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Synthesis of Highly Regioregular, Head-to-Tail Coupled Poly(3-octylesterthiophene) *via* C—H/C—H Coupling Polycondensation

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Electronic Supplementary Information

Abstract Highly regioregular, head-to-tail coupled poly(3-octylesterthiophene) was synthesized by the Pd-catalysed oxidative C—H/C—H coupling polycondensation. The regioregularity of polymer products was confirmed by the ^{1}H-NMR technique. Furthermore, the effects of various reaction factors including polymerization temperature, solvents and catalysts *etc.* on the yield, molecular weight and structural regioregularity of the resultant polymers were systematically studied. The optical, electrochemical and crystallization properties of the resultant P3OET with different HT regioregularities in solution and film state were studied by UV-Vis and fluorescent spectroscopy, cyclic voltammetry and X-ray diffraction (XRD), resepectively.

Keywords C—H/C—H coupling polymerization; Pd catalysed oxidative; Poly(thiophene)s

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INTRODUCTION

Regioregular poly(3-substitutedthiophene)s (rrP3STs) are an important class of π-conjugated polymers that can be used in a variety of applications such as field-effect transistors (FETs)[1−4], polymer light-emitting diodes (PLEDs)[5, 6], solar cells[7−11], and chemical sensors[12, 13]. Due to the fact that rrP3STs can be ordered in three dimensions: conformation ordering along the backbone, π-stacking of flat polymer chains, and lamellar stacking between chains, they exhibit unique electrical and optical properties. However, the polymerization of the non-symmetrical 3-substituted thiophene leads to a mixture of polythiophene structures containing three regiochemical linkages between repeat units (2,2′, 2,5′, 5,5′, namely, head-to-head (HH), head-to-tail (HT) and tail-to-tail (TT))[14, 15]. The 2,2′ and 5,5′ couplings are considered as defects in the polymer structure since they diminish conjugation and prevent ideal solid-state packing, thus impairing these materials' electrical and photonic properties[16−19].

In order to synthesize the pure 2,5′ (or HT coupled) regioregular P3STs, a variety of synthetic strategies including McCullough method[20], Rieke method[21], GRIM method[22], as well as Stille and Suzuki cross-coupling reaction have been reported[23−25]. Recently, the direction C—H arylation polymerization (DArP) *via* the dehydrohalogenative cross-coupling reaction of (hetero)arenes with aryl halides has been widely recognized as the atom- and step-economic method to construct π-conjugated polymers[26−29]. Despite these new advances, the above synthetic procedures usually suffer from limitations including tedious synthetic steps to prepare bifunctional aryl halides and/or organometallic monomers, a stoichiometric amount of toxic byproducts, an extra end-capping procedure for removal of terminal halogens or organometallic functional groups, and poor stabilities of some organometallic reagents.

Direct C—H/C—H coupling is obviously the best and most economical way to build new C—C bonds for new material synthesis, with many advantages such as more atom-economic, more diverse starting materials and avoiding the issue of end-capping groups[30−33]. But so far, the transition-metal-catalysed oxidative C—H/C—H coupling polymerization for the synthesis of regioregular polythiophene derivatives is still few.

More recently, we developed an efficient direct C—H/C—H coupling polymerization for the synthesis of polythiophene derivatives[33, 34]. While the mechanism of transition-metal-catalyzed oxidative C—H/C—H coupling polycondensation is still not clear at present, it is believed

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that the electron-withdrawing carbonyls directly attached to thiophene rings play a critical role in the polymerization, either through an electron-withdrawing effect to better facilitate C—H activation of the 2-position or as a directing group that coordinates with the metal palladium center. Accordingly, it is expected that the ester group attached on 3-position of thiophene ring will increase the selectivity of C—H of its 2-position, resulting in the formation of head-to-tail coupling. Herein, we wish to explore a facile and efficient synthetic strategy to build up regioregular, head-to-tail coupled poly(3-octylesterthiophene) (P3OET) through Pd-catalysed oxidative C—H/C—H coupling polycondensation of non-symmetrical 3-octylesterthiophene (Scheme 1).

