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Preparation and Properties of Fluorene-based Thienothiophene Substituted Benzothiadiazole Copolymer for the Application of Polymeric Solar Cells

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Polymer solar cells (PSCs) have been intensively studied by researchers in order to improve their power conversion efficiency (PCE). The current PCE achievement has successfully surpassed 10%, yet it is still far laging from their inorganic counterparts. Hence, there is still a lot of room for improvement of the organic photovoltaics. This work presents a new class of fluorene-donor/benzothiadiazole-acceptor copolymers with thienothiophene as the spacer. Poly(9,9-dioctyl-9H- fluorine-alt-5,6-bis(octyloxy)-4,7-di(thieno[3,2-b] thiophen-2- yl)benzo[c][1,2,5]thiadiazole) **(P1)** was synthesized through the well-known Suzuki's cross-coupling reaction and the reported M_w and PDI values were 20 kDa and 2.6, respectively. The optical and electrochemical band gaps achieved by this **P1** were 2.03 eV and 1.98 eV, respectively, which could still be narrowed down by further modification of the chemical structure. Moreover, the **P1** was found to have good thermal stability up to 433°C. This research could provide an insight into the relationship between the chemical structure and polymeric characteristics for future designation of the PSCs.

Key words: Conjugated polymers; thienothiophene; benzothiadiazole; Suzuki cross-coupling; solar cells

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Conjugated-based polymers have been widely applied in various optoelectronic devices, such as the light emitting diodes (LEDs), field effect transistors (FETs) and the active layer in solar cells due to their distinct electronic and optical characteristics [1, 2].

Fluorene is one of the donor moieties that has been commonly used to fabricate the well-known donor-acceptor conjugated copolymers for the application of polymeric solar cells [3]. This donor could either be 9-monosubstituted or 9,9-disubstituted fluorene. Various kind of fluorene derivatives has been successfully introduced by incorporated different substituents at its 9th-position. When these various substituted fluorene coupling with each other, poly(2,7-fluorene) derivatives were produced. These poly(2,7-fluorene) derivatives are found to have excellent fluorescence in the blue region. Hence, they are generally applied in many blue-light emitting devices [4, 5].

Besides poly(2,7-fluorene)s, the fluorene has been intensively studied with many different acceptor moieties to obtain the various conjugated copolymers. The fluorene (F) was coupled with thiophene(T) - benzothiadiazole(B) - thiophene(T) acceptor through Suzuki's coupling reaction. This poly(2,7-(9-dioctyl-fluroene)-alt-5,5-(4,7-di-2-thienyl-2,1,3-benzothiadiazole), (PFTBT) copolymer was further modified by introducing alkoxyl substituents at the BT, alkyl substituents at the T, and different alkyl side chains on the 9th-position of F. The band gaps and power conversion efficiency (PCE) values obtained from these copolymers were >1.86 eV and <3.1%, respectively [6].

In 2014, a research group has successfully synthesized a derivative polymer by incorporating a vinylene group in between the F donor and T-BT-T acceptor which resulted in the poly(fluorenevinylene-alt-4,7-dithienyl-2,1,3-benzothiadiazole), (PF-TBT). Meanwhile, they also replaced the thiophene spacer in PF-TBT with alkylated phenyl ring (P), which produced the poly(fluorenevinylene-alt-4,7-diphenyl-2,1,3-benzothiadiazole), (PF-DBT). The result showed that the optical band gap for the PF-DBT is relatively narrower than the PF-TBT. Hence, the PCE values achieved by the photovoltaics based on the 1:4 of PF-TBT/PCBM and 1:4 PF-DBT/PCBM blends are 1.18% and 1.64%, respectively [7]. A few years later, researchers introduced a modified conjugated polymer, known as poly[9,9-diocyl-9H-fluorene-2,7-diyl-alt-4,7-bis(E)-divinylbenzoth -iadiazole-2,2’-diyl],(PF-B-), where the thiophene spacers of the PF-TBT were replaced with the vinylene groups. The optical and electrochemical band gaps reported for this PF-B- are 2.00 eV and 2.38 eV, respectively, which are relatively higher than the band gaps reported by PF-TBT. From this research, we can conclude that the vinylene groups enhance the solubility of the resulting copolymer but are not favourable for the electron delocalization [8].

