (3,4-dimethoxythiophene, 3,4-dimethylthiophene, 3,4-thiophene dicarboxylate and 3,4-thiophene carbonitrile) were selected as the C—H comonomers, which were prepared by replacing the 3, 4 positions of thiophene by —OCH₃, —CH₃, —COOCH₃ and —CN, respectively. Besides, thiophene derivatives were selected as C—H comonomers because thiophene-based monomers are commonly used in preparation of π -conjugated polymers, and the corresponding polymers are candidates for photoelectric materials. 2,7-Dibromo-9,9-dioctylfluorene was selected as the C—Br comonomer. The dimethylacetamide (DMAc) was selected as the reaction solvent because of the high polarity rendered better service for improving molecular weight^[13]. Pivalic acid was selected as an additive because it was superior to other carboxylic acids^[14]. The polycondensations of 2,7-dibromo-9,9-dioctylfluorene with thiophene derivatives were carried out in the presence of catalyst (2 mol%), ligand (4 mol%), pivalic acid (30 mol%) and K₂CO₃ (2.5 equiv.) in dimethylacetamide (DMAc) for 24 h at 100 °C, in which the catalyst and the ligand were changed. Meanwhile, the substituent effects on polymerization and optical properties of copolymers were investigated.

EXPERIMENTAL

Materials

All the reagents and solvents were purchased from Sinopharm Chemical Reagent Limited Corporation (Beijing, China). All the raw materials were purchased from Amatek Chemical Technology Limited Corporation (Beijing, China). The solvents were dried over CaH₂ and distilled under vacuum according to standard procedures. All the reactive monomers were prepared according to known procedures.

Measurements

The GPC analysis of the copolymers was conducted on a Waters 1515 with THF as the eluent and polystyrene standards. ¹³C-NMR and ¹H-NMR were conducted on a Bruker Ascend 400 MHz nuclear magnetic resonance spectrometer. The spectra were recorded in CDCl₃ or DMSO-d₆. The data are reported as follows: chemical shifts are reported relative to trimethylsilane (TMS) as the internal standard. The UV-Vis spectra were conducted on a SHIMADZU UV-2600 spectrometer. The PL spectra were conducted on a SHIMADZU RF-5301PC spectrometer. The fluorescence quantum yields (ϕ_f) were determined in chloroform solution against 8-hydroxyquinoline aluminum (Alq₃) in *N,N*-dimethylformamide (DMF) solution assuming a quantum yield of 0.11.

Experimental details

The Four Copolymers P1, P2, P3 and P4 were prepared using the same pattern. Thiophene derivatives (0.3 mmol), 2,7-dibromo-9,9-dioctylfluorene (164.5 mg, 0.3 mmol), K₂CO₃ (103.6 mg, 0.75 mmol), catalyst (2 mol%), ligand (4 mol%) and 1 mL DMAc were transferred to a 5 mL round-bottom flask under an

atmosphere of nitrogen. The mixture was stirred for 24 h at 100 °C. After cooling to room temperature, the mixture was poured into 80 mL CH₃OH. The precipitate was separated by filtration. The product of higher molecular weight was obtained by soxhlet extraction from CH₃OH/C₃H₆O. The residual solid was dissolved in CHCl₃ and the solution was concentrated. The polymer was obtained by reprecipitation from CH₃OH.

P1: $M_n = 24000$, PDI = 1.74, Yield = 62.0% (Table 1, entry 4). ¹H-NMR (400 MHz, CDCl₃): δ = 7.80 (s, 2H), 7.46 (overlapped, 4H), 3.94 (s, 6H), 2.06 (br, 4H), 1.10 (overlapped, 20H), 0.81 (t, 6H), 0.76 (br, 4H). ¹³C-NMR (100 MHz, CDCl₃): δ = 151.6, 147.3, 140, 131.8, 125.5, 124.1, 121.1, 120, 60.4, 55.3, 40.4, 31.8, 30.1, 29.3, 29.2, 23.9, 22.6, 14.1.