EXPERIMENTAL

General Characterization

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AV400 using residual solvent peak as a reference. Number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography (SEC) in tetrahydrofuran at 25 °C using Waters 1525 with Waters Styragel HT gel columns. For the calibration, a series of monodisperse polystyrene standards (Shodex) was used. Thermogravimetric analyses (TGA) were carried out on a Netzsch TG209 instrument under a purified nitrogen gas flow with a 10 $°C\cdot min^{-1}$ heating rate. UV-Vis absorption spectra were recorded using a Shimadzu UV-2550 and drop-cast films on glass plates were used for the solid-state measurements. Optical bandgaps were determined from the onset of the absorption band. Cyclic voltammetry (CV) experiments were performed with a LK98B II microcomputer-based electrochemical analyzer. All CV measurements were carried out at room temperature with a conventional three-electrode configuration using a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. Acetonitrile was distilled from calcium hydride under dry nitrogen immediately prior to use. Tetrabutylammonium phosphorus hexafluoride (Bu_4NPF_6, 0.1 mol/L) in acetonitrile was used as the support electrolyte, and the scan rate was 100 $mV\cdot s^{-1}$. X-ray diffraction (XRD) experiments were performed on a Bruker D8 FOCUS X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å) at a generator voltage of 40 kV and a current of 40 mA.

Synthesis

$Pd(OAc)_2$, $Pd(TFA)_2$, $Pd(PhCN)_2Cl_2$, dichlorobis(tricyclohexylphosphine)palladium(II) ($Pd(dtchp)Cl_2$), *trans*-di(μ-acetato)-bis[*o*-(di-*o*-tolyl-phosphino)benzyl]dipalladium(II) (Herrmann's Catalyst), [1,1′-bis(diphenylphosphino)-ferrocene]dichloropalladium(II) ($Pd(dppf)Cl_2$) were purchased from Sigma-Aldrich. 3-Thiophenic acid, Ag_2CO_3, KOAc and other chemicals were received from commercial suppliers and used without further purification. Anhydrous dimethylacetamide (DMAc) was purchased from Kanto Chemical and used as a dry solvent. 3-Octylesterthiophene was prepared according to procedures reported in the literature[34]. All the monomers were carefully purified prior to use in the polymerization reaction.

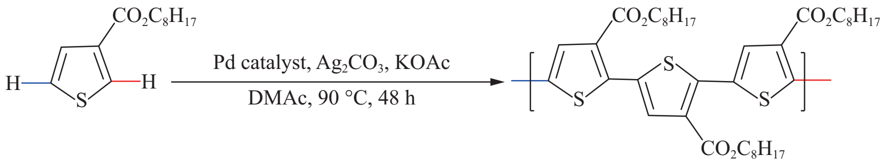
To a 25 mL round bottom flask with a reflux condenser monomer (1 equiv.), Ag_2CO_3 (2.0 equiv.), potassium acetate (2.0 equiv.) and DMAc (1 mL) were added. The mixture was stirred at 90 °C for 10 min, then degassed twice with argon followed by the addition of palladium catalyst (5 mol%) dissolving in 1 mL of DMAc. After stirring at 90 °C for 48 h under argon, the mixture was cooled to room temperature and poured in 100 mL of cold methanol. The precipitate was filtered out as the crude product. Soxhlet extraction with methanol was applied to remove the catalyst and this was followed by hexane extraction to remove the low-molecular-weight materials. The polymer products were then obtained by extraction using hot chloroform. The extract was condensed to about 2 mL and the mixture was poured into cold methanol. The precipitate was filtered, and the final polymer was isolated as a solid and dried under vacuum at 60 °C over a period of 12 h.

RESULTS AND DISCUSSION

As shown in Scheme 1, poly(3-octylesterthiophene) (P3OET) was synthesized *via* Pd-catalyzed oxidative C—H/C—H coupling reactions using various Pd as the catalyst in the presence of Ag_2CO_3 and KOAc at various temperatures. It was found that the Pd-catalyzed oxidative coupling reaction works well for polymers with asymmetric hydrogen.

