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Synthesis of carbazole-based thienothiophene substituted benzothiadiazole copolymer

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Abstract - ***Polymer based solar cells are attracting a great deal of interest. In this study we will present the preparation and characterisation of new materials for application in this area and an investigation of the photophysical and electronic properties of new series of conjugated polymers based on carbazole with thienothiophene and benzothiadiazole repeat units. A new class of alternating donor/acceptor copolymers comprising carbazole units and bis-thieno-thiophene benzothiadiazole repeat units were prepared using Suzuki coupling methods. Their electronic and photovoltaic properties in bulk heterojunction solar cells in blends with fullerene acceptors will be discussed in this contribution.***

Keywords— Conjugated polymers; thienothiophene; benzothiadiazole; solar cells.

I. INTRODUCTION (*HEADING 1*)

The science and technology of conjugated polymers continues to be a vibrant and exciting research area nearly 30 years after the initial explosion of interest in these materials.[1] The materials may combine the processability and outstanding mechanical characteristics of polymers with the readily-tailored electrical, optical and magnetic properties of functional organic molecules.[2, 3] In the late 1970s and early 1980s the rediscovery of conjugated polymers like polyacetylene, polyaniline, polypyrrole and polythiophene ignited an intense investigation of the properties of these inherently conducting materials.[4-6] Conjugated polymers are organic macromolecules which consist of alternating single and double carbon-carbon bonds along the polymer chain, where the hybridization between 2s and 2p orbitals of carbon atom leads to three sp^2 hybrid orbitals and p_z orbital which is perpendicular to other orbitals. [1, 2, 7, 8]

In particular the potential use of these materials in light-emitting diodes (LEDs), field-effect transistors (FEDs), photovoltaic cells (PV), and other opto-electronic devices has motivated the development of synthesis and processing methods of conjugated polymer materials with unique properties.[6, 9, 10] The device performance is critically dependent on the quality of the thin film of the conjugated polymer coating on these devices. Many applications for conjugated polymers rely on their facile and reversible electrochemistry, where the polymer can be oxidised and reduced with simultaneous change in properties.[11] The switchable properties are the basic of the application as transistors, sensors, re-chargeable batteries, solar cells, capacitors and even mechanical actuators.

In the 1980s, the concepts of polarons, bipolarons, and solitons were developed, in the context of both transport properties and optical properties.[7, 12] However, the photoconductivity properties of materials such as thienothiophene and selenium received the attention of researchers, not the photovoltaic properties.[13-15] During the past few years, researchers found the donor-acceptor system offers stable quinoid form of polymer, because the interactions between the two units will enhance the double bond between the units. Also, the zwitterions interaction between alternate units planarised the polymer structure and stabilized the reduced bandgap quinoid form.[16] The essential ideas about the nature of the unusual charge bearing species, and of the excited states of conjugated systems, have been discussed intensely over the past twenty years.[5, 8, 17, 18] This discovery led to develop of polymer/fullerene (Donor/Acceptor) heterojunction photovoltaic devices. It is based on mixing the donor and acceptor to increase the interfacial area, therefore the efficiency of the devices. [19-21] Other attempts were carried out to control the morphology of the active layer in devices for example disordered or ordered bulk heterojunction (BHJ) and molecular heterojuction. [22]

Recently, however, there has been a refinement of these ideas, which enables a better understanding of certain features of the electronic structure of conjugated polymers. The rather short history of BHJ solar cells can be roughly divided into three phases from the perspective of the conjugated backbones of donor polymers. Phase one centered on poly(phenylene vinylene)s (PPV), such as poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV).[23] Therefore, in phase two, a smaller-band-gap polymer, regioregular poly(3-hexylthiophene) (rr-P3HT), was thoroughly investigated. P3HT-based BHJ devices provide a noticeably higher current density (over 10 mA/cm^2), attributed to its lower band gap (1.9 eV) as well as to its increased π-stacking and crystallinity which yields a higher hole mobility.[24-27] However, due to the interplay of polymer properties such as energy levels and band gap and their correlation with V_{oc} and J_{sc}, highest V_{oc} and highest J_{sc} cannot be concurrently obtained.[21, 28]

In this work a detailed physical study is undertaken to explore the optical properties of these three conjugated polymers in order to understand the thienothiophene impact.

