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Effect of side chains on solubility and morphology of poly(benzodithiohene-alt-alkylbithiophene) in organic photovoltaics

Min Hee Choi, Kwan Wook Song, Doo Kyung Moon *, Jung Rim Haw *

Department of Materials Chemistry and Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Republic of Korea

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ABSTRACT

It was reported that the side chains play especially an important role in enhancing physical properties and energy levels. Polythiophene based on benzodithiophene has excellent carrier mobility, but high HOMO level. We synthesized polythiophenes, PBDTBiTh(2EH) and PBDTBiTh(12C), were polymerized using the Stille coupling reaction and had thiophene with a 2-ethylhexyl or n-dodecyl side chain. Upon introducing the 2-ethylhexyl side chain, the absorption coefficients of the monomers and polymers were enhanced. Also, the edge-on orientation was fortified and the HOMO level was decreased to −5.37 eV. PBDTBiTh(2EH) showed a power conversion efficiency (PCE) of 2.1%, which was double that of PBDTBiTh(12C).

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Introduction

Organic electronics, polymer light-emitting diodes (PLEDs) [1–5], polymer solar cells (PSCs) [6–10] and polymer field effect transistors (FETs) [11–14] have come into the spotlight because of their light weight, cost-effectiveness and possibility of large-scale production by the solution and roll-to-roll process. Especially, the polymer solar cells, in general, use are of the bulk hetero-junction (BHJ) type, which consist of a p-type semiconductor (conjugated polymer) as the electron donor and n-type semiconductor (fullerene derivatives) as the electron acceptor. The BHJ type of polymer solar cell had the advantages of maximizing the interface between the donor and acceptor and the facile transfer of the charge to the electrode [15]. Over the past decade, polymer solar cells have rapidly developed due to the considerable amount of research that has been done, and power conversion efficiencies (PCEs) of ~8 and ~10% have been reported in a single cell [16] and tandem cell [17], respectively. To commercialize the solar cells and adopt the solution and roll-to-roll process, the solubility and air stability of the polymer at room temperature are very important [18].

Conjugated polymers generally consist of three components, the conjugated backbone, the side chains and the substituents. The conjugated backbone is the major component that determines factors such as the physical properties, energy levels, band gap and inter/intra molecular interactions related to the PSCs [15]. The traditional concept of polymer solar cells was that the bandgap and energy levels were mainly determined by the unit of the conjugated polymer backbone and less-effected by the alkyl solubilizing groups. Therefore, it was considered that the side chains do not affect the short circuit current density (J_{sc}) and open circuit voltage (V_{oc}) in polymer-based BHJ solar cells. However, in recent studies, it was reported that the alkyl solubilizing groups play a significant role in enhancing the molecular weight, solubility and processability [19]. Additionally, these side chains were found to control the intermolecular interactions and allow for proper mixing with an electron acceptor [15]. Li and Yu reported the synthesis of polymers with different side chains and substituents using thieno[3,4-b]thiophene and benzodithiophene units as the conjugated backbone in 2009 [20]. In spite of having a similar bandgap (~1.60 eV), these polymers showed different highest occupied molecular orbitals (HOMOs), morphologies and PCEs in the range of 2.26–7.4% [20,21]. You *et al.* reported that the energy levels and polymer stacking structure were changed according to the position and length of the side chain [19,22]. In 2013, Beaujuge et al. studied the effect of the number of aliphatic carbons of benzodithiophene and N-alkyl substituted thieno[3,4-c]pyrrole-4,6-dione units and found that the polymer orientation could be engineered and a PCE of 8.5% obtained [23]. Therefore, it is important to choose the length, position and the type of the side chain.

* Corresponding author. Tel.: +82 2 450 3499; fax: +82 2 2201 6447.
E-mail addresses: dkmoon@konkuk.ac.kr (D.K. Moon), jrhaw@konkuk.ac.kr (J.R. Haw).