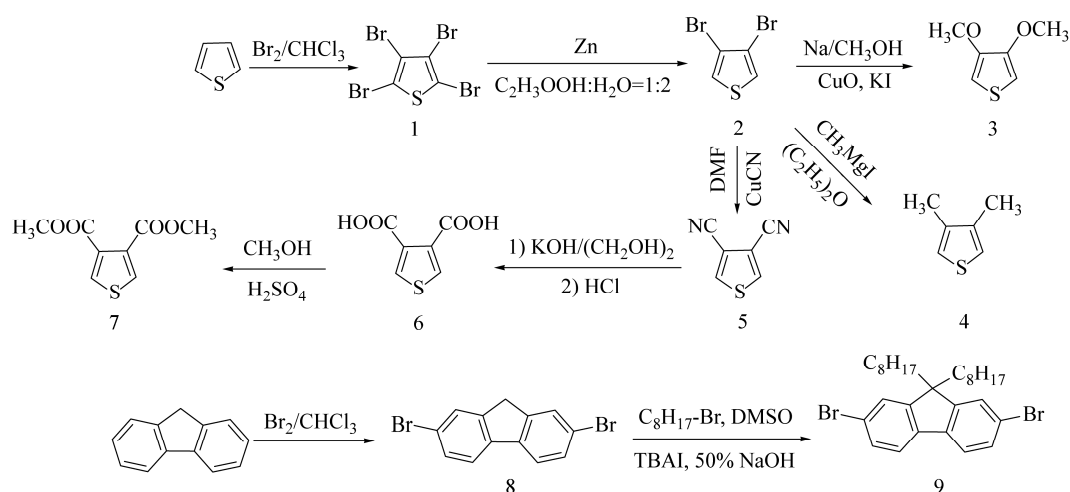
P2: $M_n = 7000$, PDI = 1.45, Yield = 73.9% (Table 2, entry 4). ¹H-NMR (400 MHz, CDCl₃): δ = 7.77 (d, 2H), 7.48 (overlapped, 4H), 2.34 (s, 6H), 2.02 (br, 4H), 1.10 (overlapped, 20H), 0.81 (t, 6H), 0.76 (br, 4H). ¹³C-NMR (100 MHz, CDCl₃): δ = 151.3, 139.9, 137.3, 134.2, 133.7, 128.1, 123.8, 119.8, 55.2, 40.4, 31.8, 30.1, 29.3, 29.2, 23.9, 22.6, 14.4, 14.1.

P3: $M_n = 23400$, PDI = 1.67, Yield = 91.4% (Table 3, entry 2). ¹H-NMR (400 MHz, CDCl₃): δ = 7.75 (s, 2H), 7.48 (overlapped, 4H), 3.76 (s, 6H), 1.98 (br, 4H), 1.07 (overlapped, 20H), 0.81 (t, 6H), 0.76 (br, 4H). ¹³C-NMR (100 MHz, CDCl₃): δ = 164.8, 153.3, 146.3, 140.9, 130.2, 128, 126.1, 123.6, 121.4, 55.5, 52.2, 40.1, 31.8, 30.1, 29.3, 29.2, 23.8, 22.6, 14.1.

P4: $M_n = 5900$, PDI = 4.54, Yield = 57.8% (Table 4, entry 3). ¹H-NMR (400 MHz, CDCl₃): δ = 7.92 (s, 2H), 7.86 (overlapped, 4H), 2.06 (br, 4H), 1.10 (overlapped, 20H), 0.81 (t, 6H), 0.76 (br, 4H). ¹³C-NMR (100 MHz, CDCl₃): δ = 153.2, 152.9, 142.5, 129.4, 127.2, 122.2, 121.5, 113.3, 108.5, 56.2, 40.1, 31.8, 29.9, 29.2, 24, 23.8, 22.6, 14.1.

