



Effects of dynamic 3D-volume of side chains in conjugated polymers on nano-scale morphology and solar cell properties



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ABSTRACT

We have synthesized a series of benzo[1,2-*b*:4,5-*b'*]-dithiophene (BDT)-co-thieno[3,4-*b*]thiophene (TT) based polymers with various alkyl side chains and bridging-atom on their TT units and studied the effects of the variation in the effective van der Waals volumes (eVol) of the side chains on the photovoltaic properties of the associated bulk heterojunction (BHJ) solar cells. eVol was found to be correlated with the degree of phase separation in the BHJ film, which affects the area of the polymer-PC₇₁BM interface and the charge mobility. The polymer has a 2-ethylhexyl group that results in a relatively optimal BHJ film morphology, with sufficient polymer-PC₇₁BM interfacial area for efficient charge generation and minimal charge mobility loss upon BHJ film formation. As a result, the solar cell device (2-ethylhexyl polymer) exhibits the highest power conversion efficiency of 8.25% because its short-circuit current density value (16.24 mA/cm²) and fill factor (0.674) are the highest of the synthesized polymers.

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1. Introduction

There have been remarkable developments in polymer solar cells (PSCs) recently [1–5] and their power conversion efficiencies (PCEs) have now exceed 10% for single-junction cells [6–8] and 11–12% for tandem cells [9–11]. These high photovoltaic performances have resulted from the development of new conjugated polymers, device architectures, and processing technologies. In particular, various polymer designs have been successfully utilized to create low bandgap polymers and improve their electrical properties, which have resulted in solar cell efficiencies [12–19]. These design strategies include the reduction of polymer backbone twist, and the incorporation of large π -conjugated aromatic systems and/or building blocks enhancing the quinoid character of the polymer [20–23].

One of the most reliable approaches to the synthesis of low bandgap conjugated polymers is the preparation of push–pull-type alternating copolymers consisting of electron-donating and electron-accepting conjugated units. Aromatic compounds with a high electron density are usually used as the electron-pushing units, and electron-deficient aromatic compounds functionalized with electron-withdrawing groups are used as the electron-pulling units [24,25]. The electrostatic interactions of push–pull type conjugated polymers increase the strength of their intermolecular interactions, which facilitates efficient charge transport by inducing long-range ordering of the polymer in the solid state [26]. In the design of push–pull type polymers, an important consideration is the introduction of appropriate side chains. Such side chains not only provide sufficient polymer solubility for solar cell device fabrication but also improve the crystallinity of the polymer, which results in increased charge mobility. Most importantly, the number of side chains and the properties of their molecular structures, such as their chain lengths and number of branching points, dramatically affect the polymer properties that determine solar cell performance, in particular the molecular orientation of the polymer and

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its miscibility with the accepting material and thereby the morphology of the bulk heterojunction (BHJ) film [27–32]. Therefore, to achieve high efficiency PSCs, it is critical to find the optimal side chains for the given chemical structure of the polymer and to understand their influence on its film morphology and photovoltaic properties. However, our understanding of the structural effects of side chains on solar cell properties is rather phenomenological and based on observations of BHJ film morphologies alone.

This study focused on the effects of varying the effective distance and volume occupied by the flexible motions of alkyl side chains on the morphologies of BHJ films. The effective van der Waals volumes were found to affect the properties of the polymers in important ways, including the solubility of the polymer, the packing structure of the polymer in the solid state, and its miscibility with fullerene derivatives in the solid state and thereby the nano-scale phase separation in the BHJ film. A series of push–pull type polymers were prepared based on 4,8-dialkoxy benzo[1,2-*b*:4,5-*b'*]-dithiophene (BDT) as the push-unit and thieno[3,4-*b*]thiophene (TT) derivatives as pull-units with various alkyl side chains. Fig. 1(a) shows that the TT unit of **PTBOBO** contains a 2-butyloctyloxy group and that in **PTBSBO** the oxygen bridging-atom of the 2-butyloctyl group is swapped with a sulfur atom. The side chain in **PTBOEH** is the less bulky 2-ethylhexyl group and in **PTBnO** is a linear octyl group. Herein, we describe the syntheses of these polymers and present our investigation of the effects of varying the effective van der Waals volumes of these TT unit side chains on the photovoltaic properties of the associated polymer devices. These polymers have different effective van der Waals volumes that depend on the molecular structures of their side chains. Our experimental and theoretical results show that the 2-ethylhexyloxy group in the TT unit of **PTBOEH** has the most appropriate van der Waals volume for the formation of the optimal morphology for charge carrier generation without sacrificing charge carrier mobility. As a result, the **PTBOEH** device exhibits a PCE up to 8.25%, which is ~20% better than the lowest PCE, 6.9%, that of **PTBOBO**.