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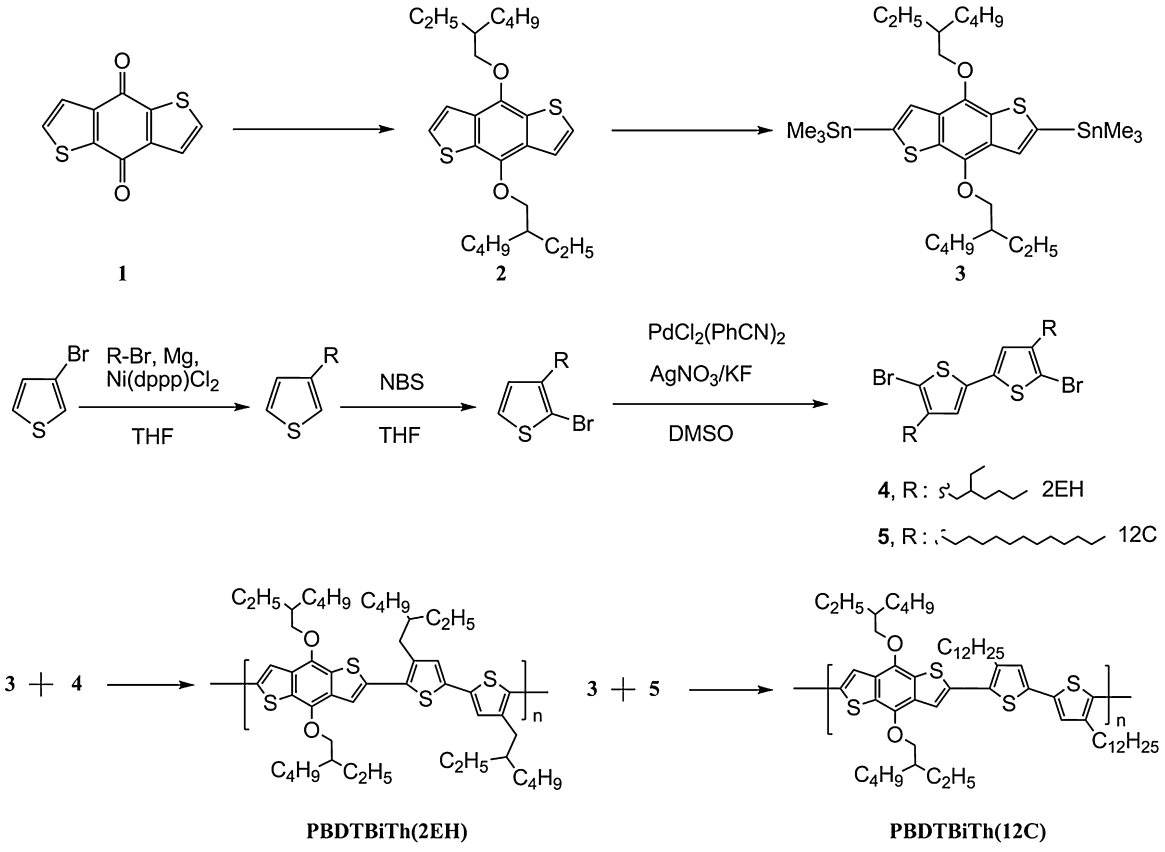
Benzodithiophene (BDT) has been widely used in the field of polymer field effect transistors (PFETs) and PSCs, because it has a low intermolecular rotation [24]. As BDT had a rigid and coplanar structure, it shows face-to-face π-stacking, good charge transfer properties and enlarged absorption region, due to its efficient conjugated length. The polythiophenes that were polymerized with BDT and thiophene moieties showed a linear backbone figure of 180°, good charge carrier mobility of 0.01 $cm^2 V^{-1} s^{-2}$ and probability of PFET [25]. The BDT units used did not have any solubilizing groups, but only two *n*-dodecyl alkyl chains introduced into bithiophene. Therefore, the polymers were only soluble in *o*-dichlorobenzene at 100 °C because of their low solubility. Also, a common issue in polymers containing BDT is that they have a high HOMO level and low air stability. The polythiophenes without a side chain showed good hole mobility, but low solubility. For example, poly (3-hexylthiophene) is a famous polymer semiconductor into which the hexyl side chain is introduced, giving it increased solubility. In recent research, it was found that a side chain, of the linear and/or branched type, must be introduced to increase the solubility and processability. Especially, studies involving the introduction of the branched type side chain were recently performed to control the electrical properties of polymer semiconductors [26]. However, according to these side chains, the studies of crystal structure and absorption coefficient of polymer were insufficient.

In this study, polythiophenes containing BDT and bithiophene were polymerized using the Stille coupling condensation. The BDT employed had 2-ethylhexyloxy side chains in the 4 and 8 positions. Also, bithiophene with either 2-ethylhexyl or *n*-dodecyl side chain in the 4 and 4′ positions was used to examine the effect of the type of side chain. The two polythiophenes, PBDTBiTh(2EH) and PBDTBiTh(12C), showed similar polymerized behavior. However, PBDTBiTh(2EH) showed enhanced solubility at room temperature, an edge-on solid phase structure and increased absorption coefficient, but decreased HOMO energy level (−5.37 eV). BHJ PSCs were fabricated using the two polymers mixed with an electron acceptor at room temperature and their increased PCE (2.1%) was confirmed.

Results and discussion

Polymer synthesis

Scheme 1 reveals the chemical structure of both the monomers and polymers and their synthetic processes. In this study, only p-type π-conjugated polymers were synthesized using 2,6-bis(trimethyltin)-4,8-di-(2-octyldodecyloxy)benzo[1,2-b:4,5-b′]dithiophene (**3**) and two bithiophene derivatives (**4** and **5**). The 2-ethylhexyl and n-dodecyl side chains were introduced into bithiophene derivatives **4** and **5**, respectively. PBDTBiTh(2EH) and PBDTBiTh(12C) were synthesized through the palladium-catalyzed Stille coupling reaction with chlorobenzene as a solvent, Pd_2dba_3 and P(o-tolyl)$_3$ as a catalyst and ligand at 90 °C for 48 h. After the polymerization concluded, the polymer was end-capped with bromothiophene and stirred for an additional 12 h. The mixtures were cooled to room temperature, washed with diluted HCl solution, the solvent evaporated and the powder re-precipitated in methanol. The obtained powders were again purified in a Soxhlet apparatus with methanol, acetone and chloroform. Finally, the chloroform-soluble portion was re-precipitated in methanol and a reddish powder obtained. The yields of PBDTBiTh(2EH) and PBDTBiTh(12C) precipitated in methanol were 73 and 98%, respectively. The PBDTBiTh(2EH) was all well soluble in tetrahydrofuran (THF), chlorobenzene and *o*-dichlorobenzene at room temperature, whereas PBDTBiTh(12C) was only soluble at elevated temperature. The structures of the



Scheme 1. Synthesis of monomers and polymers.

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