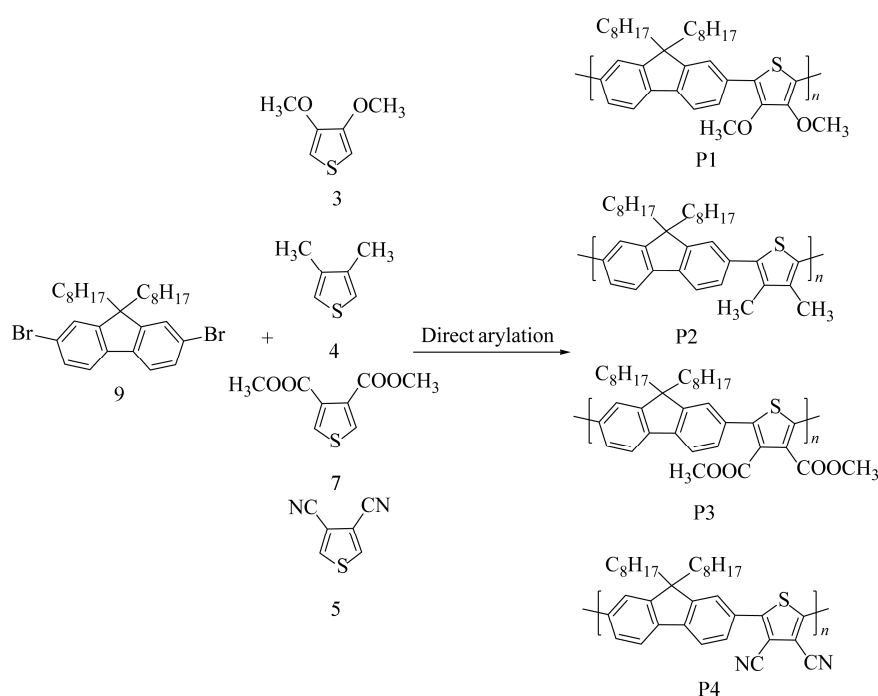
RESULTS AND DISCUSSION

Four thiophene derivatives and 2,7-dibromo-9,9-dioctylfluorene were prepared according to the literature (Scheme 1)^[15–20]. Four copolymers P1–P4 were prepared *via* direct arylation polycondensation (Scheme 2). Table 1 lists the molecular weight of copolymer P1 with six various catalytic conditions. The ligand-free condition obtained molecular weight of 8400 (yield 65.1%) using Pd(OAc)₂ (entry 1). P(*o*-MeOPh)₃ acted as ligand under the same catalyst with molecular weight of 2700 (yield 50.8%) (entry 2). To explore the effect of the ligand, PCy₃·HBF₄ was examined. Compared with P(*o*-MeOPh)₃, the molecular weight slightly promoted to 6300 (yield 82.0%) using PCy₃·HBF₄ (entry 3). The same ligand combinations were applied to Pd(OAc)(*o*-Tol).



Scheme 1 Synthesis of the monomers

The desired product was obtained with a high molecular weight of 24000 (yield 62.0%) under ligand-free (entry 4). The molecular weight of the product slipped to 7100 (yield 76.5%) when $P(o\text{-MeOPh})_3$ was added (entry 5). The fluorescent material wasn't detected within 24 h when $\text{PCy}_3\cdot\text{HBF}_4$ was added. Prolonging the reaction time to 48 h, yellow fluorescent substance was obtained with molecular weight of 10600 (yield 72.5%) (entry 6). Obviously, the ligands may weaken the catalytic ability of the catalyst in these reaction systems^[21]. Compared with ligand-free conditions, the low molecular weight polymers were obtained when ligands were added. Nevertheless, the polycondensation has taken place in both ligand catalytic systems and ligand-free catalytic systems. The experimental data suggest that 3,4-dimethoxythiophene as comonomer has high reactivity because of the low selectivity for catalyst and ligand.



Scheme 2 Synthesis of the copolymers P1, P2, P3 and P4

Table 1. The polycondensation of 3,4-dimethoxythiophene with 2,7-dibromo-9,9-dioctylfluorene^a

Entry	Catalyst	Ligand	M_n^b	PDI ^b	Yield ^c (%)
1	$\text{Pd}(\text{OAc})_2$	—	8400	2.14	65.1
2	$\text{Pd}(\text{OAc})_2$	$P(o\text{-MeOPh})_3$	2700	1.67	50.8
3	$\text{Pd}(\text{OAc})_2$	$\text{PCy}_3\cdot\text{HBF}_4$	6300	2.21	82.0
4	$\text{Pd}(\text{OAc})(o\text{-Tol})$	—	24000	1.74	62.0
5	$\text{Pd}(\text{OAc})(o\text{-Tol})$	$P(o\text{-MeOPh})_3$	7100	2.12	76.5
6 ^d	$\text{Pd}(\text{OAc})(o\text{-Tol})$	$\text{PCy}_3\cdot\text{HBF}_4$	10600	2.36	72.5

