



Random vs. alternating donor-acceptor copolymers: A comparative study of absorption and field effect mobility



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ARTICLE INFO

Article history:

Received 12 February 2014

Received in revised form

31 March 2014

Accepted 3 April 2014

Available online 15 April 2014

Keywords:

Field effect mobility

Benzothiadiazole

Donor-acceptor copolymers

ABSTRACT

The influence of the arrangement of donor and acceptor units in a conjugated copolymer chain on the absorption and field effect mobilities was studied. We synthesized a target random copolymer and compared it with two structurally relevant alternating copolymers, all consisting of 2,1,3-Benzothiadiazole (**BT**) as acceptor and 3-Hexylthiophene (**Th**) as donor units. Especially, bifunctional AB-type monomers were developed to obtain the desired randomly linked copolymer **r-BT-2Th**. We chose AA/BB-type monomers as well to obtain relevant alternating copolymers **a-BT-2Th** and **a-BT-1Th**. The systematic structural variation enables us to compare the copolymers in a precise manner. In dilute solutions **r-BT-2Th** and **a-BT-2Th** resemble closely in absorption spectra and have similar oxidation potentials regardless of random or alternating arrangement of donor and acceptor. In thin films, **a-BT-2Th** shows the lowest optical gap and depicts the highest field effect hole mobility of $1.5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

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1. Introduction

In the last few years, syntheses of π -conjugated copolymers have been attracting huge interest for the use in polymer solar cells due to their promising optical and electronic properties [1–6]. Using π -conjugated donor materials in combination with fullerene derivatives as acceptor, outstanding power conversion efficiencies of over 9 % have been already reached in single-junction and tandem cells [7]. By developing new materials and device architectures, the operational mechanism of organic photovoltaics is more and more investigated, yet it remains not fully understood [8]. To enable a rational macromolecular design with general validity for conjugated polymers, correlation of design strategy and the resulting properties has to be established. Not only a high mobility and intermolecular interaction, leading to π -electron delocalization, but also structural geometry parameters such as dihedral angle has to be taken into consideration [4,9]. One general successful strategy to extend the absorption to longer wavelengths is the strict alternation of electron-rich (donor, D) and electron-deficient (acceptor, A) units in a conjugated polymer chain [1]. But it is not verified if this strict alternation of D and A units is a

basic necessity to tune the absorption. According to the principle of orbital overlap leading to bandgap reduction, only the proximity of the D and A units is required [10]. Additionally, synthesizing the π -conjugated polymers in a random fashion would for example help to improve the solubility and processability for high molecular weight polymers. But the combination of different types of monomers in an arbitrary fashion may have an impact on the absorption, as well as on charge transport properties. We recently showed in a combined theoretical and experimental study that the specific arrangement of D and A units in well-defined low molecular weight systems has no influence on the optical absorption [11]. This raises the question whether the influence of D and A arrangement has consequences in polymer properties as well. Consequently, the following relevant questions have to be answered: Is there a difference in absorption between random and alternating copolymers? Does the sequential build-up of monomers influences the charge transport? In this contribution we address precisely these questions and compare a random copolymer with two relevant alternating copolymers. We deliberately use a combination of AB-type monomers to obtain a randomly linked copolymer, whereas conventional alternating copolymers were also obtained by AA/BB-type Suzuki polycondensation. With the use of AB-type monomers, each monomer can react with itself and the other comonomer. Due to this synthesis strategy, it is possible to obtain directly comparable random and alternating copolymers.

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We considered conjugated copolymers that incorporate 2,1,3-Benzothiadiazole units (BT) which are receiving intensive interest in recent years [12–17]. 2,1,3-Benzothiadiazole derivatives exhibit a relatively high reduction potential as well as good air and thermal stability due to their fused-aromatic ring structure [18,19]. The BT moiety in D/A conjugated copolymers is one of the most studied electron-deficient units. It is usually directly coupled with electron-rich comonomers or with two thiophenes as spacer between the BT and electron-rich units [2,20]. In BT-thiophene based random copolymers, small amounts of incorporated BT units lead towards broadening of the absorption [21]. The same tendency in optical properties has been observed on incorporating an additional acceptor unit [22].

In particular we synthesized three copolymers consisting of 2,1,3-Benzothiadiazole (as acceptor) and 3-Hexylthiophene (as donor) units via Suzuki-Miyaura polycondensation (see Fig. 1). We synthesized the random copolymer **r-BT-2Th**, where BT-1Th units (M1) are randomly linked with an additional thiophene unit (M2) (cf. Scheme 1). To obtain comparable alternating copolymers, one must consider the fact that the BT-1Th unit can react with itself and with the additional thiophene unit. This results in a randomly linked copolymer where BT units are coupled with a varying number of thiophene units in between. Therefore, we synthesized on the one hand a strict alternating **a-BT-2Th** copolymer, where BT units alternate with a bithiophene unit and on the other hand a strict alternating copolymer **a-BT-1Th** where BT units alternate with just one thiophene unit. We want to investigate any possible differences or influences of a random order of donor-acceptor units versus a strictly alternating arrangement, with respect to the optical as well as field effect mobilities. Therefore, we studied the thermal, optical and charge transport properties of these polymers and compared them under one another.