One year later, researchers proposed two modified PFDTBT by incorporating either single or three dendritic carbazoles at the terminal position of the alkyl chains of the fluorene donor which was named as PFDTBT-Cz1 and PFDTBT-Cz3, respectively. It was discovered that PCE value achieved by the PFDTBT-Cz1 was almost similar to the PFDTBT (0.62%) while the three dendritic carbazoles resulted in detrimental effect in PV efficiency of the polymer, with only 0.13% of PCE value. This is because the bulky dendritic carbazole side chains have a negative impact on the charge separation when the PFDTBT-Cz3 is blended with $PC_{61}BM$. Fortunately, the poor PV performance of these modified polymers has been compensated by the enhancement of UV capability and improvement of the hole mobility of the polymers [9]. Further research was done on the conjugated polymer with carbazole, fluorene and benzothiadiazole units. A past research was done on a series of fluorene-carbazole-benzothiadiazole-based terpolymers, and the achieved PCE values reduced in the range of 5.0% – 7.0%. The highest 7.0% PCE value was achieved by the terpolymers with 10:90 of fluorene-TTBTBTT: carbazole-TTBTBTT. From this research, it was found that the imbalance of carbazole and fluorene donors along with the polymeric backbone that contains TTBTBTT-acceptors enable the resulting terpolymers to transport high short circuit current (I_{sc}) density through a very thin film (<100 nm). This in turns enhances the photovoltaic ability of the resulting polymeric solar cell [10].

However, due to the interplay of polymer properties such as energy levels and band gap and their correlation with V_{oc} and J_{sc}, the highest V_{oc} and highest J_{sc} could not be concurrently obtained. In order to achieve the highest possible PCE, it is crucial to balance out the V_{oc} and J_{sc} via judicious control over physical properties of the conjugation.

EXPERIMENTAL SECTION

Materials

Materials used for the preparation of monomers were purchased from commercial suppliers and used as received unless otherwise stated. All solvent used for the reaction were dried through appropriate drying agents (mainly CaH_2) and all reactions for preparing monomers were carried out under nitrogen atmosphere and the reaction for preparing polymer was carried under Argon atmosphere. 9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester **(5)** was purchased from Sigma-Aldrich. An intermediate 4,7-dibromo- 5,6-bis(octyloxy)benzo[c][1,2,5] thiadiazole **(1)** (1.00 g, 1.817 mmol) was prepared according to published procedures [10] and trimethyl(thieno[3,2-b]thiophen-2-yl)stannane was prepared according to Prim and Kirsch [12].

Characterization

Polymer solutions in tetrahydrofuran (THF) at 100°C were used as samples for gel permeation chromatography (GPC) analysis. The GPC curves were recorded on the equipment consisting of Waters Model 515 HPLC Pump, GILSON Model 234 Auto injector, MILLIPORE Waters Lambda-Max Model 481 LC Spectrometer, Erma ERC-7512 RI Detector, PLgel 5 m 500A Column, and PLgel 10 m MIXED-B Column using THF as the eluent at a rate of 1 cm^3 $minute^{-1}$. The GPC curves were obtained by the RI-detection method which was calibrated with a series of polystyrene narrow standards (Polymer Laboratories). Nuclear magnetic resonance (NMR) spectra were recorded on Bruker DRX-500 MHz NMR spectrometers and had variable temperature capabilities of ca. ± 100°C in 1,1,2,2-tetrachloroethane-d_2 solution. FTIR absorption spectra were recorded on the Nicolet Model 205 FT-IR spectrometer using a Diamond ATR attachment for solid sample analysis. Elemental analysis was carried out by the Perkin Elmer 2400 CHN Elemental Analyser for CHN analysis and by the Schöniger oxygen flask combustion method for anion analysis. The weights of the samples submitted for analysis were approximately 5 mg for CHN analysis and approximately 5 mg for each anion analysis. UV-visible absorption spectra were measured by Hitachi U-2010 Double Beam UV / Visible Spectrophotometer. The absorbance of polymers was measured in solution of toluene (spectrophotometric grade) and THF (spectrophotometric grade) at ambient temperature using rectangular quartz cuvettes (light path length = 10 mm) purchased from Sigma-Aldrich. Samples of pristine polymer thin films for UV-visible absorption spectra measurements were prepared by dip coating quartz plates into 1 mg cm^{-3} polymer solutions in chloroform (HPLC grade) and the measurements were carried out at ambient temperature. Cyclic voltammograms (CV) were recorded using a Princeton Applied Research Model 263A Potentiostat/Galvanostat. Measurements were carried out under an inert argon atmosphere at 25 ± 2°C. Tetrabutylammonium perchlorate ($TBAClO_4$) 10 cm^3 solution in acetonitrile (HPLC grade) (0.1 mol dm^{-3}) was used as the electrolyte solution. A three electrode system was used consisting of an Ag/Ag^+ reference electrode (silver wire in 0.01 mol dm^{-3} silver nitrate solution in the electrolyte solution), a platinum working electrode (2 mm diameter smooth platinum disc, area = 3.14×10^{-2} cm^2), and a platinum counter electrode (platinum wire). Polymer thin films were formed by drop casting 1.0 mm^3 of polymer solutions in dichloromethane (HPLC grade) (1 mg cm^{-3}) onto the working electrode, then dried in air. Ferrocene was employed as a reference redox system according to IUPAC's recommendation. Polymer thin films were formed by drop-casting 1.0 mm^3 of polymer solutions in dichloromethane (DCM) (analytical reagent, 1 mg cm^{-3}) onto the working electrode and dried in the air.