^a Reactions were run with catalyst (2 mol%), ligand (4 mol%), pivalic acid (30 mol%), and K_2CO_3 (2.5 equiv.) in dimethylacetamide (DMAc) for 24 h at 100 °C; ^b Estimated by GPC calibration based on polystyrene standards; ^c The products were obtained by soxhlet extraction from $\text{CH}_3\text{OH}/\text{C}_3\text{H}_6\text{O}$; ^d Prolonging the reaction time to 48 h

The same catalytic conditions were employed in preparing P2, P3 and P4. Table 2 lists the molecular weight of copolymer P2 with six various catalytic conditions. The ligand-free condition obtained molecular weight of 5400 (yield 47.3%) using $\text{Pd}(\text{OAc})_2$ (entry 1). With the same catalytic condition, Takaki obtained molecular weight of 10700 (yield 78%)^[21]. The main reason is that the processing of removing water and oxygen results in a decline in the mole ratio of the monomers due to the strong volatility of 3,4-dimethylthiophene, which reduces

degree of polymerization. Compared with ligand-free condition, the molecular weight of the product slipped to 5200 (yield 72.8%) and 4400 (yield 37.1%) when $P(o\text{-MeOPh})_3$ and $PCy_3 \cdot HBF_4$ were added, respectively (entry 2 and entry 3). The same ligand combinations were applied to $Pd(OAc)(o\text{-Tol})$. The polycondensation could only occur in entry 4 with the molecular weight of 7000 (yield 73.9 %). The ligands still weaken the ability of the catalyst in these reaction systems. Compared with 3,4-dimethoxythiophene, 3,4-dimethylthiophene as comonomer has lower reactivity because entry 5 and entry 6 have no product and the products of lower molecular weight are obtained with the same catalytic conditions (entries 1–4). Table 3 lists the molecular weight of copolymer P3 with six various catalytic conditions. The polycondensation didn't take place with ligand-free condition (entry 1 and entry 4). Meanwhile, the products were not generated using $Pd(OAc)(o\text{-Tol})$ as catalyst (entries 4–6). The merited products were obtained with high molecular weight of 23400 (yield 91.4%) and 20000 (yield 84.4%) when $P(o\text{-MeOPh})_3$ and $PCy_3 \cdot HBF_4$ were added respectively using $Pd(OAc)_2$ as catalyst (entry 2 and entry 3). The experimental data demonstrate that the effect of ligand can be magnified in these reaction systems^[22]. The entry 2 and entry 3 obtained higher molecular weight, which was only due to a good synergistic reaction between catalyst and ligand^[13]. Although the products of higher molecular weight were obtained, the polycondensation didn't take place under ligand-free condition. This result suggests that 3,4-thiophene dicarboxylate as comonomer demands better synergistic reaction between catalyst and ligand. Furthermore, it suggests that 3,4-thiophene dicarboxylate as comonomer has lower reactivity than 3,4-dimethylthiophene. Table 4 lists the molecular weight of copolymer P4 with six various catalytic conditions. Not unexpectedly, the polycondensation could only occur in this catalytic condition, in which $PCy_3 \cdot HBF_4$ acted as ligand and $Pd(OAc)_2$ acted as catalyst (entry 3). The product with the molecular weight of 5800 (yield 57.8%) was obtained. According to the above result, 3,4-thiophene carbonitrile as comonomer has the lowest reactivity among the four thiophene derivatives in the same reaction condition.

Table 2. The polycondensation of 3,4-dimethylthiophene with 2,7-dibromo-9,9-dioctylfluorene^a

Entry	Catalyst	Ligand	M_n^b	PDI ^b	Yield ^c (%)
1	$Pd(OAc)_2$	—	5400	2.03	47.3
2	$Pd(OAc)_2$	$P(o\text{-MeOPh})_3$	5200	1.66	72.8
3	$Pd(OAc)_2$	$PCy_3 \cdot HBF_4$	4400	1.62	37.1
4	$Pd(OAc)(o\text{-Tol})$	—	7000	1.45	73.9
5 ^d	$Pd(OAc)(o\text{-Tol})$	$P(o\text{-MeOPh})_3$	—	—	—
6 ^d	$Pd(OAc)(o\text{-Tol})$	$PCy_3 \cdot HBF_4$	—	—	—