Polymer Structural Analyses

^{1}H-NMR spectroscopy was used to characterize the structure of resultant P3OET and determine the regioregularity. Fig. 1 shows the typical NMR spectra of P3OET with HT regioregularity of 90.5% synthesized with the condition of $Pd(dppf)Cl_2$ as catalyst and DMAc as solvent at 90 °C (entry 2 in Table 1). As shown in Fig. 1, two sets of peaks at δ = 4.30/4.28 and 4.14/4.12 ppm assigned to the CH_2 groups (H_b) close to ester group are observed, which should be designated to the HT and HH dyads, respectively[35−37]. This assignment method has been widely used to confirm the regioregularity of HT coupling for various new



Scheme 1 Pd-catalysed oxidative C—H/C—H coupling polymerization of 3-octylesterthiophene. Reaction conditions: 3-octylesterthiophene (1 equiv.), oxidant (2.0 equiv.) and additive (2.0 equiv.) in 2 mL of solvent at 90 °C for 48 h.

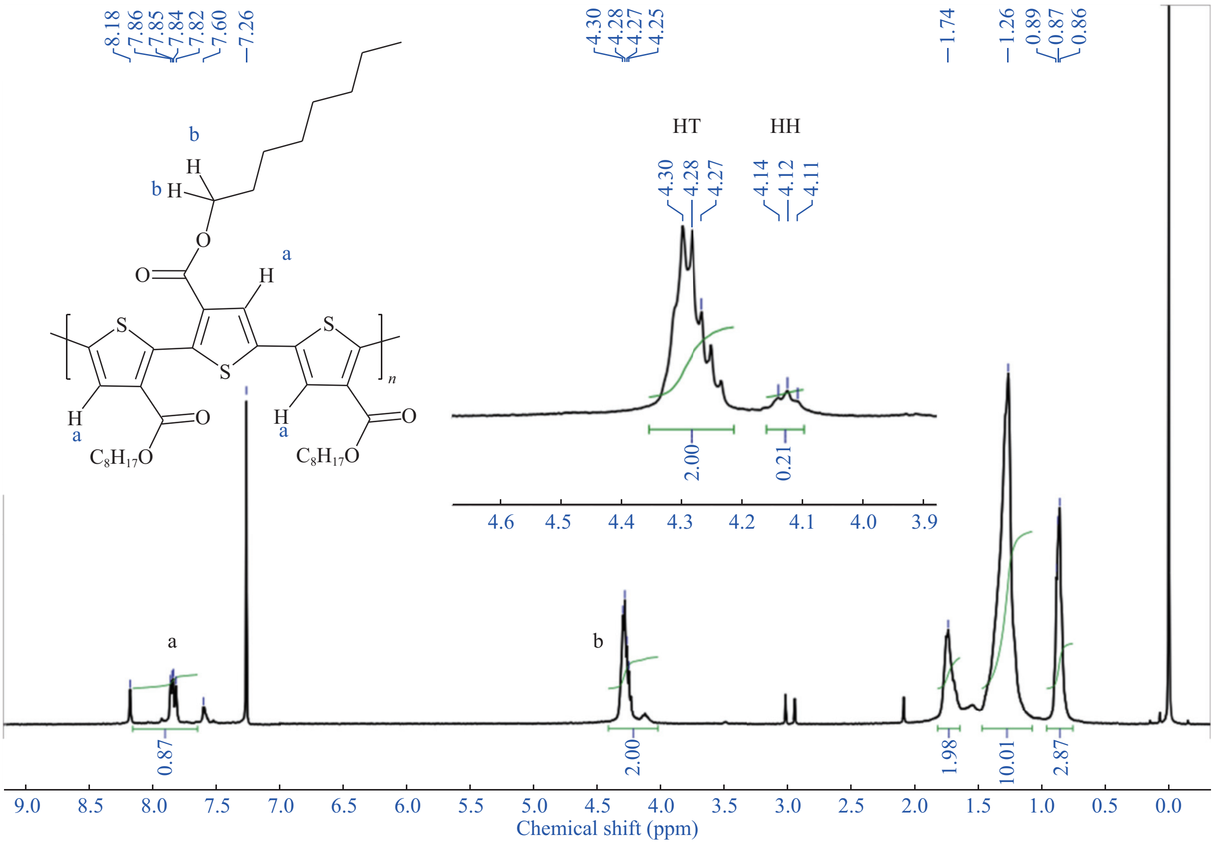


Fig. 1 ^{1}H-NMR spectrum of P3OET synthesized according to the reaction conditions listed as entry 2 in Table 1 (Inset: the enlarged spectrum in the range of 4.00–4.60 ppm for determination of the regioregularity of product P3OET.)

polythiophene derivatives through determining the integral area ratio of HT and HH dyad peaks in their ^{1}H-NMR[14, 38]. Based on this method, the HT regioregularity of P3OET is about 90.5%. The greater amount of HT dyads seems to be reasonably indicated from the benzene series, in which strong electron withdrawing groups activate the *ortho* position in the Ullmann coupling reaction[14, 39].