Synthetic Procedures

Monomers synthesis. The monomers **(3)** and **(4)** were synthesized through modified procedures from a previous study [10].

Synthesis of 5,6- bis(octyloxy)-4,7 -di(thieno[3,2-b]thiophen-2-yl)benzo[c][1,2,5] thiadiazole **(3)**.

A mixture of 4,7-dibromo- 5,6-bis(octyloxy) benzo[c][1,2,5] thiadiazole **(1)** (1.00 g, 1.817 mmol) and trimethyl(thieno[3,2-b]thiophen-2-yl)stannane **(2)** (2.11 g, 6.963 mmol) were introduced to a round bottom flask under argon. Dried toluene (5 ml) was added into the mixture, and the mixture, and the mixture was degassed. To this mixture $Pd(PPh_3)_2Cl_2$ (0.10 g, 0.142 mmol) was added under an inert argon atmosphere and then degassed and heated to 110°C for 72 h. The crude product which was purified by open column chromatography on silica and used 40–60 petroleum ether:ethyl acetate: triethylamine (4 : 1 : 0.03) to eluted compound **(3)** as an orange solid (1.24 g, 84%). TLC: R*f* = 0.74 in 40–60 petroleum ether/ethyl acetate (9:1). Melting point: 80–82°C. ^1H NMR ($CDCl_3$), (δH/ppm): 8.86 (s, 2H), 7.50 (d, *J* = 5.0 Hz, 2H), 7.37 (d, *J* = 5.0 Hz, 2H), 4.21 (t, *J* = 7.0 Hz, 4H), 2.06–1.99 (m, 4H), 1.54–1.48 (m, 4H), 1.45–1.26 (m, 16H), 0.98–0.91 (m, 6H). ^{13}C NMR ($CDCl_3$), (δC/ppm): 152.0, 150.9, 141.4, 139.3, 136.3, 128.3, 123.0, 119.4, 118.1, 74.7, 31.8, 30.4, 29.5, 29.3, 26.0, 22.7, 14.1. FT-IR (cm^{-1}): 3119, 3079, 3006, 2950, 2915, 2850, 2357, 2319, 1727. Mass (EI+): *m/z* 670, 669, 668 (100 %); (calculated for $C_{34}H_{40}N_2O_2S_5$: 669.01). Elemental Analysis (%) calculated for $C_{34}H_{40}N_2O_2S_5$: C, 61.04; H, 6.03; N, 4.19; O, 4.78; S, 23.96. Found: C, 59.74; H, 5.73; N, 3.91; S, 23.80.

Synthesis of 4,7-bis(5-bromothieno [3,2-b] thiophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5] thiadiazole **(4)**.