2. Experimental section

2.1. Materials and methods

All reactions were carried out in dry glassware and under inert atmosphere of purified argon using Schlenk techniques. The reagents and solvents were purchased from Aldrich, ABCR, Acros or TCI. All reagents were used without further purification unless otherwise noted. Solvents used for precipitation and column chromatography were distilled under normal atmosphere. 4-[(Trimethylsilyl)ethynyl]phenylboronic acid pinacol ester was synthesized similar to a published procedure. [23] $^1\text{H-NMR}$ (300 MHz) spectra were recorded on a Bruker AC 300 spectrometer at room temperature. Chemical shifts for $^1\text{H-NMR}$ spectra are referenced relative to residual protons in the deuterated solvents (CDCl_3 $\delta = 7.26$ ppm, CD_2Cl_2 $\delta = 5.33$ ppm, $\text{C}_2\text{Cl}_4\text{D}_2$ $\delta = 5.91$ ppm). Abbreviations used for splitting patterns are s (singlet), d (doublet), t (triplet), m (multiplet) and b (broad). Mass spectroscopic data (MS) were obtained from a FINNIGAN MAT 8500 instrument. Differential scanning calorimetry experiments were conducted at a heating rate

of 40 Kmin^{-1} under a nitrogen atmosphere with a Perkin–Elmer Diamond DSC, calibrated with indium. Thermogravimetry measurements were conducted on a Mettler Toledo TGA/SDTA 851 under a nitrogen atmosphere at a heating rate of 10 Kmin^{-1} . Temperature decomposition ($T_{d-5\%}$) correlates to the respective temperature at 5 % weight loss. UV/Vis spectra of solutions in *o*-Dichlorobenzene with a concentration of 0.02 mg mL^{-1} and of films were recorded on a JASCO V-670 spectrophotometer at room temperature. Size exclusion chromatography (SEC) measurements were carried out in THF with two Varian Mixed-Columns ($300 \times 7.5 \text{ mm}$) at room temperature and a flow rate of 0.5 mL min^{-1} using UV (Waters model 486) with 254 nm detector wavelength for **a-BT-2Th**. Polystyrene standards and *o*-Dichlorobenzene as an internal standard were used for calibration. SEC measurements were carried out in 1,2,4-Trichlorobenzene with three PLgel Olexis-Columns ($300 \times 7.5 \text{ mm}$) at $150 \text{ }^\circ\text{C}$ using RI detector for **r-BT-2Th** and **a-BT-1Th**. Cyclic voltammetry measurements were carried out under moisture and oxygen free conditions using a standard three-electrode assembly connected to a potentiostat (model 263A, EG&G Princeton Applied Research) at a scanning rate of 50 mV s^{-1} . A Pt milli-electrode was used as working electrode. A platinum wire in the respective solvent plus conducting salt (tetra-*n*-butylammoniumhexafluorophosphate, 0.1 M) was used as a counter electrode. The quasi-reference electrode consisted of an Ag-wire in a $\text{AgNO}_3/\text{acetonitrile}$ solution (0.1 M). Each measurement was calibrated with the internal standard ferrocene/ferrocenium. For **r-BT-2Th** and **a-BT-2Th** methylene chloride and for **a-BT-1Th** a mixture of *o*-Dichlorobenzene/acetonitrile (10/1; v/v) was used as solvent with 0.1 M conducting salt. The HOMO energy levels were calculated using the empirical relation: $E_{\text{HOMO}} = [-e(E^{1/2} \text{ (vs. Ag/AgNO}_3) - E^{1/2}(\text{Fc/Fc}^+ \text{ vs. Ag/AgNO}_3))] - 5.16 \text{ eV}$ for **r-BT-2Th** and **a-BT-2Th** and $E_{\text{HOMO}} = [-e(E^{1/2} \text{ (vs. Ag/AgNO}_3) - E^{1/2}(\text{Fc/Fc}^+ \text{ vs. Ag/AgNO}_3))] - 5.25 \text{ eV}$ for **a-BT-1Th**. The oxidation potentials of 5.16 eV and 5.25 eV for ferrocene/ferrocenium oxidation versus zero vacuum level are obtained from solvent dependent redox potentials [24].

2.2. Synthesis of polymers

2.2.1. Synthesis of r-BT-2Th

In a 20 mL high pressure microwave reactor tube, equipped with a sealed septum **M1** (227 mg, 0.448 mmol) and monomer **M2** (167 mg, 0.448 mmol) were dissolved in tetrahydrofuran (6 mL) and an aqueous solution of K_2PO_4 (2 M, 1.05 mL) were added to the solution and degassed with Argon for 5 min. Afterwards $\text{Pd}_2(\text{dba})_3$ (16.4 mg, 0.0179 mmol) and $[(t\text{-Bu})_3\text{PH}]\text{BF}_4$ (10.4 mg, 0.0358 mmol) were added, then the tube was sealed and degassed with Argon for 15 min. The reaction was heated 39 h at $80 \text{ }^\circ\text{C}$ (oil bath temperature). The end-capping procedure was performed in 2 separate steps. After cooling to room temperature, a degassed solution of 4-[(Trimethylsilyl)ethynyl]phenylboronic acid pinacol ester (268 mg, 0.895 mmol) in 3 mL tetrahydrofuran was added first, followed by heating for 27 h at $80 \text{ }^\circ\text{C}$. After cooling to room temperature,

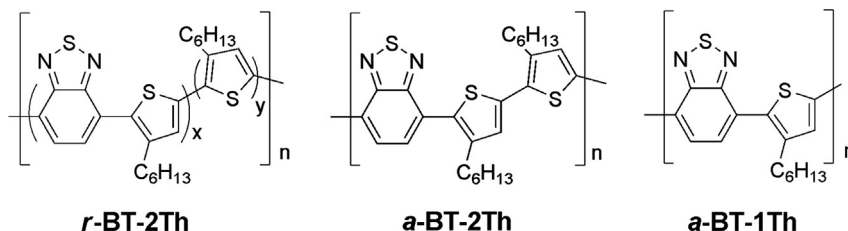


Fig. 1. Random and alternating BT-Th based donor-acceptor conjugated copolymers.

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