



# Synthesis and characterization of poly(3-hexylthiophene)-*block*-poly(dimethylsiloxane) for photovoltaic application



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## ABSTRACT

A diblock copolymer poly(3-hexylthiophene)-*block*-poly(dimethylsiloxane) (P3HT-*b*-PDMS) was synthesized as a donor material for organic photovoltaic devices. The regioregular poly(3-hexylthiophene) (P3HT) with a bromo-terminal was prepared via Grignard metathesis polymerization, and poly(dimethylsiloxane) (PDMS) with a silane terminal was obtained by anionic polymerization. Finally, the coupling reaction of these homopolymers via hydrosilylation afforded P3HT-*b*-PDMSs with different lengths of the PDMS segment. Device evaluation of photovoltaic cells based on P3HT-*b*-PDMS blended with [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) revealed that the incorporation of PDMS segment effectively increase the photocurrent compared to a P3HT/PCBM system. From AFM and SEM observations for P3HT-*b*-PDMS/PCBM blend films, it was clearly revealed that the phase-separated structure within several tens nanometer scale was obtained, and that the aggregation of PCBM was sufficiently suppressed by the introduction of PDMS. These facts indicate that the PDMS segment is probably assembled into the interface between P3HT and PCBM to relieve the mismatch of the surface free energy.

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## 1. Introduction

Organic solar cells have several advantages such as light weight, low cost, and short energy payback time compared to silicon-based inorganic ones, and have attracted attention as an alternative clean energy source [1]. Intensive research on developing appropriate organic donor and acceptor materials has been carried out for improving their power conversion efficiency (PCE). Semi-conducting materials based on polymers have an advantage of facile solution processing such as spin-coating and ink jetting to fabricate a thin active layer in solar cells, which enables a large area production. Numerous polymeric materials, especially donor polymers combined with [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) as an acceptor, with a wide range of absorption band have been developed for harvesting the sufficient solar photons to increase the photocurrent [2,3].

Controlling morphology in the active layer of organic solar cells is also of great importance in order to achieve an efficient photon-

to-electron conversion. Most of recent works have employed bulk heterojunction structures constructed in a mixture of donor/acceptor materials affording large interface area between donor/acceptor domains where the photo-induced exciton undergoes charge dissociation into a hole and an electron, respectively. The photovoltaic device based on the bulk heterojunction structure have been intensively investigated using a famous combination of poly(3-hexylthiophene) (P3HT) and PCBM in terms of the morphological effect on PCE, device life time, and so on [4–7]. Since the diffusion length of the exciton is limited within 5–10 nm, the phase-separated structure of donor/acceptor within several tens nanometer scale is favorable for effective charge generation [8]. The self-assembling nature of block copolymers can be exploited to create suitable morphology for organic solar cells because of the scale of domains matching the size of exciton diffusion. A number of the charge transporting block copolymers have been synthesized in a combination of donor-acceptor segments, crystalline-amorphous segments, and so on [9,10]. The block copolymers consisting of P3HT as a typical donor material have also been prepared [11–33]. Instead of polymer/PCBM blend systems, donor-acceptor (DA) type block copolymers can be alternative candidates to create stable phase-separated structures

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[11,14,20,21,23,25,34]. For example, Zhang et al. demonstrated that the P3HT block copolymer containing polyacrylate with perylene diimide pendant groups as an acceptor block showed a microphase-separated structure in the thin films, yet low PCE in comparison to the conventional P3HT-based solar cells [11,14]. A rod–rod type block copolymer consisting of P3HT and poly(*p*-phenylene) was also found to be a good component for creating a well-defined double channel network nanostructure in a blend with PCBM [32]. On the other hand, it was revealed that adding small amount of the P3HT-based block copolymer as a surfactant into P3HT/PCBM solar cells exclusively changed their morphology resulting in improvement of the PCE [13,19,22,26].