A mixture of 5,6- bis(octyloxy)-4,7-di(thieno[3,2-b]thiophen-2-yl)benzo[c] [1,2,5]thiadiazole **(3)** (618 mg, 0.923 mmol), *N*-bromosuccinimide (NBS) (337 mg, 1.892 mmol) and chloroform (15 ml) was degassed and stirred in dark for 48 h at room temperature. A further amount of chloroform (10 ml) was added and the mixture stirred for 1 h. The formed precipitate was filtered then washed with water (150 ml) to obtain 4,7-bis(5-bromothieno[3,2-*b*]thiophen-2-yl) -5,6-bis(octyloxy) benzo[*c*][1,2,5] thiadiazole **(4)** as a bright red solid (652 mg, 85 %). TLC: R*f* = 0.5 in 40–60 petroleum ether/toluene (8:2). Melting point: 125–127°C. ^{1}H-NMR ($CDCl_3$), (δH/ppm): 8.74 (s, 2H), 7.32 (s, 2H), 4.16 (t, *J* = 7.0 Hz, 4H), 2.03–1.95 (m, 4H), 1.53–1.43 (m, 4H), 1.42–1.27 (m, 16H), 0.93 (t, *J* = 7.0 Hz, 6H). ^{13}C-NMR ($CDCl_3$), (δC/ppm): 151.8, 150.6,140.2, 139.5, 135.6, 134.6, 122.2, 117.7, 114.7, 74.8, 31.8, 30.4, 29.5, 29.3, 26.0, 22.7, 14.1. FT-IR (cm^{-1}): 3122, 2917, 2850, 2159, 1972, 1561. Mass (EI+): *m/z* 826 (100 %); (calculated for $C_{34}H_{38}Br_2N_2O_2S_5$: 826.81). Elemental Analysis (%) calculated for $C_{34}H_{38}Br_2N_2O_2S_5$: C, 49.39; H, 4.63; Br, 19.33; N, 3.39; O, 3.87; S, 19.39. Found: C, 48.81; H, 4.61; Br, 19.18; N, 3.31; S, 19.59.

Polymer Synthesis.

Synthesis of poly(9,9-dioctyl-9H- fluorine-alt-5,6-bis (octyloxy)-4,7-di(thieno[3,2□b] thiophen-2- yl) benzo[c][1,2,5]thiadiazole) **(P1)**.

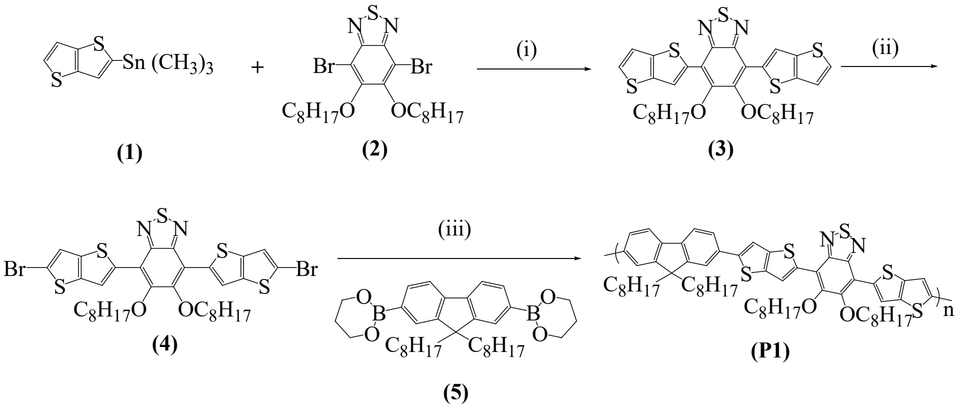
A single-necked flask under argon containing 4,7-bis(5-bromothienylthiophen-2-yl)-5,6- bis(octyl oxy)benzo[c][1,2,5]thiadiazole **(4)** (0.800 g, 0.968 mmol), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester **(5)** (0.540 g, 0.968 mmol), was degassed. To the mixture toluene (21 ml) and then tetraethylammonium hydroxide (20% wt, 7.0 ml, degassed) was added and degassed. To this solution $Pd(OAc)_2$ (8.0 mg) and tri(o-tolyl)phosphine (21.7 mg) were added, degassed and heated to 90°C for 48 h. The mixture was cooled to room temperature and bromobenzene (0.1 ml) were added, degassed and heated 90°C for 1 h. Again, the mixture was cooled to room temperature and phenylboronic acid (150 mg) was added, degassed and heated to 90°C for 3 h. After cooling to room temperature, the mixture was dissolved in $CHCl_3$ (300 ml) and to this solution ammonia (200 ml, 35%) was added, heated at reflux temperature for 3 h, cooled to room temperature. The organic phase was separated then ethylenediamine tetraacetic acid disodium salt dihydrate (300 mg) was added and stirred overnight. The mixture was washed with distilled water (2 × 200 ml), the organic phase was separated and concentrated to about 50 ml and poured into degassed methanol/water (10:1, 500 ml). The resulting mixture was then stirred overnight and filtered through a membrane filter. The collected solid was cleaned using a Soxhlet extraction with solvents in order methanol (250 ml), acetone (250 ml), hexane (250 ml), and toluene (250 ml), respectively. The toluene fraction was concentrated to about 50 ml and then poured into degassed methanol (500 ml). The resulting mixture was stirred overnight and the red powder polymer **P1** was collected by filtration (347.3 mg, 34 %). GPC (1, 2, 4- trichlororbenzene at 100°C): M_w = 20 000, M_n = 7600, PDI = 2.6. ^{1}H-NMR ($C_2D_2Cl_4$), (δH/ppm): 8.77 (d, 2H); 7.81–7.58 (bm, 8H); 4.23 (b, 4H); 2.18–1.89 (bm, 8H); 1.54 (b, 4H); 1.4–1.05 (bm, 40H); 0.98–0.68 (d, 12H). FT-IR (cm^{-1}): 3118, 3081, 3056, 3008, 2953, 2921, 2851, 2158, 2023, 1968, 1887, 1673, 1607, 1563. Elemental analysis (%) calculated for $C_{63}H_{78}N_2O_2S_5$: C, 71.68; H, 7.45; N, 2.65; Br, 0.00. Found: C, 79.01; H, 12.18; N, 4.11; Br, 0.00.

