

Impact of the Alkyl Side Chains on the Optoelectronic Properties of a Series of Photovoltaic Low-Band-Gap Copolymers

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ABSTRACT: The design of novel low-band-gap conjugated polymers with appropriate frontier orbital energy levels and good charge transport is needed to improve the conversion efficiency of organic photovoltaic devices. In this article, we describe the synthesis and structure-property relationships of a series of photovoltaic copolymers with a common conjugated backbone and differing solubilizing side chains. The copolymer optoelectronic properties and the related photovoltaic device performances are reported. Our results clearly show that the side chains have a major impact on the material and device properties. The electronic band gap can be varied by more than 0.3 eV, the charge mobilities by orders of magnitude, and the optimized fullerene content of photovoltaic devices by a factor of 4 by barely changing the side-chain positioning and/or by switching from linear to branched alkyl chains. A power conversion efficiency of 2.7% could be achieved with devices using the most promising polymer.

Introduction

Organic photovoltaic (OPV) devices based on blends of π -conjugated polymers and fullerene derivatives have been the focus of intense research activities over the past decade. The device performances increase continuously, and energy conversion efficiencies above 10% seem within reach for the near future.¹ Yet, the persistence of this progress depends crucially on the development of new materials with improved optoelectronic and physicochemical properties. In particular, the material solar photon harvesting capacity, charge collection efficiency, and related device open-circuit voltage could still be enhanced. Since these properties are strongly correlated to the polymer π -electron system, they can be controlled, at least to some extent, by macromolecular engineering. The design of alternate copolymers from specific conjugated monomers is a possible, wellrecognized route that can be followed to engineer the polymer frontier orbitals and the related optoelectronic properties.² Recently, Liang et al.¹ succeeded for instance to increase the polymer ionization potential, while keeping constant the polymer bandgap, by combining benzo[1,2-b:4,5-b']dithiophene and thieno-[3,4-b]thiophene units substituted with electron-withdrawing functional groups. This allowed them to increase the open-circuit voltage (V_{oc}) and to reach energy conversion efficiencies above 7.4%. Another illustrative example is given by the insertion of highly planar thieno[3,2-b]thiophene moieties into polythiophenes. Such a combination has led to the development of polymers with record hole mobilities.³ The solubilizing side chains on a given conjugated monomer may as well have a considerable impact on the resulting material properties. The chain nature (linear or ramified) and position not only fix the material solubility in common solvents. They may also change the molecular

optoelectronic properties.^{4,5} Moreover, in polymer/fullerene blends, the side chains participate in the molecular interactions between the blend components and contribute to the resulting blend morphology, an essential feature for charge generation and transport.⁶ For instance, Mayer et al. observed recently that in polymer/fullerene OPV devices fullerene intercalation among the polymer side chains affects the optimal fullerene content (i.e., the content necessary for achieving the highest energy conversion efficiency).⁷ It is thus obvious that for a given conjugated polymer backbone the nature and positioning of the side chains are crucial to the polymer properties and need to be investigated thoroughly.

In a recent publication, we described the structure-property relationships of a new copolymer family based on 2,1,3-benzothiadiazole electron acceptor units and electron-rich thiophene and thieno[3,2-b]thiophene units.⁸ The alternation of electron donor (D) and acceptor (A) groups is known to lower the polymer energy band gap and is therefore of interest for photovoltaic applications. The presence of thieno[3,2-b]thiophene within the molecular backbone is believed to stabilize the HOMO level and to planarize the molecule, leading to strong π -stacking interactions.^{3,8,9} Photovoltaic devices using first members of this copolymer family as electron donor and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as electron acceptor led to a promising $V_{\rm oc}$ of 0.74 V with a long wavelength absorption edge (related to the polymer band gap) comparable to that of poly(3-hexylthiophene) (P3HT). However, in spite of the increase in opencircuit voltage, the energy conversion efficiency remained lower than that of P3HT:PCBM-based reference devices. Low hole mobilities and high optimal fullerene contents (1:4 copolymer/ fullerene weight ratio) are possible causes for this discrepancy. As pointed out above, both properties are linked to the polymer side chains in a nontrivial way. This led us to investigate further the impact of the side-chain nature and positioning on the material properties for this copolymer family.

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Scheme 1. Chemical Structures of the Different Copolymers Studied in the Present Work



In this work, we describe the synthesis and structure—property relationships of a series of copolymers with a common conjugated backbone but different solubilizing side chains. The copolymer optoelectronic properties, in solution and in thin films, as well as the related photovoltaic device performances are reported. Our results clearly show that the side chains have a major impact on the material and the related device properties. In particular, the electronic band gap can be varied by more than 0.3 eV, the charge mobilities by orders of magnitude, and the fullerene content of optimized photovoltaic devices by a factor of 4 by barely changing the side-chain positioning on the thiophene units and/ or by switching from linear to branched alkyl chains. A power conversion efficiency of 2.7% could be achieved with devices using the most promising polymer as electron donor material.

Experimental Section

Materials. The molecular structure, synthesis methodology, and nomenclature of the investigated copolymers are presented in Scheme 1. The acronym "PTBzT²" is used for all the polymers and refers to a polymer (P) which is formed by the alternation of a trimer (T), derived from a central 2,1,3-benzothiadiazole (Bz) unit surrounded by two alkylthiophene units, and a thieno[3,2-*b*]thiophene (T²) unit. The acronym extension highlights the side-chain nature and positioning: C8, C12, and CEH correspond to octyl, dodecyl, and 2-ethylhexyl alkyl chains respectively, whereas the α and β indexes designate chains that are either in the third position (α) or the fourth position (β).