2. Results and discussion

2.1. Polymer syntheses

As shown in Fig. 1(b), **PTBOBO** and **PTBSBO** were prepared via the Stille coupling polymerizations [33] of 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy) benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT-EH) with 2-butyloctyl 4,6-dibromo-3-fluorothieno[3,4-*b*]thiophene-2-carboxylate (TT-BO) and 2-butyloctyl 4,6-dibromo-3-fluorothieno[3,4-*b*]thiophene-2-thiolate (TT-SBO) respectively. **TT-SBO** was synthesized via a DCC (*N,N'*-dicyclohexylcarbodiimide) coupling reaction from fluorothieno[3,4-*b*]thiophene-2-carboxylic acid and 2-butyloctylthiol. 2-Butyloctyl thiol was prepared by reacting 2-butyloctyl bromide with thiourea under basic conditions, as shown in Scheme S1; during this reaction, a side product, the oxidized bisulfide of the thiol product, was observed and recovered to the desired product by reducing it with lithium aluminum hydride after the reaction. The detailed reaction conditions and procedures are described in the Supplementary Data. After polymerization, the synthesized polymers were precipitated in methanol and purified by performing successive Soxhlet extractions with methanol, hexane, and chloroform. The molecular weights of **PTBOBO**, **PTBSBO**, **PTBOEH**, and **PTBnO** were determined with gel permeation chromatography (GPC) at 80 °C and found to be $M_n = 69, 26.6, 71.3, \text{ and } 76.3$ kg/mol with polydispersity indices (PDI) of 2.8, 2.9, 3.6, and 2.6, respectively.

2.2. Optical and electrochemical properties of the polymers

Fig. 2 shows the UV–vis absorption spectra of the polymers in the film state and their characteristic data are summarized in Table 1. Compared with the polymers with branched alkoxy chains (**PTBOBO** and **PTBOEH**), the polymer with a linear octyl chain, **PTBnO**, has a red-shifted spectrum with a maximum absorption (λ_{max}) of 680 nm and an absorption onset point (λ_{onset}) of 749 nm, which are 4–5 nm red-shifted from those of **PTBOBO** and

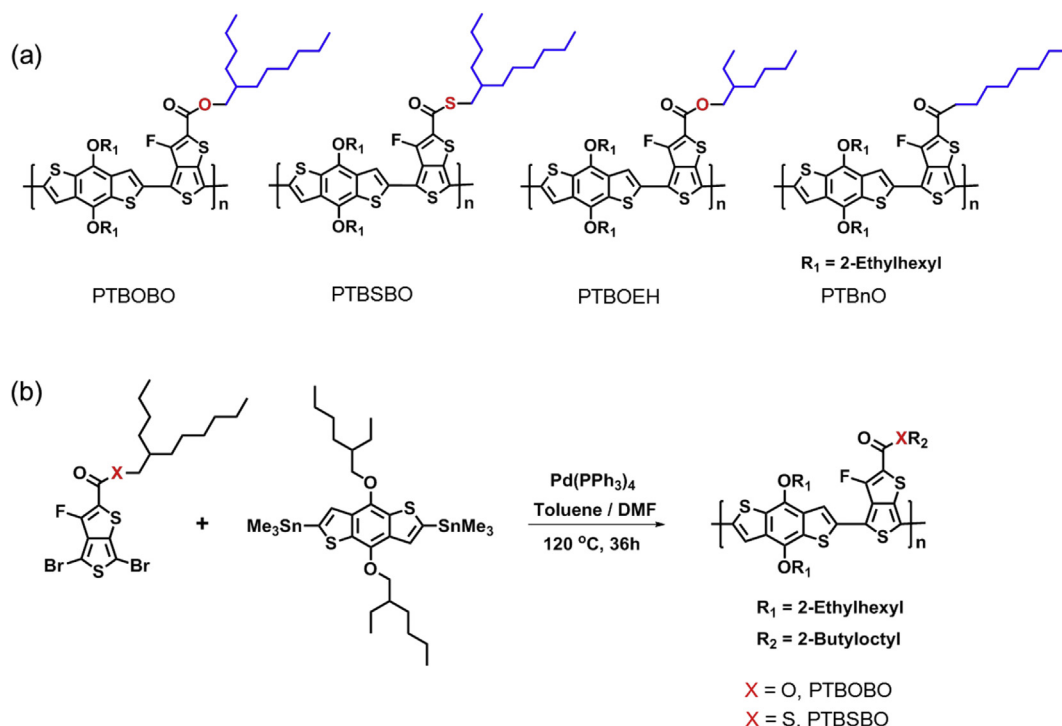


Fig. 1. (a) Structures of **PTBOBO**, **PTBSBO**, **PTBOEH**, and **PTBnO**, (b) Synthesis of **PTBOBO** and **PTBSBO**.

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