RESULTS AND DISCUSSION

^{1}H-NMR studies conducted at 100°C in 1,1,2,2-tetrachloroethane-d_2 on **P1** confirmed its assigned structure. The ^{1}H-NMR spectrum of **P1** is shown in Figure 1, it revealed in the aromatic region the proton of the fluorene hydrogen with multiplet signal at 8.78 ppm, and 7.77 ppm assigned to protons a and b, respectively.

The FTIR spectrum of the **P1** had similar patterns to those of its constituent monomers with some assignments of different bands/peaks. It can be seen the characterizing peak at 3118 cm^{-1} and 3081 cm^{-1} which fall with aromatic benzene groups =C–H stretch. The characteristic peaks at 2953 cm^{-1}, 2921 cm^{-1}, and 2851 cm^{-1} are assigned to the alkyl stretching frequencies of the methylene groups.

The characteristic overtones are seen from about 2158–1887 cm^{-1}. The assignment of different peaks compared to monomer **(4)** was observed at 1456 cm^{-1}, 1424 cm^{-1} and 1375 cm^{-1} and it has a mixture



Scheme 1. Synthesis routes for poly(9,9-dioctyl-*9H*-fluorene-*alt*-5,6-bis(octyloxy)-4,7-di(thieno[3,2-b] thiophen-2- yl)benzo[*c*][1,2,5]thiadiazole) **(P1)**. (i) $Pd(PPh_3)_2Cl_2$, 110°C, 72 h; (ii) NBS, $CHCl_3$, 1h; (iii) $Pd(OAc)_2$, tri(o-tolyl)phosphine, tetraethylammonium hydroxide, bromobenzene, phenylboronic acid.

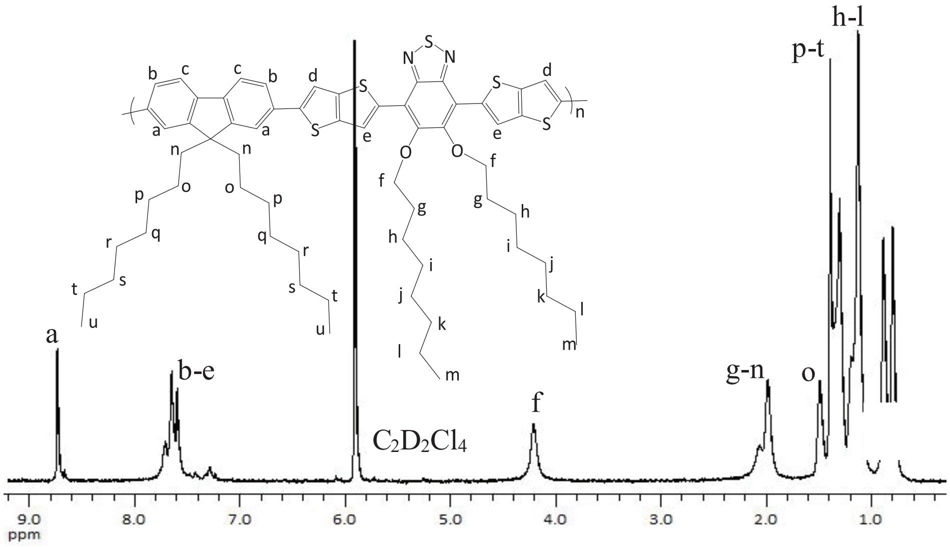


Figure 1 . The ^{1}H-NMR spectrum of **P1** in $C_2D_2Cl_4$ at 100°C.