The synthesis of 3-dodecylthiophene, 3-octylthiophene, 4,7dibromo-2,1,3-benzothiadiazole,¹⁰ and 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene³ have been done following procedures reported in the literature. The 3-dodecylthiophene derivative and the 4,7-bis(5-bromo-3-alkylthiophen-2-yl)-2,1,3-benzothiadiazole synthesis have been described in our previous work.⁸ Tetrahydrofuran (ACS grade), toluene (ACS grade), and diethyl ether (ACS grade) were distilled over sodium while dichloromethane (ACS grade) and acetonitrile were distilled over calcium hydride, prior to use. All other chemicals were purchased from Aldrich and used without further purification.

NMR Characterization. ¹H and ¹³C NMR spectra were recorded on a Bruker 300 UltrashieldTM 300 MHz NMR spectrometer and a Bruker 400 UltrashieldTM 400 MHz NMR spectrometer, with an internal lock on the 2H signal of the solvent (CDCl₃).

Synthesis. 3-(2-Ethylhexyl)thiophene (1). To magnesium turnings (5.81 g, 0.24 mol) in dry THF (5 mL) was added 2-ethylhexyl bromide (39 mL, 0.22 mol) in THF (55 mL) at a rate sufficient to maintain reflux. After addition, the reflux was maintained for 2 h. The Grignard reagent was then added dropwise through a canula to a solution of 3-bromothiophene (30.00 g, 0.18 mol) and Ni(dppp)Cl₂ (1.84 mmol) in THF (110 mL). The mixture was refluxed under argon and stirred overnight. Next, the mixture was hydrolyzed by careful addition of water followed by 38% aqueous HCl and extracted with CH₂Cl₂. The brown organic phase was washed with saturated sodium chloride and then with water and dried over sodium sulfate. After removing the solvent under reduced pressure, the crude product was distilled to provide a colorless oil (bp 30 °C at 1.3 mbar) (26 g, yield: 73%). ¹H NMR

(300 MHz, CDCl₃, ppm): δ = 7.26 (dd, 1H, ⁴*J* = 4.9 Hz, ³*J* = 3.0 Hz), 6.93 (m, 2H, ⁴*J* = 4.9 Hz), 2.59 (d, 2H, ³*J* = 6.8 Hz), 1.58 (m, 1H, ³*J* = 6.1 Hz), 1.29 (m, 10H), 0.90 (t, 6H, ³*J* = 4.9 Hz). ¹³C (75 MHz, CDCl₃, ppm): δ = 143.40, 128.42, 125.15, 119.88, 32.04, 30.72, 30.44, 29.59, 29.51, 29.42, 22.82, 14.25.

2-(Trimethylstannyl)-4-alkylthiophene (2). Under an argon atmosphere, 3-alkylthiophene (35.6 mmol) was dissolved in dry THF (240 mL) and cooled to -78 °C. In another flask, under argon, diisopropylamine (39.2 mmol) was solubilized in dry THF (20 mL) cooled to -78 °C. Then nBuLi (37.4 mmol, 2.5 M in hexane) was added dropwise, and the solution was kept at -78 °C for 10 min, heated for 10 min at -20 °C, and then cooled again to -78 °C. The lithium diisopropylamide so synthesized was added slowly to the alkylthiophene solution, keeping the temperature below -60 °C. The cooling bath was removed, allowing the temperature to reach 0 °C (ice bath). The solution was then cooled back to -78 °C before the addition of trimethyltin chloride (41 mmol, 1 M in THF). The mixture was stirred overnight and allowed to reach room temperature. The mixture was quenched with water and extracted with diethyl ether, and the organic phase washed with water and dried over sodium sulfate. The solvent was removed under reduced pressure and was further dried under high vacuum, providing an oil containing a non-negligible amount of nonreacted 3-alkylthiophene. This monostannylated compound was used without further purification (yield: 80%).

2-(*Trimethylstannyl*)-4-*dodecylthiophene* (2*a*). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.22 (s, 1H), 7.04 (s, 1H), 2.67 (t, 2 H, ³J = 7.4 Hz), 1.66 (m, 2H), 1.30 (m, 18H), 0.91(t, 3H, ³J = 6.3 Hz), 0.39 (s, 9H).

2-(*Trimethylstamyl*)-4-(2-ethylhexyl)thiophene (**2b**). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.19 (s, 1H), 6.99 (s, 1H), 2.61 (d, 2 H, ³J = 6.8 Hz), 1.59 (m, 1H), 1.30 (m, 8H), 0.90 (t, 6H, ³J = 7.4 Hz), 0.38 (s, 9H).

4,7-Bis(4-alkylthiophen-2-yl)-2,1,3-benzothiadiazole (3). General procedure: 5-(trimethylstannyl)-3-alkylthiophene (21 mmol) and 4,7-dibromobenzo-2,1,3-thiadiazole (7 mmol) were dissolved in dry toluene (100 mL). Then, Pd(PPh₃)₄ (0.5 mmol) was added, and the reaction mixture was stirred at 110 °C for 24 h under an argon atmosphere. Then, the reaction mixture was filtered through a pad of Celite, and the toluene solution was evaporated and dried under high vacuum. The crude product was purified by column chromatography on silica gel with cyclohexane/toluene 9/1 as eluent to give an orange compound (93%).

4,7-Bis(4-dodecylthiophen-2-yl)-2,1,3-benzothiadiazole (**3a**). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.99 (s, 1H), 7.85 (s, 1H), 7.06 (s, 1H), 2.71 (t, 2H, ³J = 7.8 Hz), 1.72 (m, 2H, ³J = 7.6 Hz), 1.28 (m, 18H), 0.9 (t, 3H, ³J = 6.8 Hz). ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 152.65, 144.38, 139.00, 129.01, 126.04, 125.54, 121.53, 33.13, 31.92, 30.66, 30.51, 29.65, 29.62, 29.49, 29.36, 22.69, 14.12.