The notes follow Table 1

Table 3. The polycondensation of 3,4-thiophene dicarboxylate with 2,7-dibromo-9,9-dioctylfluorene^a

Entry	Catalyst	Ligand	M_n^b	PDI ^b	Yield ^c (%)
1 ^d	$Pd(OAc)_2$	—	—	—	—
2	$Pd(OAc)_2$	$P(o\text{-MeOPh})_3$	23400	1.67	91.4
3	$Pd(OAc)_2$	$PCy_3 \cdot HBF_4$	20000	1.71	84.4
4 ^d	$Pd(OAc)(o\text{-Tol})$	—	—	—	—
5 ^d	$Pd(OAc)(o\text{-Tol})$	$P(o\text{-MeOPh})_3$	—	—	—
6 ^d	$Pd(OAc)(o\text{-Tol})$	$PCy_3 \cdot HBF_4$	—	—	—

The notes follow Table 1

Table 4. The polycondensation of 3,4-thiophene carbonitrile with 2,7-dibromo-9,9-dioctylfluorene^a

Entry	Catalyst	Ligand	M_n^b	PDI ^b	Yield ^c (%)
1 ^d	$Pd(OAc)_2$	—	—	—	—
2 ^d	$Pd(OAc)_2$	$P(o\text{-MeOPh})_3$	—	—	—
3	$Pd(OAc)_2$	$PCy_3 \cdot HBF_4$	5900	4.54	57.8
4 ^d	$Pd(OAc)(o\text{-Tol})$	—	—	—	—
5 ^d	$Pd(OAc)(o\text{-Tol})$	$P(o\text{-MeOPh})_3$	—	—	—
6 ^d	$Pd(OAc)(o\text{-Tol})$	$PCy_3 \cdot HBF_4$	—	—	—

The notes follow Table 1

It is noted that the higher molecular weight and yield are not merely associated with the reactivity of monomer or comonomer because many factors may influence the direct arylation polycondensation, for example, Schlenkline technical^[22], the synergistic reaction between catalyst and ligand^[23], additive^[14], solvent^[13], reaction temperature and time^[12], *etc.* Nonetheless, the polycondensations of 2,7-dibromo-9,9-dioctylfluorene with thiophene derivatives were carried out under the same conditions, in which the catalyst and the ligand were changed. The substituent can affect the electron cloud density of the active C—H bond in thiophene derivative, which can be monitored by the NMR chemical shift. Figures 1(a) and 1(b) show the ¹H- and ¹³C-NMR spectra of the four thiophene derivatives, respectively. The NMR data showed that the chemical shift of the active C—H bond in thiophene derivatives increased with increasing the electron withdrawing ability of the substituent. The above results show that the reactivity of thiophene derivatives decreases with increasing chemical shift of active C—H bond in the four thiophene derivatives, and thus can promote the direct arylation polycondensation.

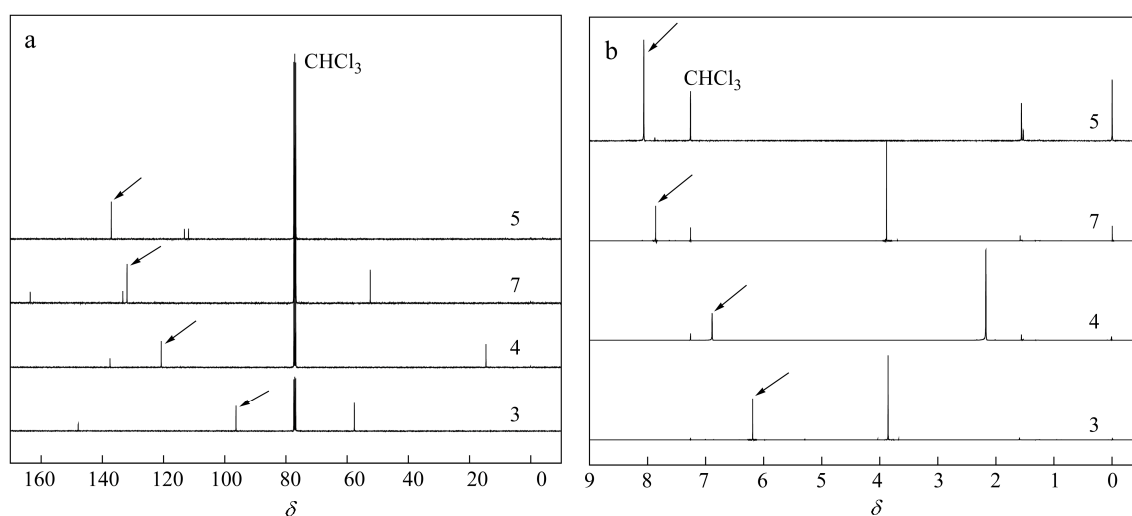


Fig. 1 The ¹³C-NMR spectra (a) and the ¹H-NMR spectra (b) of the four thiophene derivatives