By the comparison for NMR in the aromatic region of P3OET with that of its monomer (Fig. S3, in electronic supplementary information, in ESI), the signals at δ = 8.18 (H_d), 7.86 (H_a) and 7.6 ppm (H_c) should be assigned to the 2-, 4- and 5- position protons on the terminal unit of P3OET, respectively. The slight difference of chemical shifts between the terminal units and the monomer should be due to the formation of the polymer chain, as widely observed in polymers. The ratios of the H_a:H_c and H_a:H_d were 11.11 and 6.67 for P3OET, respectively. These results further indicate that the C—H/C—H coupling polymerization reaction of 3-octylesterthiophene occurred on 2,5 sites of 3-octylesterthiophene. It is important to note that the 4-position H (H_a) on the thiophene ring of the polymer is split into three sets of peaks at δ = 7.92, 7.86 and 7.60 ppm, respectively. Especially, when the ^{1}H-NMR spectrum is zoomed in, it showed many more peaks, up to about 12–16 peaks and shoulders as observed by Pomerantz *et al*[14]. It is well known that there are four triads (HT-HT, HT-HH, HT-TT, HH-TT) to be considered with respect to the ^{1}H-NMR spectra in the case of many 3-substituted polythiophenes such as poly(3-alkylthiophenes), so P3OET should expect four peaks. The observation of many more than four peaks for P3OET suggests that pentads rather than triads must be considered (see Fig. S13, in ESI). This is because of the strong electron-with drawing ability of the ester group which enables it to induce ^{1}H chemical shift of H_a in the polythiophene.

Optimization of Polymerization Conditions

Firstly, the polymerization of 3-octylesterthiophene was conducted according to the reaction conditions optimized in the previous work[31, 32], *i.e.*, 2.0 equiv. of Ag_2CO_3 as oxidant, 2.0 equiv. of KOAc, *N*,*N*-dimethylacetamide (DMAc) as a solvent at 110 °C for 48 h in the presence of Herrmann's catalyst or $Pd(OAc)_2$ (entries 1 and 8, Table 1). Only polymer products with moderate regioregularities were obtained (80.4% for Herrmann's catalyst and 65.4% for $Pd(OAc)_2$). As pointed out by Huggin *et al.*, the polymerization temperature had a significant effect on the stereoregularity of polymer products and the lower polymerization temperature was beneficial to stereoregularity of polymer products[40]. However, lowering the reaction temperature should decrease the undesired activation of the less reactive β-protons relative to more reactive α-protons[41]. Thus, we focused on the effect of reaction temperature on the polymerization of 3-octylesterthiophene. Pd-catalysed oxidative C—H/C—H coupling polycondensation of 3-octylesterthiophene was conducted at 110, 90 and 60 °C,

Table 1 Reaction conditions for the polymerization of P3OET through Pd-catalyzed oxidative C—H/C—H coupling[a]

Entry	Catalyst	Solvent	Temperature (°C)	Yield [b] (%)	M_n [c] (kDa)	M_w [c] (kDa)	PDI [c]	HT [d] (%)
1	Herrmann's cat.	DMAc	110	73	7.0	12.4	1.77	80.4
2	Herrmann's cat.	DMAc	90	83	5.4	7.1	1.32	90.5
3	Herrmann's cat.	DMAc	60	99	11.2	25.9	2.32	85.4
4	Herrmann's cat.	DMAc	30	Trace	–	–	–	–
5	Herrmann's cat.	THF	90	Trace	–	–	–	–
6	Herrmann's cat.	Toluene	90	Trace	–	–	–	–
7	Herrmann's cat.	Xylene	90	Trace	–	–	–	–
8	$Pd(OAc)_2$	DMAc	110	64	6.8	11.6	1.70	65.4
9	$Pd(OAc)_2$	DMAc	90	76	5.8	8.4	1.45	83.3
10	$Pd(OAc)_2$	DMAc	60	72	5.6	7.4	1.32	85.0
11	$Pd(OAc)_2$	DMAc	30	Trace	–	–	–	–
12	$Pd(TFA)_2$	DMAc	90	83	11.6	26.3	2.26	78.7
13	$Pd(PhCN)_2Cl_2$	DMAc	90	47	6.5	10.9	1.68	84.0
14	$Pd(dtchp)Cl_2$	DMAc	90	81	11.0	23.8	2.17	80.0
15	$Pd(dppf)Cl_2$	DMAc	90	46	5.1	6.5	1.26	88.5
16 [e]	$Pd(dppf)Cl_2$	DMAc	90	99	9.6	33.3	3.47	86.2
17	$FeCl_3$ [f]	$CHCl_3$	45	Trace	–	–	–	–