4,7-Bis(4-(2-ethylhexyl)thiophen-2-yl)-2,1,3-benzothiadiazole (**3b**). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.97 (s, 1H), 7.86 (s, 1H), 7.04 (s, 1H), 2.66 (d, 2H, ³J = 6.9 Hz), 1.68 (m, 1H), 1.35 (m, 6H), 0.92 (t, 6H, ³J = 7.4 Hz). ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 152.67, 143.06, 138.82, 129.48, 126.05, 125.49, 122.43, 40.33, 34.70, 32.53, 28.91, 25.68, 23.07, 14.14, 10.86.

4,7-Bis(5-bromo-4-alkylthiophen-2-yl)-2,1,3-benzothiadiazole (4). General procedure: compound 3 (3.59 mmol) was solubilized in DMF (60 mL) under argon in the dark. N-Bromosuccinimide (NBS) (7.35 mmol) was added portionwise. The resulting solution was stirred at room temperature under argon overnight. Water and diethyl ether were added, and the resulting solution was stirred for 2 h. The organic phase was separated from the water phase and extracted with brine (3×100 mL). The organic phase was dried with sodium sulfate and filtered, and the solvent evaporated under reduced pressure and further dried under high vacuum. The crude product was purified by column chromatography on silica gel with cyclohexane as eluent, providing the compound 4 as an orange coumpound (yield: 82%). *Orange Solid* C12β (4a). ¹H NMR (300 MHz, CDCl₃, ppm): $\delta = 7.78$ (d, 2H, ⁵J = 5.5 Hz), 2.65 (t, 2H, ³J = 7.4 Hz), 1.69 (m, 2H), 1.28 (m, 18H), 0.89 (t, 3H, ³J = 6.9 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm): $\delta = 152.27$, 143.09, 138.51, 128.11, 125.36, 124.89, 111.61, 31.92, 29.76, 29.68, 29.59, 29.43, 29.35, 29.27, 22.68, 14.11. Elemental analysis results: C, 57.07; H, 6.85; S, 12.10; Br, 20.11; N, 3.52. Calcd for C₃₈H₅₄S₃Br₂N₂: C, 57.42; H, 6.85; S, 12.10; Br, 20.11; N, 3.52.

Orange Oil EHβ (**4b**). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.77 (d, 2H, ⁵*J* = 4.6 Hz), 2.60 (t, 2H, ³*J* = 7.2 Hz), 1.72 (m, 1H), 1.35 (m, 8H), 0.93 (t, 6H, ³*J* = 7.4 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 152.18, 142.22, 138.21, 128.58, 125.24, 124.75, 112.27, 40.01, 33.91, 32.52, 28.80, 25.74, 23.09, 14.14, 10.87. Elemental analysis results: C, 52.85; H, 5.73; S, 13.43; Br, 22.95; N, 4.06. Calcd for C₃₀H₃₈S₃Br₂N₂: C, 52.78; H, 5.61; S, 14.1; Br, 23.41; N, 4.10.

Polymer Synthesis General Procedure. 2-Trimethylstannylthieno-[3,2-b]thiophene (1.36 mmol) and compound **4** (1.36 mmol) were dissolved in dry toluene (70 mL). Then, tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (0.02 equiv) was added, and the reaction mixture was stirred at 110 °C under an argon atmosphere for 17 h. The polymer was then precipitated in a solution of methanol, filtered, and washed on a Soxhlet apparatus with methanol, cyclohexane, and chloroform. The chloroform fraction was evaporated under reduced pressure, and the polymer was precipitated in methanol, filtered, and finally dried under high vacuum, providing a film with a metallic shine.

*PTBzT*²-*C12β*. ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.92 (m, 1H), 7.80 (m, 1H), 7.33 (m, 1H), 2.76 (m, 2H), 1.62 (m, 2H) 1.27 (m, 18H), 0.87 (m, 3H).

*PTBzT*²-*CEHβ*. ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.97 (m, 1H), 7.83 (m, 1H), 7.39 (m, 1H), 2.85 (m, 2H), 1.81 (m, 1H), 1.34(m, 8H), 0.92 (m, 6H).

Computational Study. In order to get an additional insight into the influence of the alkyl side chain nature and positioning on the copolymer optoelectronic properties, density functional theory (using Gaussian 03 package¹¹ at the B3LYP/6-311+G* level of theory in vacuum)¹² was utilized to model the structural and electronic properties of relevant molecular structures. In particular, the HOMO and LUMO level positions and related electron distributions were calculated on three repeating units.¹³ To keep the computational time within a reasonable range, the alkyl chains were replaced by methyl groups. It is thereby assumed that the electronic coupling between alkyl chains and the π -electron system is negligible. CH₃ groups were placed at both ends, and the dihedral angle between the last carbon atom and the methyl group was kept fixed in order to mimic the rigidity of the actual polymer.

Materials Characterizations. UV-vis. UV-visible absorption spectroscopy measurements were done using a Shimadzu UV-2101 spectrophotometer. The absorption spectra were measured on both *o*-DCB polymer solutions and polymer thin films spin-coated on glass substrates.

GPC. Gel permeation chromatography measurements were performed in trichlorobenzene (TCB) with a Waters Alliance GPCV 2000 instrument (two PL-gel 5 mm mixed-C, a 5 mm 100 Å columns or a PLgel Olexis column); two detectors (viscosimeter and refractometer) in trichlorobenzene (flow rate: 1 mL/min) at 150 °C. The system was calibrated with polystyrene standards using universal calibration.