II. EXPERIMENTAL

A. *Materials*

Materials used for the preparation of monomers were purchased from the commercial suppliers and used as received unless otherwise stated. All solvent used for the reaction were dried and all reactions for preparing monomers were carried out under Nitrogen atmosphere and the reaction for preparing polymer was carried under Argon atmosphere.

B. *Measurements*

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 Autoinjector, MILLIPORE Waters Lambda-Max Model 481 LC Spectrometer, Erma ERC-7512 RI Detector, PLgel 5m 500A Column, and PLgel 10m 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 has 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 samples 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 approx. 5 mg for CHN analysis and approx. 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) (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.

C. *9-(Heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole*

Synthesis of 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*9H*-carbazole was performed using a modified procedure by Blouin *et al.*[23], Yamato *et al.*[29] and Sonntag *et al.*[30] 2,7-Dibromo-9-(heptadecan-9-yl)-*9H*-carbazole (4.70 g, 8.34 mmol), bis(pinacolato)diboron (7.42 g, 29.21 mmol), potassium acetate (4.90 g, 49.93 mmol) and (diphenylphosphino) ferrocene palladium dichloride, $Pd(dppf)Cl_2$ (0.40 g, 0.49 mmol) in DMF (100 ml) was heated to 100 °C for 36 h. The reaction mixture was cooled to room temperature, then poured into H_2O (100 ml) and extracted with diethyl ether (3 × 100 ml). The organic phases were combined, then washed with H_2O (2 × 100 ml) and dried over $MgSO_2$. The crude product was purified *via* recrystallisation, the crude product was dissolved in the minimum amount of acetone and then precipitated in hot methanol which had been ran through a basic column. The product was a white solid. Yield: 4.75 g (87 %). TLC: $R_f = 0.45$ in 40 - 60 petroleum ether/ ethyl acetate (10:1). Melting point: 141-143°C. ^1H NMR ($CDCl_3$), (δ_H/ppm): 8.13 (t, J=8.5 Hz, 2H), 8.02 (S, 1H), 7.89 (S, 1H), 7.66 (d, J=5.5 Hz, 2H), 4.70(t, J = 5.0 Hz, 1H), 2.33 (m, 4H), 1.61 (m, 4H), 1.39 (S, 20H), 1.19 (br, 24 H), 0.98 (t, J = 6.5 Hz, 6H). ^{13}C NMR ($CDCl_3$), (δ_C/ppm): 142.0, 138.8, 126.4, 126.4, 126.3, 126.3, 126.2, 124.8, 119.8, 120.1, 118.2, 115.5, 83.8, 56.4, 33.9, 29.4, 26.9, 25.0, 22.6, 14.2. Mass (EI+): *m/z* 657; (calculated for $C_{41}H_{65}B_2NO_4$: 657.58). Elemental Analysis (%) calculated for $C_{41}H_{65}B_2NO_4$: C, 74.89; H, 9.96; B, 3.29; N, 2.13; O, 9.73. Found: C, 74.70; H, 10.13; N, 2.20.

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

Synthesis of 4,7-bis(5-bromothieno[3,2-*b*]thiophen-2-yl)-5,6-bis(octyloxy)benzo[*c*][1,2,5] thiadiazole was obtained from a modified procedure by Ding *et al.*[31] A mixture of 5,6-bis(octyloxy)-4,7-di(thieno[3,2-*b*]thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (618 mg, 0.923 mmol), 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 as a bright red solid. Yield: 652 mg (85 %). TLC: R_f = 0.5 in 40-60 petroleum ether/toluene (8:2). Melting point: 125-127 °C. ^{1}H NMR ($CDCl_3$), (δ_H/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 ($CDCl_3$), (δ_C/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.