[a] Reaction conditions: Substrate (1 equiv.), catalyst (0.05 equiv.), oxidant Ag_2CO_3 (2.0 equiv.), additive KOAc (2.0 equiv.) in 2 mL of different solvents at various temperatures for 48 h, unless otherwise noted; [b] Isolated yield after purification; [c] Estimated by SEC measurements (eluent: THF, standard: polystyrene); M_n = Number-average molecular weight, M_w = Weight-average molecular weight, PDI = Polydispersity index; [d] Estimated by ^1H-NMR; [e] PCy_3-HBF_4 (0.2 equiv.) was used; [f] $FeCl_3$ (6 equiv.). It does not work as catalyst, but as oxidant.

respectively, using Herrmann's catalyst and $Pd(OAc)_2$ as catalyst with constant catalyst loading and reaction time of 48 h. As shown in Table 1 and Fig. 2, the regioregularity of P3OET was affected by reaction temperature significantly. In the same catalyst system, as the reaction temperature decreased from 110 °C to 60 °C, the regioregularity of P3OET increased gradually. For example, as decreasing the temperature from 110 °C to 60 °C, the regioregularity significantly increased from 65.4% to 85.0% in the presence of $Pd(OAc)_2$ (entries 8–11, Table 1 and Fig. 2a). However further decreasing the reaction temperature to 30 °C, only trace product was obtained. It can be explained that the reaction temperature is too low to activate the α-protons. On the other hand, it was found that the reaction temperature also had an obvious influence on the polymer yield as shown in Table 1 and Fig. 2(b). In the case of Herrmann's catalyst, when the reaction temperature decreased from 110 °C to 60 °C, the corresponding polymer yield increased from 73% to 99% as shown in Fig. 2(b). In summary, the optimized conditions using Herrmann's catalyst in 90 °C for 48 h give the best regioregularity up to 90.5% with moderate yield and average molecular weight.

In order to screen the most appropriate solvents for Herrmann's catalyst-catalyzed direct coupling polymerization, we have systematically studied the C—H direct coupling polymerization in various solvents, which were widely used in various cross-coupling reactions, such as DMAc, THF, toluene and xylene (entry 2, 5–7 in Table 1). The results showed that the Herrmann's catalyst has relatively higher reactivity in polar solvents (for example DMAc, entry 2 in Table 1) than nonpolar solvents (for example toluene and xylene, entries 6 and 7 in Table 1). These results could be explained as follows: (1) the activity of C—H on the 2 and 5-position of the monomer is lower in nonpolar solvents than that in polar ones; (2) the inorganic salts of oxidants and additives such as Ag_2CO_3 and KOAc have poor solubility in nonpolar solvents, thus reducing their ability of oxidation and capturing hydrogen. In addition, the chemical characteristics of palladium catalysts, also known