The above phenomenon is explained by the electrophilic aromatic substitution (S_EAr) mechanism^[24]. The generally catalytic cycle mechanism of direct arylation has been studied experimentally and computationally, including the oxidative addition, electrophilic aromatic substitution (S_EAr) and reductive elimination^[25]. Figure 2 shows the catalytic cycles and takes the coupling of thiophene derivative and bromobenzene as an example. Bromobenzene generates complex 1 by oxidative addition. Additives can play the role of the ligand to generate similar complex 1 with ligand-free catalytic condition^[26]. Under the action of carboxylate anion, complex 1 transforms into more stable complex 2. The sulfur atom on the thiophene derivative acts as the nucleophilic reagent attacking the complex 2 to generate transition state TS1 because the sulfur atom has more intensive electron cloud^[27]. The TS1 exists in instable seven-membered heterocycle and will transform into transition state TS2, which is more stable and more consistent with the principle of lowest energy^[28]. High density of electron cloud at active site is conducive to promote formation of transition state TS2 and avoids reversible reaction. The cooperative capability of ligand and catalyst also promotes formation of transition state TS2^[23]. The complex 3 then removes a member carboxylic acid while generates complex 4. Finally, the aryl coupled product is generated by reductive elimination. The S_EAr process plays an important role in the whole catalytic cycle and determines the feasibility of polycondensation. The metal atom of the complex 2 should be susceptible to attack by nucleophilic reagents. The thiophene derivative as nucleophilic reagents attacks the complex 2 to generate transition state TS2. Stronger nucleophilic ability can promote formation of transition state TS2 in the same reaction condition^[29]. Thus, the reactivity decreases with increasing chemical shift of active C—H bond in four thiophene derivatives and can promote the direct arylation polycondensation.

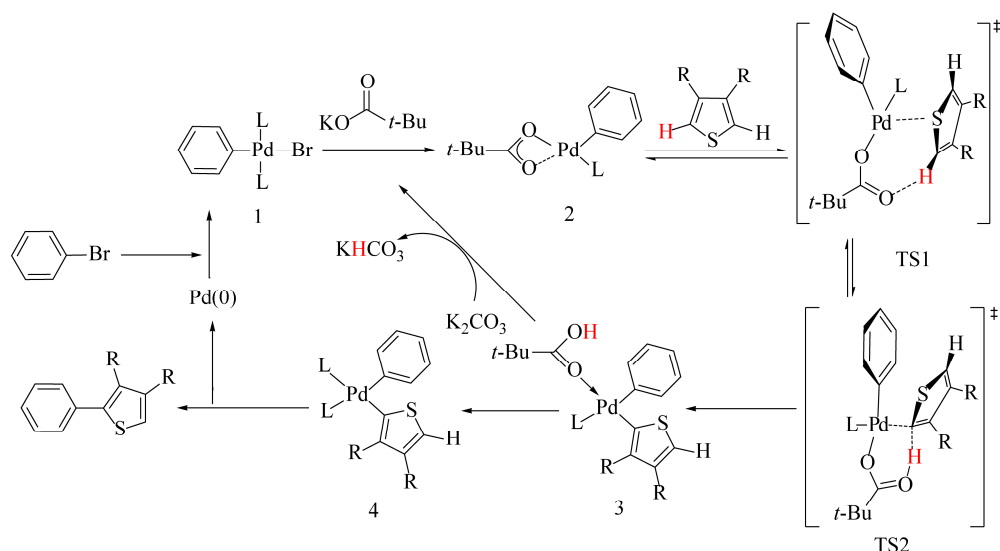


Fig. 2 The catalytic cycles for cross coupling between thiophene derivative and bromobenzene