E. Preparation of Poly(9-(heptadecan-9-yl)-9H-carbazole-alt-5,6-bis(octyloxy)-4,7-di(thieno[3,2-b]thiophen-2-yl)benzo[c][1,2,5]thiadiazole)[PCTTB]

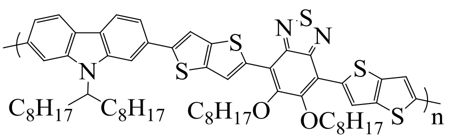

Fig. 1. Chemical structure PCTTB.

9-(Heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*9H*-carbazole [PCTTB] (0.120 g, 0.183 mmol) and 4,7-bis(5-bromothieno[3,2-*b*]thiophen-2-yl)-5,6-bis(octyloxy)benzo [*c*][1,2,5] thiadiazole (0.151 g, 0.183 mmol) were introduced to 100 mL round bottom flask under argon. To the mixture was added toluene (5 ml) and the mixture was degassed. Then 20 wt % tetraethyl ammonium hydroxide 20 % (1.0 ml, 1.356 mmol, previously 2.5 h degassed) was added. To this mixture was added $Pd(OAc)_2$ (1.2 mg, 5.3 x 10^{-3} mmol) and tri(*o*-tolyl)phosphine (3.3 mg, 1.08 x 10^{-2} mmol) under an inert argon atmosphere and it was heated to 95 °C for 72 h. The mixture was cooled to room temperature and bromobenzene (0.05 ml, 61.0 mg; 0.3877 mmol) was added. It was then degassed and heated to 90 °C for 1 h. The mixture was cooled to room temperature and phenylboronic acid (50 mg; 0.4076 mmol) was added. The mixture was degassed and heated to 90 °C for 1 h. After cooling to room temperature, $CHCl_3$ (200 ml) was added to solubilise the polymer. An ammonium hydroxide solution (28 % in H_2O, 50 ml) was then added and the mixture was stirred overnight. The organic phase was separated and washed with distilled water (2 x 100 ml). It was then concentrated to about 50 ml in volume and added drop-wise into a methanol/water mixture (10 : 1, v/v, 300 ml). The resulting mixture was then stirred overnight and filtered through a membrane filter. The collected solid was cleaned using a Soxhlet extraction under an inert argon atmosphere with methanol (250 ml), acetone (250 ml), hexane (250 ml), toluene (250 ml) and chloroform (250 ml), respectively. The toluene and chloroform fractions were concentrated to about 50 ml and then poured into degassed methanol (200 ml). The resulting mixtures were stirred overnight and the solids collected by filtration to afford polymer PCTTB (see Fig. 1) fractions as a dark purple powders. Yield: 142.6 mg (73 %). Toluene fraction: (25.4 mg, 13 %), GPC (1, 2, 4-trichlororbenzene at 100 °C): M_w = 20000, M_n = 8500, PD = 2.4. Chloroform fraction: (117.2 mg, 60 %), GPC (1, 2, 4-trichlororbenzene at 100 °C): M_w = 63000, M_n = 27000, PD = 2.3. ^{1}H NMR ($C_2D_2Cl_4$), (δ_H/ppm): 8.78 (d, 2H); 8.09 (b, 2H); 7.88 (b, 2H); 7.74-7.54 (bm, 4H); 4.71 (b, 1H); 4.28 (b, 4H); 2.41 (b, 4H); 2.02 (bm, 4H); 1.58 (b, 4H); 1.38-1.18 (bm, 40H); 1.0-0.85 (bm, 12H). FT-IR (cm^{-1}): 3079, 3009, 2949, 2920, 2851, 2160, 2032, 1977, 1621, 1595, 1562. Elemental analysis (%) calculated for $C_{63}H_{79}N_3O_2S_5$: C, 70.67; H, 7.44; N, 3.92; Br, 0.00. Found: C, 78.00; H, 8.03; N, 4.22; Br, 0.00.