Voltammetry. Cyclic voltammetry analyses were carried out with a BioLogic VSP potentiostat using platinum electrodes at a scan rate of 20 mV/s. The measurements were performed on polymer thin films drop-casted from *o*-DCB solutions onto a platinum working electrode. A Pt wire was used as counter electrode and Ag/Ag^+ as reference electrode in a 0.1 mol L⁻¹ solution of tetrabutylammonium perchlorate in acetonitrile. Ferrocene was used as internal standard to convert the values obtained with Ag/Ag^+ reference to the saturated calomel electrode scale (SCE).

DSC. Differential scanning calorimetry analyses were performed on a DSC 2910 apparatus from TA Instruments. The analyses were carried out under air at a heating rate of $10 \,^{\circ}\text{C min}^{-1}$.

TGA. Thermogravimetric analyses were performed on a Hi-Res TGA 2950 apparatus from TA Instruments. The analyses were carried out under a mixture of 75% N₂ and 25% O₂ at a heating rate of 20 °C min⁻¹ for PTBzT²-C12 α and under air at a heating rate of 10 °C/min for PTBzT²-C12 β and PTBzT²-CEH β .

XRD. X-ray diffraction experiments were carried out on the BM26B beamline¹⁴ at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, with a Frelon CCD camera. The films obtained directly from synthesis procedure were measured both in normal and transverse directions. The modulus of the scattering vector s ($s = 2 \sin \theta / \lambda$, where θ is the Bragg angle and λ the wavelength) was calibrated using several diffraction orders of silver behenate.

Field-Effect-Mobility Measurements. Bottom contact fieldeffect transistors (FETs) were elaborated on commercially available prepatterned test structures whose source and drain contacts were composed of 30 nm thick gold and 10 nm thick indium tin oxide (ITO) bilayers. A 230 nm thick silicon oxide was used as gate dielectric and n-doped (3 \times 10¹⁷/cm³) silicon crystal as gate electrode. The channel length and channel width were 20 μ m and 10 mm, respectively. The test structures were cleaned in acetone and isopropyl alcohol and subsequently for 15 min in an ultraviolet ozone system. Then, hexamethyldisilazane (HMDS) was spin-coated (500 rpm for 5 s and then 4000 rpm for 50 s) under nitrogen ambient and followed by an annealing step at 130 °C for 5 min. Finally, 4 mg/mL anhydrous o-dichlorobenzene (o-DCB) polymer solutions were spin-coated (1250 rpm for 60 s and 2000 rpm for 120 s) to complete the FET devices. The samples were then left overnight under vacuum $(<10^{-6} \text{ mbar})$ to remove residual solvent traces. Both the FET elaboration and characterizations were performed in nitrogen ambient.

Preparation of Photovoltaic Devices. Bulk heterojunction devices were elaborated using the PTBzT² polymers as electron donor and C60-PCBM as electron acceptor. The standard device structure was the following: ITO/PEDOT:PSS(~40 nm)/polymer:PCBM(~100 nm)/Al(~120 nm). Indium tin oxide-coated glass with a surface resistance lower than 20 Ω / sq was used as transparent substrate. ITO was cleaned sequentially by ultrasonic treatments in acetone, isopropyl alcohol, and deionized water. After an additional cleaning for 45 min under ultraviolet generated ozone, a highly conductive polyethylene dioxythiophene:polystyrenesulfonate PEDOT:PSS was spincoated (1500 rpm: 40 nm) from an aqueous solution and dried for 30 min at 120 °C under vacuum before being transferred to the nitrogen-filled glovebox. The dichlorobenzene polymer: PCBM solutions were stirred at 70 °C for 48 h before spincoating. Unless otherwise stated, the solution had a total concentration of 40 mg/mL with a polymer:fullerene weight fraction ranging from 1:1 to 1:4. Finally, a 120 nm thick aluminum layer was thermally evaporated and used as cathode. The device active area was 9 mm², while each sample included four independent diodes. With the most promising polymer, an extra series of devices were elaborated with specific thermal annealing conditions (130 °C for 15 min prior to cathode deposition) and an additional LiF (0.5 nm) layer between the active layer and the aluminum cathode. Current versus voltage (J-V) characteristics were measured under darkness and under AM1.5 (100 mW/cm²) illumination using an Oriel 150 W solar simulator.

Results and Discussion

Materials Synthesis. Two new copolymers with an identical conjugated backbone, composed of alternating thieno[3,2-*b*]-thiophene and 4,7-bisthiophene-2,1,3-benzothiadiazole segments functionalized with alkyl side chains of various types (linear and branched) on the β position of the thiophene units, have been

Scheme 2. Synthesis of Monomers and Polymers



synthesized by Stille cross-coupling polycondensation (Scheme 2). The syntheses of PTBzT²-C8 α and PTBzT²-C12 α (see Scheme 1), where linear side chains of various lengths are introduced on the α position of the thiophene rings, have been published recently by us.⁸ In order to obtain the 4,7-bis(4alkylthiophene)-2,1,3-benzothiadiazole derivatives (3a, 3b) (β position), selectively deprotonation of the 3-alkylthiophene in the 5-position has been performed by the addition of 1 equiv of the lithium diisopropylamide (LDA) base. The high basicity and the steric hindrance of the LDA provide selectively the 2-(trimethylstannyl)-4-alkylthiophene derivatives (2a, 2b) after addition of Me₃SnCl. This synthetic approach is different than the one followed for the synthesis of 2-(trimethylstannyl)-3alkylthiophene derivatives, which have been obtained by a selective nucleophilic substitution of 3-alkylthiophene in the 2-position by n-BuLi.⁸ Then, the trimer-based derivatives (**3a**, **3b**) were effectively synthesized by the Stille coupling between either the 2a, 2b, and 4,7-dibromo-2,1,3-benzothiadiazole. Finally, the desired functional monomers 4a and 4b were provided upon subsequently dibromination of 3a and 3b using N-bromosuccinimide (NBS) as the bromine agent.