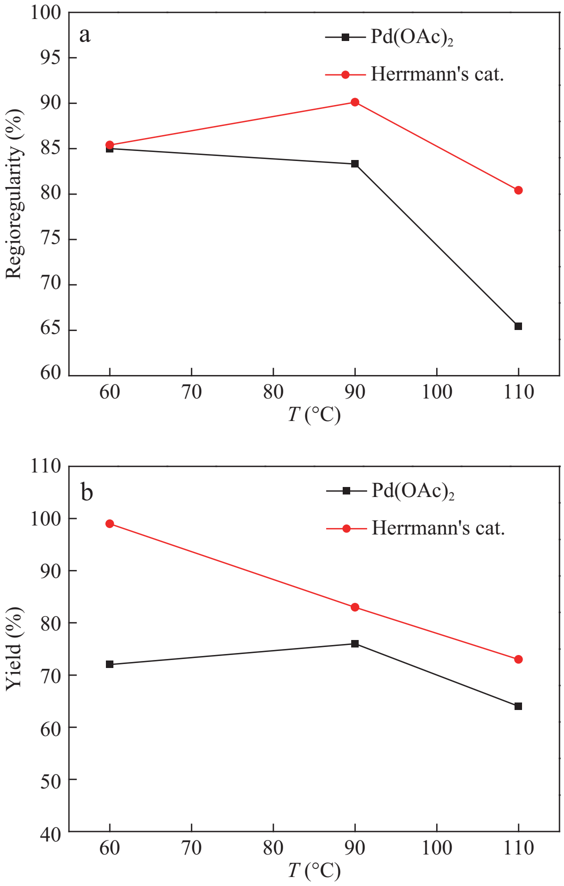


Fig. 2 Influence of reaction temperature on the regioregularity of polymer products (a) and polymer yield (b) (entries 1–4 and entries 8–11 in Table 1. Reaction conditions: catalyst loading amount of 5%, reaction time of 48 h.)

as catalytic precursors, are important to determine their activity in a coupling reaction. The activities of different palladium complexes for the polymerization of 3-octylesterthiophene were also investigated. As shown in Table 1 (entries 2, 9 and 12–15), the polymerization using Herrmann's catalyst in DMAc resulted in P3OET with the best regioregularity of 90.5%. It was noted that the steric hindrance of palladium ligands probably slightly affected the regioregularity of the polymer products. With the gradual increase of the ligand size of palladium catalyst from $Pd(OAc)_2$, $Pd(TFA)_2$, $Pd(PhCN)_2Cl_2$, $Pd(dtchp)Cl_2$, $Pd(dppf)Cl_2$ to Herrmann's catalyst, the regioregularity of polymer products exhibits gradual increase from 83.3% to 90.5%. Compared with Herrmann's catalyst, other catalyst systems led to similar stereoregularity with an improved number-average molecular weight (M_n) and weight-average molecular weight (M_w) but relatively broader PDI. According to the mechanism of C—H/C—H coupling polycondensation reported in our previous work[42, 43], the first step of C—H/C—H coupling polymerization comes from the Pd metalation at the neighboring C—H site. Herrmann's catalyst has a larger ligand (*o*-tolylphosphinobenzyl) than other catalysts (acetate, trifluoroacetate, benzonitrile and diphenylphosphino-ferrocene). So it may have a steric effect to form a relatively stable intermediate with six-member ring. This is beneficial for the stereoselectivity in C—H direct coupling polymerization. A phosphine ligand, tricyclohexylphosphine tetrafluoroborate (PCy_3-HBF_4), was found to significantly improve the regioregularity of poly(3-hexylesterthiophene)s[38]. So, PCy_3-HBF_4 was also selected as additive to conduct our polymerization reaction in this work. However, only 86.2% HT regioregularity was obtained (entry 16 in Table 1) with improved weight-average molecular weight (M_w) (3.33×10^4 Da) but a considerably broader PDI of 3.47. Importantly, ferric chloride ($FeCl_3$), which was the most widely used oxidant for the polymerization of thiophene, could not work for the polymerzation of 3-octylesterthiophen (entry 17 in Table 1). The result is consistent with the previously reported ones, that is, the carbonyl-containing heterocycle is incompatible with chemical oxidative polymerization with $FeCl_3$. Thus, the oxidative C—H/C—H coupling polycondensation method should give promising alternative to acquire these corresponding polymers.