III. RESULTS AND DISCUSSIONS

The polymerization of PCTTB was performed in different conditions, either in THF as solvent and $NaHCO_3$ as base, or in toluene solvent and tetraethylammonium hydroxide as base, due to the high boiling point of toluene, the average molecular weight of the polymers obtained from these polymerizations was higher than these using THF.

^{1}H-NMR studies conducted at 100 °C in 1,1,2,2-tetrachloroethane-d_2 ($C_2D_2Cl_4$) on PCTTB confirmed its assigned structure. The ^{1}H-NMR spectrum of PCTTB is shown in Fig. 2, it reveals in the aromatic region the protons of the carbazole hydrogen with multiplet signal at 8.76 ppm, 8.16 ppm and 7.82 ppm assigned to protons a, b and c respectively.

The two protons on the thienothiophene repeat units are observed at broad peak 7.61 ppm and 7.58 ppm assigned to protons d and e respectively. The broad peak at 4.71 ppm corresponds to the proton on the carbon atom at position f. The peak at 4.25 ppm corresponds to the protons on the carbon atoms that are connected to the oxygen atoms in the octyloxy chains (position g). Other peaks correspond to alkyl chains which are connected to carbazole and benzothiadiazole units.

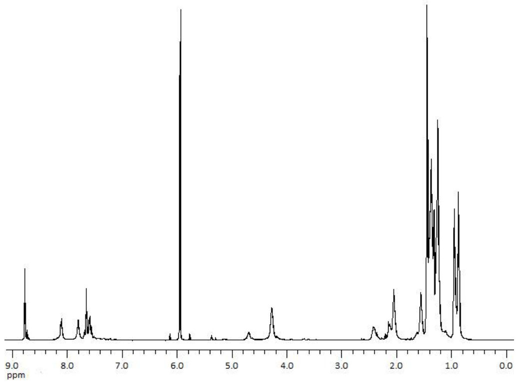

Fig. 2. The proton NMR spectra of [PCTTB] in $C_2D_2Cl_4$ at 100 °C.

The IR spectrum of the PCTTB showed similar patterns to those of its constituent monomers with some assignments of different bands/peaks. The characterizing peaks at 3079 cm^{-1} and 3009 cm^{-1} due to aromatic benzene groups =C–H stretch can be observed. The characteristic peaks at 2949 cm^{-1}, 2920 cm^{-1} and 2853 cm^{-1} are assigned to the alkyl stretching frequencies of the methylene groups.

The characteristic overtones are seen from about 2159-1977 cm^{-1}. The assignment of different peaks compare to monomer 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*9H*-carbazole was observed at 1471 cm^{-1}, 1410 cm^{-1} and 1310 cm^{-1} and its has a mixture of peaks related to the combination bands and also the deformations bands of the aromatic –CH groups and methylene $–CH_2-$ groups.

The peak originally at 1037 cm^{-1}, attributed to $C_{aromatic}$-Br linkage in the spectrum of monomer 4,7-bis(5-bromothieno[3,2-*b*]thiophen-2-yl)-5,6-bis(octyloxy)benzo[*c*][1,2,5] thiadiazole disappeared. And also peaks at 1327 cm^{-1} and 1296 cm^{-1} (B-O stretch), and 1140 cm^{-1} (B-C stretch) present in the spectrum of 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*9H*-carbazole did also disappear from the spectrum of PCTTB due to the consumption of the corresponding functional groups in the Suzuki cross-coupling reaction.

The yields of the different fractions of the polymers after Soxhlet extraction are also shown. Gel permeation chromatography measurements were taken in 1, 2, 4-trichlororbenzene (TCB) at 100 °C as at lower temperatures it was not possible to solubilise all the higher molecular weight polymers to obtain the true molecular weights.