Molecular Characterizations. Because of the high tendency of these conjugated copolymers to aggregate in room temperature solutions, their molecular weights had to be determined by GPC experiments carried out at 150 °C in trichlorobenzene solutions (see Table 1). Most polymers have a comparable molecular weight distribution with a number-average molecular weight (M_n) close to 15 kg/mol except for the PTBzT²-C8 α , whose M_n is twice as high.

All the polymers exhibit good thermal stability with 5% weight-loss temperatures higher than 275 °C.

The DSC measurements were featureless up to 300 °C (highest achievable temperature with our setup) for all the polymers. It is likely that the pronounced backbone rigidity as well as the strong interchain interactions induced by the thieno[3,2-*b*]thiophene units may lead to melting temperatures above this limit. A similar observation on thieno[3,2-*b*]-thiophene containing copolymers has been reported before by Liang et al.¹⁵

Properties of Polymers in Solution. The normalized UV-vis absorption spectra of the copolymers in *o*-DCB are presented in Figure 1, and the corresponding optoelectronic properties are summarized in Table 3. Each polymer is characterized by two major absorption peaks, a feature which is commonly observed for alternating donor-acceptor copolymers. The low-wavelength peak can be attributed to a π - π * transition while the high-wavelength transition is believed to be related to an intramolecular D-A charge

Table 1. Polymer Characterization

polymer	$M_{\rm w}({ m g/mol})^a$	$M_{\rm n}~({\rm g/mol})^a$	PDI^{a}	$T_{\rm d} (^{\circ}{\rm C})^b$
PTBzT ² -C12α	23 000	16000	1.4	352
PTBzT ² -C8α	46 000	30 000	1.5	304
$PTBzT^2-C12\beta$	55000	14000	3.9	277
$PTBzT^2-CEH\beta$	32 000	12 000	2.7	307

^{*a*} Determined by GPC with polystyrene as standard and TCB as eluent. ^{*b*} Temperature with 5% weight loss determined by TGA at a scan rate of 10 °C/min under air.



Figure 1. Normalized UV-vis absorption spectra for all polymers in o-DCB solution. The continuous line corresponds to PTBzT²-C8 α , the open squares to PTBzT²-C12 α , the filled circles to PTBzT²-C12 β , and the crosses to PTBzT²-CEH β .

transfer.¹⁶ Increasing the chain length, from C8 to C12, leaves constant the polymer absorption spectra. Also, replacing C12 by CEH does not significantly perturb the lowenergy peak position. However, the high-energy peak is blueshifted by 26 nm. This shift may indicate a larger twist between the thiophene and thieno[3,2-b]thiophene units induced by to the more bulky CEH side chains. When changing the side chains from the α to the β position, independent of the side-chain nature, the low-energy peak is significantly red-shifted while the high-energy peak remains almost unchanged. These results suggest that the β position induces less sterical twisting on the conjugated backbone and thereby leads to a more pronounced coupling between the D and A units, enhancing charge transfer and reducing the HOMO-LUMO gap. The slightly higher red shift observed for PTBzT²-C12 β , in comparison to PTBzT²-CEH β , supports



Figure 2. Calculated HOMO (c, d) and LUMO (a, b) distributions for alkyl side chains in α (left: a, c) or β (right: b, d) position.

-2.8



the assertion that the steric hindrance is lower for linear chains. The pronounced high wavelength shoulder seen only for PTBzT²-C12 β may reveal the presence of small aggregates in solution and indicates a lower polymer solubility in comparison to PTBzT²-CEH β .

14

-4.6

1 - 2

1 - 2

β

Our density functional theory investigations done on single molecules in vacuum corroborate these conclusions. The molecular structures together with the calculated frontier orbital electronic distributions are displayed in Figure 2. The results can be considered as representative of the molecular conformation in dilute solutions, where intermolecular $\pi - \pi$ interactions are negligible. The theoretical dihedral angles (see Scheme 3) as well as the HOMO and LUMO levels are reported in Table 2.

A highly twisted molecular backbone, with R_1 and R_2 values as high as 50°, are found with the alkyl chains on the α position, while these angles are negligible for the β position. Note however that, due to the longer alkyl chain synthesized polymers, the actual dihedral angles are possibly somewhat higher. The model also highlights the influence on the sidechain positioning on the frontier orbital distributions. The highest delocalization is found in β position molecules. The resulting theoretical estimations of the HOMO–LUMO energy gap (2.3 eV for the α position and 1.8 eV for the β position) are close to the optical band gaps measured



Figure 3. Normalized UV–vis absorption spectra for spin-coated films. The open squares correspond to PTBzT²-C12 α , the filled circles to PTBzT²-C12 β , and the crosses to PTBzT²-CEH β .

in solution (2.1 and 1.7 eV for the α and β position, respectively). This concurrence strengthens the consistency of our model molecular structure.