of peaks related to the combination bands and also the deformations bands of the aromatic –CH groups and methylene $–CH_2$- groups.

The peak initially at 1037cm^{-1}, attributed $C_{aromatic}$-Br linkage in the spectrum of monomer **(4)** disappeared. Also peaks at 1327 cm^{-1} and 1296 cm^{-1} (B-O stretch), and 1140 cm^{-1} (B-C stretch) presented in the spectrum of **(4)** disappeared from the spectrum of **P1** due to the consumption of the corresponding functional groups in the Suzuki cross-coupling reaction.

Polymer **P1** was obtained as a red solid in 34% yield. GPC analysis of the polymer **P1** which was extracted by chloroform gave the M_w = 20 000 and M_n = 7600 with a polydispersity of 2.6. Table 1 shows the GPC data for the **P1** while the elemental data is reported in Table 2.

The UV-Vis absorption spectra of the polymer were measured in chloroform and in solid state as thin films. UV-Vis analysis of **P1** in Figure 2 and Table 3 shows two absorption band at $\lambda_{max\ 1}$ = 355 nm and $\lambda_{max\ 2}$ = 487 nm in chloroform solution, and at $\lambda_{max\ 1}$ = 380 nm and $\lambda_{max\ 2}$ = 519 nm in solid state.

This slight red shift in the solid state for the same polymer was again observed in all polymers, and this is because of the structure of polymers in a solid state more planar, thus more conjugation and lower band gap. Therefore, all calculations and comparisons will be based on the solid state results. The optical band gaps were calculated from the onset of absorption of the polymer in the solid state. The optical band gap of polymer **P1** as determined from the start of its absorption spectra in the solid state has a value $E_g = 1.98$ eV.

Table 1. Gel permeation chromatography data of **P1**.

Fraction	Yield (%)	M_w	M_n	PDI
Toluene	34	20000	7600	2.6

Table 2. Elemental analysis data of **P1**.

Formula weight	Molecular weight		Elemental analysis (%)			
			C	H	N	Br
$(C_{63}H_{78}N_2O_2S_5)_n$	$(1055.63)_n$	Calculated	71.68	7.45	2.65	0
		Found	79.01	12.18	4.11	0

Table 3. UV-Vis data of **P1**.

λ_{max} solution (nm)		λ_{max} thin film (nm)		λ onset abs. (nm)	E_g optical (eV)
1	2	1	2		
355	487	380	519	625	1.98

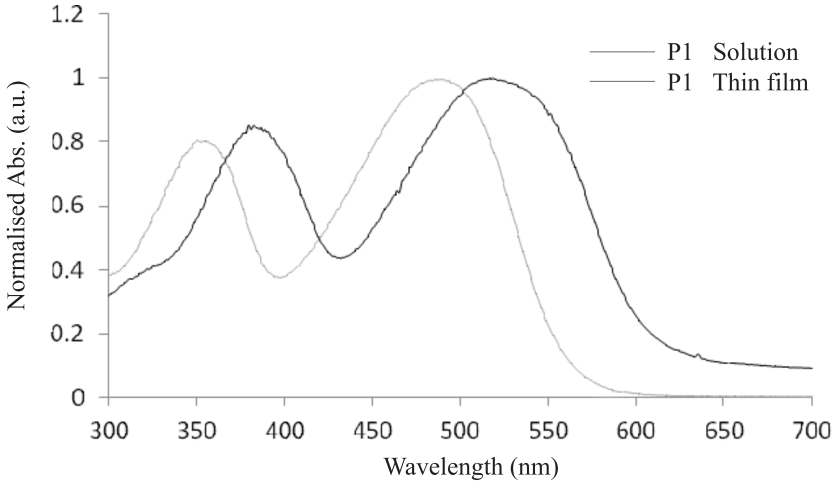


Figure 2 . Normalised UV-Vis spectra of **P1** in chloroform (grey line) and a thin film (black line).