Polymer PCTTB was obtained as a red solid in 73 % overall yield. GPC analysis of polymer PCTTB which was extracted by toluene gave as M_w = 20000 and M_n = 8500 with a polydispersity of 2.4. The chloroform fraction GPC analysis of PCTTB gave the M_w = 63000 and M_n = 27000 with a polydispersity of 2.3.

The UV-Vis absorption spectra of the polymer were measured in chloroform and in solid state as thin films. UV-Vis analysis of PCTTB in Fig. 3 shows two absorption band at $\lambda_{max\ 1}$ = 373 nm and $\lambda_{max\ 2}$ = 466 nm in chloroform solution, and at $\lambda_{max\ 1}$ = 410 nm and $\lambda_{max\ 2}$ = 545 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 solid state is 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 polymers in the solid state The optical band gap of polymer PCTTB as determined from the onset of its absorption spectra in the solid state has a value E_g = 1.89 eV.

Based on the TGA curves for of the thermal degradation of the polymer PCTTB, the onset of the degradation occurs at 444 °C, the onset of second degradation is 566 °C with a weight loss of 73.8 %. The percentage of residual weight 26.2 % is consistent with percentage weight of PDI units and polymer backbone.

Thermal gravimetry analysis measurements revealed the remarkable stability of the polymer up to 566 °C, which indicated that these polymers are thermally very stable. The subsequent degradation and weight loss of the polymer beyond 566 °C was proportional to the mass of its a alkyl-group substituents. The polymer did not show any further weight loss up to a temperature of 800 °C.

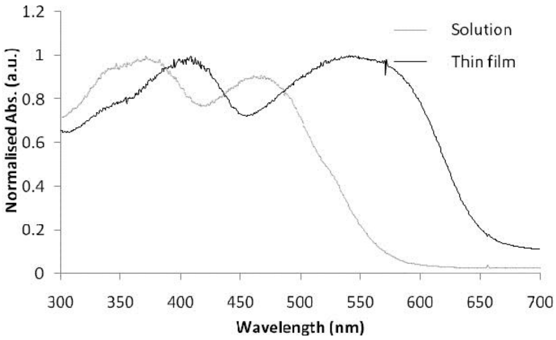

Fig. 3. Normalised UV-Vis spectrum of PCTTB in chloroform (grey line) and a thin film (black line).

Table 1 summarises the results from the thermo gravimetric analysis (TGA) and the differential scanning calorimetry (DSC). In applications that can experience temperature extremes, it is important to know what will happen when these polymers are exposed to variants in temperature and how they will affect the mechanical behaviour of the polymer.

Table 1. The TGA and DSC data for PCTTB.

TGA Analysis			DSC Analysis
Onset degradation temp. (°C)		Wt. loss at 800 °C (wt. %)	T_g (°C)
1st degradation	2nd degradation		
444	566	73.8	75

IV. CONCLUSIONS

Poly(9-(heptadecan-9-yl)-9H-carbazole-alt-5,6-bis(octyloxy)-4,7-di(thieno[3,2-b]thiophen-2-yl)benzo[c][1,2,5]thiadiazole)

PCTTB composed of alternating carbazole donor unit and acceptor unit were successfully prepared. The polymer was synthesised by Suzuki cross coupling, in order to investigate its suitability for application in photovoltaic cell. GPC results from polymerisation have shown that PCTTB had a weight average molecular weight values M_w of 63000 Da with a polydispersity of 2.3.

UV-Vis analysis showed the polymer absorbed at high wavelengths λ_{max} 466 nm in solution and 545 nm in the solid state and the band gap of PCTTB in solid state is 1.89 eV. CV measurements estimated the band gap as 2.26 eV from the onset of oxidation and reduction. The HOMO and LUMO levels can be estimated as -5.27 eV and -3.01 eV respectively.

TGA of PCTTB showed good stability, the thermal stability, up to 566 °C. DSC analysis of PCTTB exhibited T_g peak at 75 °C. These results are in agreement with the design procedures for the use of these materials in photovoltaic applications.

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