Optical Properties

UV-Vis absorption spectra were employed to investigate P3OET's optical properties (M_w = 7.1 kDa, HT = 90.5%, entry 2 in Table 1). As shown in Fig. 3, P3OET exhibited broad absorption in the range of 300–550 nm with maximum absorption band at 421 nm in chloroform solution (5×10^{-5} mol·L^{-1}). Compared with the solution absorption spectra, the absorption spectra of P3OET solid film exhibited an obvious red shift by 33 nm, which was attributed to the intermolecular interactions between the polymer chains and the planarization effect of the *p*-conjugated polymer backbone[44−46]. In the film state, P3OET's optical band gaps could be determined by extrapolation of the absorption onsets, and the estimated value was 2.14 eV, which was close to the electrochemical bandgap of 2.36 eV measured by cyclic voltammetry (CV) method as shown in Fig. S11 (in ESI). Fluorescence spectra of P3OET in the solution and film states are shown in Fig. 3(b). Similar to the results of UV-Vis absorption spectra, obvious red-shift of fluorescence spectra was observed in the film states compared with solution states.

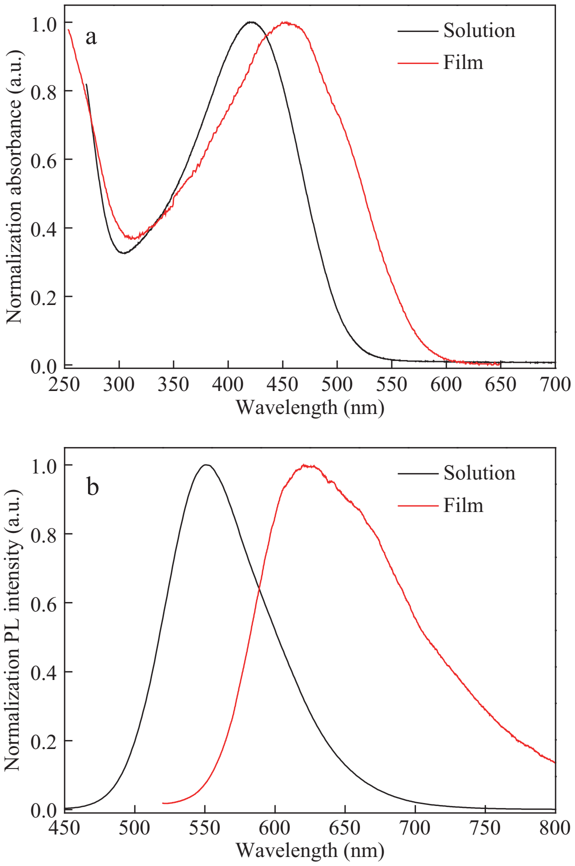


Fig. 3 Normalized UV-Vis absorption spectra (a) and fluorescence spectra (b) of P3OET in dilute chloroform solution (black line) and in the thin film state (spin-cast from chloroform solution) (red line), respectively

As well known, the HT regioregularity of 3-substitued polythiophenes has a significant effect on their self-assembly behavior, thus resulting in obvious changes in optical properties for the polymer products. In the present study, UV-Vis absorption spectra of P3OET with 90.5% HT regioregularity (entry 2 in Table 1) and 65.4% HT regioregularity (entry 8 in Table 1) in $CHCl_3$/MeOH mixed solutions were collected and compared with each other (Fig. 4). As shown in Fig. 4(a), P3OET with 65.4% HT regioregularity exhibits the absorption peak around 421 nm, which should be associated with the random-coil conformation of polythiophene derivates. With the increase of MeOH ratio in the mixture solution, the absorption maximum of P3OET was gradually red-shifted to about 438 nm. Compared with the results of P3OET with 65.4% HT regioregularity, the more significant red-shift by 60 nm was observed for P3OET with higher HT regioregularity (for example 90.5%). This distinct shift is the characteristic of