Polymer **P1** exhibited an oxidation wave at E_{pa} = 0.95 V and a reduction wave at E_{pa} = –1.45 V, and their associated reduction and oxidation waves at E_{pc} = 0.70 V and E_{pc} = –1.71 V, respectively. From the onset of oxidation (0.52 V) and the onset of reduction (–1.51V), the HOMO level is at –5.32 eV and the LUMO level is at –3.29 eV for the polymer backbone (on the basis that ferrocene/ferrocenium has an IP of 4.8 eV below the vacuum level and the oxidation occured at 0.082 V relative to Ag/Ag^+), therefore the electrochemical band gap of the polymer was 2.03 eV.

Thermal gravimetry analysis measurements revealed the remarkable stability of the polymer up to 433°C, which indicated that these polymers are thermally very stable. The subsequent degradation and weight loss of the polymer beyond 433°C was proportional to the mass of its a alkyl-group substituent. The polymer did not show any further weight loss up to a temperature of 800°C. Figure 3 shows the TGA curves for of the thermal degradation of the polymer **P1**, the onset of the degradation occurs at 321°C, the beginning of second degradation was 433°C with a weight loss of 71.1%. The % of residual weight 28.9% was consistent with the percentage weight of PDI units and polymer backbone.

The thermal degradation temperatures and the glass transition temperature (T_g) of **P1** were obtained from the thermogravimetric analysis (TGA) and the differential scanning calorimetry (DSC), as summarized in Table 4. The glass transition (T_g) indicated the polymeric backbone flexibility. It is vital to study the mechanical behaviour of polymer when it was exposed to the high temperature.

CONCLUSION

Poly(9,9-dioctyl-9H-fluorene-alt-5,6-bis(octyloxy)-4,7-di(thieno[3,2-b]thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole) **(P1)** composed of alternating carbazole donor unit and 5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole acceptor unit were successfully prepared. The result showed that the **P1** had M_w of 20 000 Da with PDI 2.6 and the HOMO and LUMO energy levels are –5.32 eV and –3.29 eV, respectively, which resulted in 2.03 eV electrochemical band gap. The λ_{max} of **P1** in solution and solid state are 487 nm and 519 nm, respectively, while the optical band gap of **P1** was 1.98 eV. Besides that, the **P1** was found to exhibit good thermal stability up to 433°C. This **P1** showed a remarkable decrease in the band gap compared to their analogous thiophene-based copolymers which made these materials more promising to be applied in solar cell fabrication. Furthermore, it is reasonable to enlarge this family of copolymers and find whether the use of alkyl substituents of different sizes could enhance the photovoltaic performance of the polymers.

Table 4. The TGA and DSC data for **P1**.

TGA analysis			DSC analysis
Onset degradation temp./ ºC		Weight loss at 800ºC (wt. %)	T_g/ºC
1st degradation	2nd degradation		
321	433	71.1	71

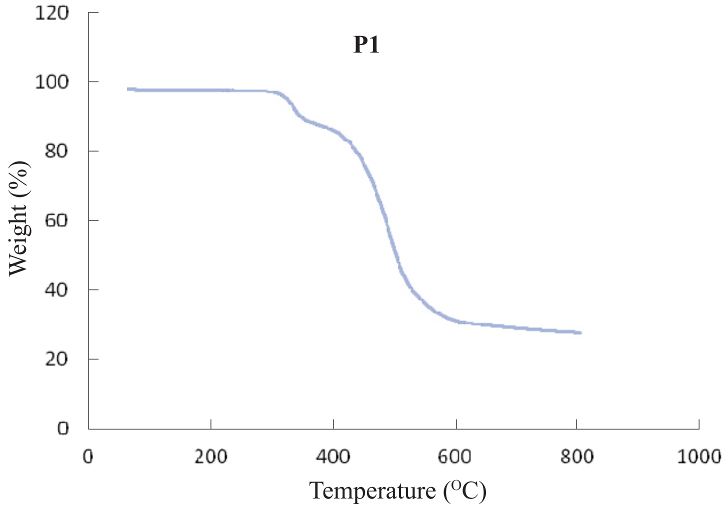


Figure 3. The TGA thermogram of **P1**.

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