Polymer Thin Film Optoelectronic Properties. Because of the poor film quality of PTBzT²-C8 α , only PTBzT²-C12 α , PTBzT²-C12 β , and PTBzT²-CEH β thin film UV-vis absorption spectra were investigated. The results are shown in Figure 3, and the corresponding peak positions and optical band gaps (deduced from the long wavelength absorption edge) are reported in Table 3. Similarly to what has been observed in solution, the absorption spectra are mostly affected by the side-chain positioning, rather than by the chain chemical structure (compare $PTBzT^2$ -C12 α with PTBzT²-C12 β and PTBzT²-C12 β with PTBzT²-CEH β). All the peaks are red-shifted when going from solution to the solid state, with the most pronounced changes occurring for the low-energy peak. Such a bathochromic shift is generally attributed to π -stacking interactions and in our case points out that these interactions are stronger for the polymers with alkyl side chains in the β -position polymers. This is consistent with the more planar molecular conformation of these polymers deduced from the solution absorption data and from our theoretical modeling (Table 2). Interestingly, the

Table 3. Absorption Maxima and Optical Band Gap on Thin Films

polymer	λ_{\max} sol (nm)	λ_{\max} film (nm)	$E_{\rm g}^{ m opt}\left({ m eV} ight)$
PTBzT ² -C8α	405/513		
PTBzT ² -C12a	407/510	416/540	1.88
$PTBzT^2-C12\beta$	419/577	424/614	1.56
$PTBzT^2-CEH\beta$	393/561	428/617	1.56
	Table 4 Fleetreah	omical Desults	

polymer	Eosset/HOMO (eV)	E _{onset} /LUMO (eV)	$E_{\rm g}^{\rm ec}~({\rm eV})$
PTBzT ² -C12α	0.9/5.3	-1.2/3.2	2.1
$PTBzT^2-C12\beta$	0.6/5.0	-1.2/3.2	1.8
$PTBzT^2-CEH\beta$	0.6/5.0	-1.3/3.1	1.9

high-energy peak positions of both β -position-based polymers almost coincide in solid state, canceling the blue shift (with respect to the α -position-based polymers, PTBzT²-C12 α and PTBzT²-C8 α) observed in solution. This points out that in this case (alkyl side chains in β -position) the intermolecular interactions of the conjugated backbones are strong enough to outdo the influence of the side chains on the π - π * transitions.

Changing alkyl side chains from α to β position leads, as expected, to a significant reduction (0.32 eV) of the polymer energy band gap. The resulting 1.56 eV optical band gap of both PTBzT²-C12 β and PTBzT²-CEH β is close to the optimal value for single-junction photovoltaic devices¹⁷ and makes these polymers highly promising for photovoltaic applications.

Quasi-reversible oxidation and reduction waves could be observed by cyclic voltammetry on all polymer thin films (see Supporting Information). The corresponding oxidation and reduction onsets are summarized in Table 4.

As can be seen from the above results, the side-chain positioning drastically influences the HOMO levels of the polymers, whereas the LUMO levels remain almost unaltered. Interestingly, the LUMO level is close to that of a structurally related polymer, PPBzT²-C12 α (3.2 eV), reported earlier, whose donor segment includes two additional thiophene rings.⁹ These results, along with the density functional theory investigations, point out that the LUMO level is localized on the 2,1, 3-benzothiadiazole.

On the opposite, by passing from PTBzT²-C12 α to PTBzT²-C12 β an 0.34 eV higher-lying HOMO level is obtained. A small drop in the open-circuit voltage (V_{oc}) of the corresponding polymer-fullerene OPV devices should thus be expected when using the PTBzT²-C12 β or PTBzT²-CEH β instead of PTBzT²-C12 α as electron donor materials (see Photovoltaic Devices section). Nevertheless, for both positions, the frontier orbital energy levels should allow an efficient photoinduced charge transfer to PCBM (whose LUMO and HOMO levels are estimated to 4.3 and 6 eV, respectively⁸).

Preliminary X-ray scattering measurements have been performed on bulk α - and β -position polymer samples in order to evaluate the influence of the side-chain positioning on the π -stacking interactions. A more in-depth structural analysis of our polymer thin films is out of scope of the present article and will be reported elsewhere. For all polymers, well-defined diffraction peaks could be observed, indicating the semicrystalline nature of the materials (see Supporting Information). The corresponding π -stacking distances for PTBzT²-C12 α , PTBzT²-C12 β , and PTBzT²-CEH β could be estimated to 0.41, 0.37, and 0.35 nm, respectively. These results thus further substantiate the assertion that the π -stacking interactions are most pronounced for the β -position polymers.

Table 5. Field-Effect Mobility Values

polymer	annealing conditions	$\begin{array}{c} \mu_{\rm h}~(\rm cm^2/\\ (V~s)) \end{array}$	annealing conditions	μ _h (cm ² / (V s))
PTBzT ² -C12 α PTBzT ² -C12 β	as cast as cast	5×10^{-4} 7×10^{-6}	130 °C, 15 min 180 °C, 15 min	1×10^{-4} 1×10^{-5}
PTBzT ² -CEH β	as cast	1×10^{-3}	130 °C, 15 min	1×10^{-3}

Finally, the polymer hole mobilities (μ_h) have been investigated in bottom-contact field-effect-transistors (FET) on as-deposited as well as annealed thin film devices. The results obtained in the saturation regime are summarized in Table 5. Mobility values measured in the linear regime were in the same range.