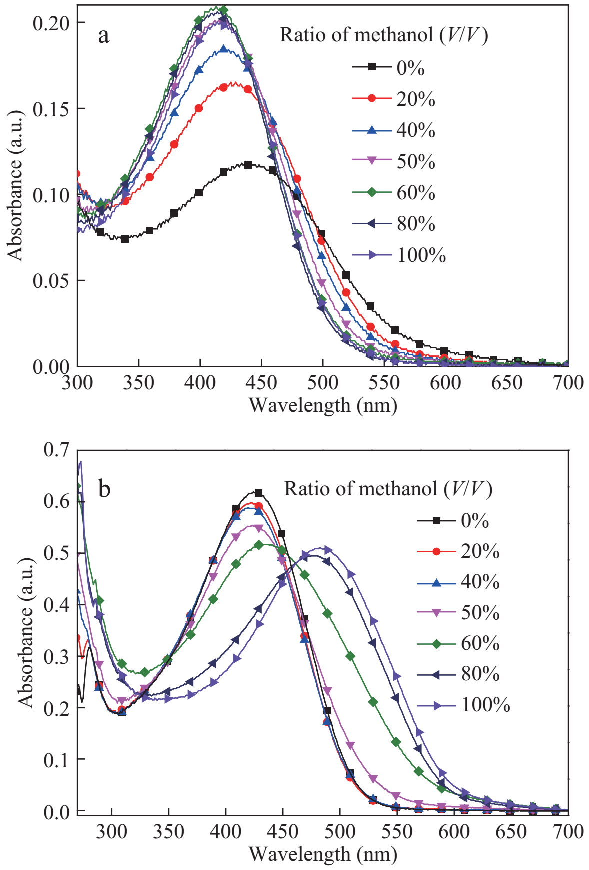


Fig. 4 UV-Vis absorption spectra of P3OET with HT regioregularity of 65.4% (a) and 90.5% (b) in $CHCl_3$/MeOH mixture solutions

aggregation of the PT backbone[47]. Obviously, P3OET with higher HT regioregularity will favor self-assembly to form ordered microstructure.

Electrochemical Properties and Thermal Stability

The electrochemical properties of P3OET with the best HT regioregularity of 90.5% prepared according to reaction conditions listed as entry 2 in Table 1 were investigated by cyclic voltammetry (CV). Ferrocene/ferrocenium of the (Fc/Fc^+) redox couple (4.8 eV below the vacuum level) was used as the internal calibration. As shown in Fig. S11 (in ESI), the HOMO and LUMO energy levels of P3OET were calculated from the onset oxidation and reduction potential, and the corresponding values were −5.74 and −3.38 eV, respectively. So the electrochemical band gap of P3OET is estimated to be 2.36 eV.

The thermal stability of P3OET was also studied by thermal gravimetric analysis (TGA) (Fig. S12, in ESI). The results revealed that the onset decomposition temperatures of the polymer were around 351 °C under N_2 atmosphere, indicating that the synthesized P3OET were quite thermally stable and could be used as functional material for optoelectronic devices.

X-ray Diffraction Study

XRD measurements were employed to investigate the crystallinity of P3OET with different HT regioregularities, such as 65.4% and 90.5% (Fig. 5). As seen from Fig. 5, P3OET with 90.5% HT regioregularity exhibited distinct diffraction peak at $2\theta = 3.76°$, corresponding to an interchain lamellar *d*-spacing of 23.4 Å. Compared with the X-ray data of typical HT regioregular poly(3-hexylthiophene) (rrP3HT) films where the well-ordered lamellar structure has an interlayer spacing of 16.0 Å, the farer interlayer distance should be related to steric effect originated from bulky ester groups directly attached to the thiophene ring. In addition, P3OET with low HT regioregularity of 65.4% did not show any diffraction peak in the tested region. Thus, the regioregularity of P3OET has an important effect on its crystallinity property.

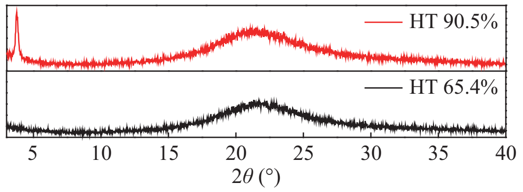


Fig. 5 Thin film X-ray diffraction profiles of P3OET with 90.5% HT regioregularity and 65.4% HT regioregularity

CONCLUSIONS

In conclusion, highly regioregular, head-to-tail coupled poly(3-octylesterthiophene)s have been successfully prepared by the novel direct C—H/C—H coupling polymerization method. Very importantly, the highest HT regioregularity (90.5%) for 3-ester substituted polythiophenes was achieved to date. Furthermore, the effects of reaction conditions including the types of catalyst, reaction temperatures and solvents on the HT regioregularity, yield, and average molecular weight of the resultant polymers were investigated in detail. The new C—H/C—H coupling polymerization method avoids many issues using the conventional organometallic intermediates and provides a simple, effective and environmental friendly strategy for the synthesis of many versatile functional polymers for various optoelectronic applications.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-018-2116-9.

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