The UV-Vis spectra of the four copolymers in chloroform solutions and thin films are shown in Fig. 3. A summary of the absorption is given in Table 5. As shown in Fig. 3 and Table 5, the spectra and the band gap of the polymers varied with the different substituents at thiophene group. The four copolymers in chloroform solution display absorption band from 300 to 500 nm, which is ascribed to the π - π^* transition derived from the polymer backbone^[30]. Compared with that of P2 (about 371 nm), the maximum absorption peaks of P1, P3 and P4 obviously red-shifted, which was due to the elongation of the conjugation length and the increased charge-transfer character induced by the electron donating or electron withdrawing substituent^[31]. Compared with that of P4 (about 410 nm), the maximum absorption peaks of P1 and P3 red-shifted, too. The presence of higher molecular weight or better planarization of the copolymer backbone for P1 and P3 may account for the spectral shifts. P1 and P3 have the similar absorption spectra in solution. The absorption spectra undergo red shifts for P1-P4 on going from the solutions to thin films, but their relative order of the values of maximum absorption peak retain the same as observed in solutions (Table 5). This is due to intermolecular π - π stacking of the polymer backbone in thin films^[32]. From the onset of absorption, we can estimate its optical band gap (Table 5)^[33]. The optical band gaps of copolymers P1, P3 and P4 are lower than that of P2 because either strong electron-donating or electron-withdrawing substituent on π -electron ring system can promote π -electron delocalization^[31].

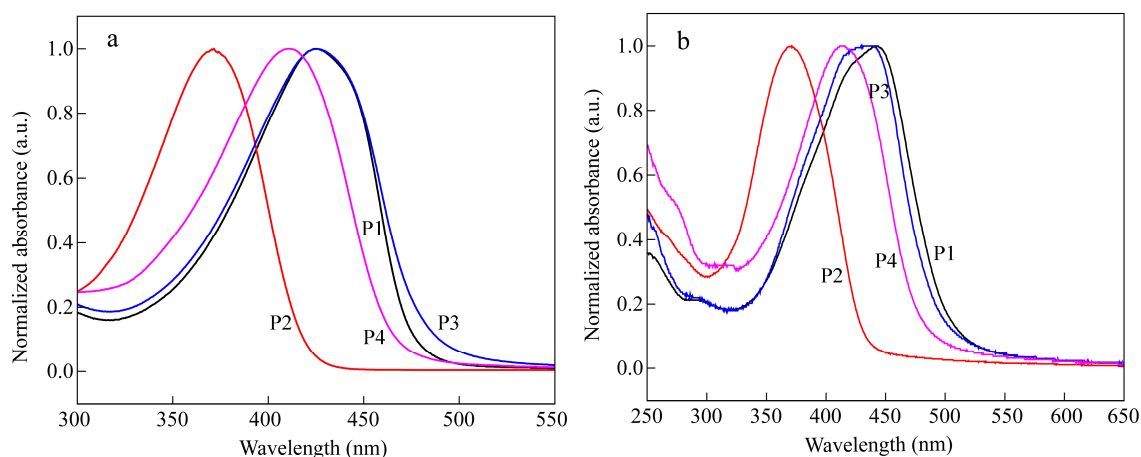
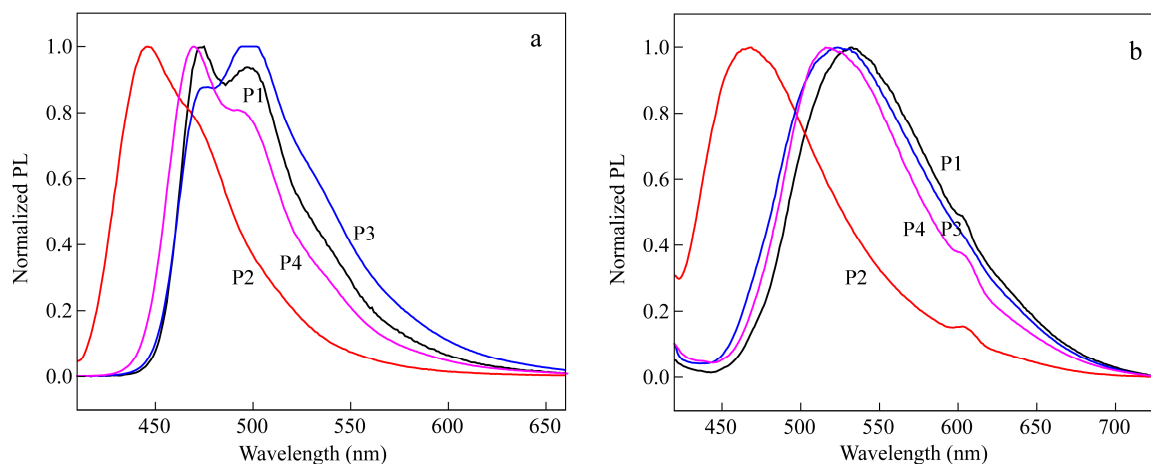