Note that the hole mobility measured on PTBzT²-C12 α is one order of magnitude above our previously published results which had been measured in air and on top-contact FETs without an HMDS surface pretreatment. We may attribute the improvement in mobility reported here to the better film quality at the dielectric interface when using HMDS.⁸

The FET results clearly show that the side-chain position can have a major influence on the charge transport, leading to orders of magnitude variations in the field-effect mobility. This result is consistent with the structural properties (i.e., π -stacking distances) discussed above. The 2 orders of magnitude difference in $\mu_{\rm h}$ observed for both β -position polymers is more surprising since both UV-vis and X-ray investigations led to comparable π -stacking interactions and conjugation lengths. However, the X-ray data obtained on the bulk samples (thick films) show more regular ordering of PTBzT²-CEH β chains compared to polymers bearing linear side groups. Moreover, the calculated crystalline density of PTBzT²-CEH β (1.59 g/cm³) is significantly higher than the density of PTBzT²-C12 α and PTBzT²-C12 β crystal (1.33 and 1.26 g/cm³, respectively). It is documented that the charge mobility is crucially dependent not only on the π -stacking distance but also on the intermolecular distance in the direction normal to the π -stacking.¹⁸ Therefore, the smallest π -stacking distance and the highest lateral chain packing could explain why the mobility in the PTBzT²-CEH β sample is so much different from that of the other two polymers. Nevertheless, in such analysis one should also take into account the morphology of the films used in the studies and not only the structure of the bulk material since they can be very different.19,20

Photovoltaic Devices. Polymer-fullerene photovoltaic devices have been elaborated using the newly synthesized polymers as electron donor. Different polymer:PCBM weight ratios have been investigated as well as different annealing conditions. For PTBzT²-CEH β devices we used a low molecular mass fraction to improve the film homogeneity. For PTBzT²-CEH β and PTBzT²-C12 β , the thickness of the active layer was kept close to 110 nm. The best results were obtained after a 15 min postelaboration heat treatment at 200 and 130 °C for PTBzT²-C12 β and PTBzT²-CEH β , respectively. The properties of PTBzT²-C12 α -based devices have already been published before, and the results obtained for devices with a comparable thickness of 135 nm are reported in Table 6. The measured average photovoltaic results obtained on devices with optimal fullerene content and for similar active layer thicknesses are also summarized in Table 6 as well as the parameters measured on a series of optimized PTBzT²-CEH β -based devices.

As expected, the polymer-fullerene weight ratio has a major impact on the device performances. As shown in Figure 4, the normalized power conversion efficiency (PCE) varies by more than a factor of 3, when the weight ratio changes from 1:1 to 1:4. Interestingly, for the linear



Figure 4. Normalized average PCE obtained on polymer:PCBM photovoltaic devices using PTBzT²-C12 α (filled triangles), PTBzT²-C12 β (open squares), and PTBzT²-CEH β (crosses). The normalization was performed on the (1:4) polymer: C₆₀-PCBM weight ratio and the dotted line are used to guide the eye.

Table 6. Average and Best (Indicated by Asterisk) Photovoltaic Parameters

ratio	thickness (nm)	$V_{\rm oc}\left({\rm V} ight)$	$J_{\rm sc}~({\rm mA/cm^2})$	FF (%)	PCE (%)
]	PTBzT ² -C	212α (pristine)		
1:4	135	0.67	2.17	32	0.46
	PTBzT ² -C	$C12\beta$ (ann	ealed 15 min at 2	200 °C)	
1:4	110	0.55	1.88	41	0.42
	PTBzT ² -C	$EH\beta$ (ann	ealed 15 min at	130 °C)	
1:1 1:1*	120 120	0.55 0.67	5.67 7.80	40 52	1.24 2.71

alkyl chain polymers, the PCE increases with fullerene content, while the opposite is observed for the branched side chain. The high PCBM loading required to achieve the optimal efficiency is distinctive for a large variety of poly-mers reported in the literature^{21,22} and has been tentatively attributed by McCulloch et al. to the intercalation of the fullerene between the polymer side chains.⁷ In this case, the high fullerene content is believed to achieve a continuous electron pathway necessary to support electron transport efficiently. Accordingly, our results support the idea that linear alkyl side chains, in both α and β position, make these polymers prone to fullerene intercalation. Furthermore, the more bulky 2-ethylhexyl chains could hamper fullerene intercalation, allowing efficient electron transport to take place at a lower fullerene content. Additional charge transport and structural analyses on the polymer-fullerene blends are however necessary to corroborate this assertion.

The highest PCE value on LiF free devices (see Supporting Information) is achieved with PTBzT²-CEH β and correlates with the large short-circuit-current (J_{sc}) obtained with this polymer. The higher J_{sc} value in turn results from the lower optimal polymer:fullerene ratio (1:1 instead of 1:4 for both linear dodecyl based polymers), the lower optical band gap (in comparison to PTBzT²-C12 α), and the higher hole mobility (in comparison to PTBzT²-C12 β). The open-circuit voltages (V_{oc}) of both PTBzT²-CEH β - and PTBzT²-C12 β -based devices are comparable and slightly lower (by 0.12 V) than the V_{oc} of the PTBzT²-C12 α -based device. This voltage drop can be linked to the less stable HOMO level of the β -position polymers with respect to the α -position polymer. Note however that the value estimated from the empirical linear relationship between V_{oc} and the polymer HOMO level in

polymer-fullerene bulk heterojunctions reported by Scharber et al. leads to a $V_{\rm oc}$ of 0.4 V, well below our experimental findings.²³ The actual $V_{\rm oc}$ is close to the value typical for P3HT:PCBM devices (~0.6 V). A significant increase in PCE (from 1.5 to 2.7%) is achieved on PTBzT²-CEH β devices when including a LiF layer and an annealing step prior to cathode deposition (Supporting Information). This result highlights the potential of this polymer and opens the way to further optimization.

Conclusion

The synthesis and characterization of a series of donor-acceptor alternate low-band-gap copolymers with a common conjugated backbone, including 2,1,3-benzathiadiazole, thiophene, and thieno-[3,2-*b*]thiophene units, decorated by different solubilizing side chains allowed us to investigate quantitatively the relationships between the polymer optoelectronic and photovoltaic properties and the positioning and molecular structure of the side chains.

The results show that the polymer side chains can have a profound impact on the target polymer functionalities, such as the light harvesting capacity, ionization potential and electron affinity, charge carrier mobilities, or intermolecular interactions in polymer:fullerene blends.

The spectral and electrochemical measurements, as well as the density functional calculations of model oligomers, point out that these variations are related to the degree of twisting along the molecular backbone. The side chains on the fourth position of thiophene rings (β position) induce less steric hindrance and thus a more planar molecular structure which enhances the π -electron delocalization and favors intermolecular interactions. Moreover, using ethylhexyl side chains instead of linear alkyl side chains modifies the interaction between the polymer and the fullerene molecules, leading to opposite dependences of the photovoltaic performances on the fullerene intercalation between the side chains is at the origin of the frequently observed high optimal fullerene content in polymer:fullerene bulk heterojunction devices.

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Supporting Information Available: GPC chromatograms, cyclic voltammogram scans, X-ray diffraction spectrum, OFET characteristics, and I/V curves. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

- Liang, Y.; Xu, Z.; Xia, J.; Tsai, S.-T.; Wu, Y.; Li, G.; Ray, C.; Yu, L. Adv. Mater. 2010, 22, E135–E138.
- (2) Kroon, R.; Lenes, M.; Hummelen, J. C.; Blom, P. W. M.; De Boer, B. Polym. Rev. 2008, 48, 531–582.
- (3) McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; MacDonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W.; Chabinyc, M. L.; Kline, R. J.; McGehee, M. D.; Toney, M. F. *Nature Mater.* 2006, *5*, 328–333.
- (4) Nguyen, L. H.; Günes, S.; Neugebauer, H.; Sariciftci, N. S.; Colladet, K.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Gelan, J.; Vanderzande, D. E. P. J. Appl. Phys. 2006, 36, 219–224.

- (5) Li, W.; Qin, R.; Zhou, Y.; Andersson, M.; Li, F.; Zhang, C.; Li, B.; Liu, Z.; Bo, Z.; Zhang, F. *Polymer* **2010**, *51*, 3031–3038.
- (6) Müller, C.; M. Ferenczi, T. A.; Campoy-Quiles, M.; Frost, J. M.; Bradley, D. D. C.; Smith, P.; Stingelin-Stutzmann, N.; Nelson, J. Adv. Mater. 2008, 20, 3510–3515.
- (7) Mayer, A. C.; Toney, M. F.; Scully, S. R.; Rivnay, J.; Brabec, C. J.; Scharber, M.; Koppe, M.; Heeney, M.; McCulloch, I.; McGehee, M. D. Adv. Funct. Mater. 2009, 19, 1173–1179.
- (8) Biniek, L.; Chochos, C. L.; Leclerc, N.; Hadziioannou, G.; Kallitsis, J. K.; Bechara, R.; Lévêque, P.; Heiser, T. J. Mater. Chem. 2009, 19, 4946–4951.
- (9) Biniek, L.; Chochos, C. L.; Hadziioannou, G.; Leclerc, N.; Lévêque, P.; Heiser, T. Macromol. Rapid Commun. 2010, 31, 651–656.
- (10) Pilgram, K.; Zupan, M.; Skile, R. J. Heterocyl. Chem. **1970**, *6*, 629–633.
- (11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Jr., Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G.A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P.Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox,

- (12) (a) Becke, A. D. J. Chem. Phys. 1993, 98, 5648–5652. (b) Lee, C. T.;
 Yang, W. T.; Parr, R. G. Phys. Rev. B 1988, 37, 785–789.
- (13) Zhang, L.; Zhang, O.; Ren, H.; Yan, H.; Zhang, J.; Zhang, H.; Gu, J. Sol. Energy Mater. Sol. Cells 2008, 92, 581–597.
- (14) Bras, W.; Dolbnya, I. P.; Detollenaere, D.; van Tol, R.; Malfois, M.; Greaves, G. N.; Ryan, A. J.; Heeley, E. J. Appl. Crystallogr. 2003, 36, 791–794.
- (15) Liang, F.; Lu, J.; Ding, J.; Movileanu, R.; Tao, Y. Macromolecules 2009, 42, 6107–6114.
- (16) Roquet, S.; Cravino, A.; Leriche, P.; Alévêque, O.; Frère, P.; Roncali, J. J. Am. Chem. Soc. 2006, 128, 3459–3466.
- (17) Wûrfel, P. In Physics of Solar Cells; Wiley-VCH: Weinheim, 2005.
- (18) Park, Y. D.; Kim, D. H.; Jang, Y.; Cho, J. H.; Hwang, M.; Lee, H. S.; Lim, J. A.; Cho, K. Org. Electron. 2006, 7, 514–520.
- (19) Zhu, X.; Mourran, A.; Möller, M.; Beginn, U.; Anokhin, D. V.; Ivanov, D. A. Phys. Chem. Chem. Phys. 2010, 12, 1444–1452.
- (20) Gospodinova, N.; Ivanov, D. A.; Anokhin, D. V.; Mihai, I.; Vidal, L.; Brun, S.; Romanova, J.; Tadjer, A. *Macromol. Rapid Commun.* 2009, *30*, 29–33.
- (21) Hoppe, H.; Sariciftci, N. S. J. Mater. Chem. 2006, 16, 45-61.
- (22) Shi, C.; Yao, Y.; Yang, Y.; Pei, Q. J. Am. Chem. Soc. 2006, 128, 8980–8986.
- (23) Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. Adv. Mater. 2006, 18, 789–794.
- (24) Clarke, T. M.; Durrant, J. R. Chem. Rev. 2010, ASAP, DOI: 10.1021/cr900271s.