Fig. 3 The UV-Vis spectra of the four copolymers in solutions (a) and in thin films (b)

Table 5. The UV-Vis data and PL data of the four copolymers

Polymer	Solution		Thin film		PL $\lambda_{\max}$ (nm)		E_g (eV)	$\phi_{(n)}$ (%)
	$\lambda_{\max}$ (nm)	λ_{onset} (nm)	$\lambda_{\max}$ (nm)	λ_{onset} (nm)	solution	film		
P1	425	479	442	515	474, 498	530	2.41	84.9
P2	371	423	372	439	446, 470	468	2.82	40.6
P3	425	494	441	511	501, 474	523	2.42	62.6
P4	410	470	413	485	470, 494	516	2.56	32.2

Figure 4(a) shows PL spectra of the four copolymers in dilute chloroform solutions (1×10^{-5} mol·L⁻¹) on irradiation at 365 nm and Fig. 4(b) shows PL spectra of the four copolymers in thin films on irradiation at 400 nm, and the PL emission peaks are listed in Table 5. Among the four copolymers, P2 showed typical blue-emission peak and other polymers showed typical green-emission peaks in solution. For all copolymers, the PL spectra exhibited a main emission peak and a shoulder peak, which were attributed to the π - π^* transition along the copolymer backbone. The emergence of shoulder peaks was due to the 0-1 or 0-2 singlet transition of the copolymer backbone^[34]. Compared in solutions, the four copolymers in thin films displayed broad red-shifts (> 20 nm), it was due to the more heteroaromatic ring packing in solid state. The weak shoulder peaks at about 603 nm for all copolymers were observed, this was due to formation of the excimer because of the aggregation of the polymers in thin films. Comparing to P2, the red shifts of PL spectra in the other copolymers were as expected due to the electron donating or electron withdrawing substituent effect. The electron-donating or electron-withdrawing substituent on π -electron ring system can promote π -electron delocalization and enhance the conjugation length. This is in accordance with the UV-Vis results. However, in thin films, P2 emits blue-green light and the other polymers emit yellow light. The fluorescence quantum yields (ϕ_f) of the four copolymers in CHCl₃ were estimated, and the results are summarized in Table 5. The fluorescence quantum yields of P1–P4 in CHCl₃ are 84.9%, 40.6%, 62.8% and 32.3%, respectively, by reference to the DMF solution of Alq₃ ($\phi = 0.11$) as the standard solution^[35]. The fluorescence quantum yield of P1 is the highest. It demonstrates that the higher molecular weight and electron donating substituent may improve the luminescence efficiency. Thus, these alternating fluorene-thiophene copolymers with different substituents are good fluorescent materials and promising in PLED applications.

**Fig. 4** The PL spectra of the four copolymers in solutions (a) and in thin films (b)

CONCLUSIONS

Four copolymers P1–P4 *via* direct arylation polycondensation were prepared in six different catalytic systems to investigate the substituent effects. The substituent can affect the electron cloud density of the active C–H bond, which can be monitored by the NMR chemical shift. The experimental results show that the reactivity decreases with increasing the chemical shift of active C–H bonds in the four thiophene derivatives, and thus can promote

the direct arylation polycondensation. This phenomenon is explained by the electrophilic aromatic substitution (S_EAr) mechanism. The optical properties of the copolymers demonstrate that either strong electron-donating or electron-withdrawing substituent can influence the emission band and optical band gap. In thin films, P2 emits blue-green light and the other polymers emit yellow light. Thus, these alternating fluorene-thiophene copolymers with different substituents are good fluorescent materials and promising in PLED applications.

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