In our previous reports, we designed donor diblock copolymers based on P3HT attached with a short soft segment such as poly(ethylene oxide) (PEO) [35,36] or polystyrene [37]. The strategy is the formation of discrete and thermodynamically stable phase-separated structures in block-copolymer/PCBM blend films. The soft second segment is aimed to assist not only the stabilization of PCBM domain in nanoscale but also the vertical orientation of each donor and acceptor domain to the film plane for the effective charge transportation. In the blend films of P3HT-*b*-PEO and PCBM, lamellar phase-separated structures with perpendicular alignment in some extent were obtained with the aid of the soft PEO segment [36]. The PCE using this blend films became slightly higher than the device using P3HT/PCBM system. In this article, a diblock copolymer consisting of P3HT and poly(dimethylsiloxane) (PDMS) was designed for morphological control in the blend film with PCBM. The synthesis of poly(3-hexylthiophene)-*block*-poly(dimethylsiloxane) (P3HT-*b*-PDMS) in this work employed the polymer coupling reaction between P3HT and PDMS homopolymers with a reactive chain end. A similar procedure to synthesize P3HT-*b*-PDMS have been reported in the recent work by Manners et al., in which they used relatively longer PDMS chains [38]. In contrast, P3HT-*b*-PDMS in this work possesses a short PDMS block (less than 2000 of the molecular weight) in order not only to assist the formation of a suitable phase separation in the blend with PCBM but also not to disturb an efficient charge transportation by the insulating PDMS domains. PDMS possesses a relatively low surface free energy of 22.6 mN m<sup>-1</sup> [39], and can relieve the mismatch between those of P3HT (16.8 mN m<sup>-1</sup>) and PCBM (30.1 mN m<sup>-1</sup>) at the interface [40], which is likely to cause a segregation into the large crystalline domains. Furthermore, due to its low surface free energy, PDMS tends to segregate at the surface of the film. It was reported that the surface thin layer of the PDMS additive improved the PCE of P3HT/PCBM solar cells, possibly because of suppression of charge carrier recombination at the organic/metal interface [41]. The effect of introduction of PDMS segment on the photovoltaic device performance based on P3HT/PCBM system as well as the thin film morphology was investigated in detail.

## 2. Experimental section

### 2.1. Materials

Tetrahydrofuran (THF) was used as freshly distilled over sodium and benzophenone. Toluene was distilled over calcium hydride and stored under nitrogen. 2,5-Dibromo-3-hexylthiophene (**1**) was synthesized from 3-hexylthiophene according to the literature [42]. Poly(dimethylsiloxane)s with a Si–H terminal (PDMS-SiH) were prepared by anionic polymerization of hexamethylcyclotrisiloxane followed by treating with chlorodimethylsilane according to the reported procedure [43]. PCBM (purity: 99%) was purchased from ATR company (Chiba, Japan) and used as received without purification. A solution of poly(3,4-

ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) (Clevios P Al 4083, conductivity:  $\sim 10^{-3}$  S cm<sup>-1</sup>) was purchased from H. C. Stark GmbH (Goslar, Germany), and diluted with deionized water (PEDOT:PSS/water = 2/1 in volume) with 5 wt% of dimethyl sulfoxide before use. The other solvents and reagents were purchased from Wako Pure Chemical Industries (Osaka, Japan) or Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and used as received.

### 2.2. Synthesis of regioregular poly(3-hexylthiophene) (P3HT-Br)

To a two-necked flask equipped with a stirring bar, a condenser, and a three-way stopcock were added 2,5-dibromo-3-hexylthiophene (**1**) (3.26 g, 10.0 mmol) and anhydrous THF (100 mL) under nitrogen. To this solution was added 2 M *tert*-butylmagnesium chloride solution in THF (5.10 mL, 10.2 mmol), and the mixture was gently refluxed for 1.5 h. After the solution was allowed to room temperature, [1,3-bis(diphenylphosphino)propane]nickel(II) dichloride (Ni(dppp)Cl<sub>2</sub>) (0.081 g, 0.15 mmol) was added as a suspension in anhydrous THF (3.5 mL). The mixture was stirred at room temperature for 17 min, and the reaction was quenched by adding a small amount of methanol. The solution was concentrated by a rotary evaporator, and poured into methanol. The precipitate was filtered, and extracted with in the order of methanol, hexane, and chloroform using a Soxhlet extractor apparatus. Then the extract in chloroform was concentrated by a rotary evaporator, and reprecipitated in methanol. The precipitate was filtered and dried to give a dark-purple polymer. The yield was 1.13 g (69%).

### 2.3. Synthesis of vinyl-terminated poly(3-hexylthiophene) (P3HT-VN)

To a two-necked flask equipped with a stirring bar, a condenser, and a three-way stopcock were added P3HT-Br (0.300 g, 0.025 mmol of thiophene unit), 4-vinylphenylboronic acid (0.0250 g, 0.16 mmol), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>) (9.0 mg, 6.9 μmol), 3 M potassium carbonate aq. (3.0 mL, 9.0 mmol), and toluene (15 mL) under nitrogen. The mixture was subject to freeze-pump-thaw cycles to eliminate the air. Then the mixture was stirred at 100 °C for 24 h. The mixture was extracted with chloroform and washed by water. The organic layer was dried with magnesium sulfate, concentrated by a rotary evaporator, and poured into methanol. The precipitate was filtered and dried to give a dark-purple polymer. The yield was 0.263 g (87%).

### 2.4. Synthesis of poly(3-hexylthiophene)-*block*-poly(dimethylsiloxane) (P3HT-*b*-PDMS)

To a two-necked flask equipped with a stirring bar, a condenser, and a three-way stopcock were added P3HT-VN (0.250 g, 0.020 mmol of thiophene unit) and dry toluene (8 mL) under nitrogen. To this solution were added PDMS-SiH (0.400 g, 0.20 mmol) and platinum(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (2 drops, solution in polydimethylsiloxane), and the mixture was stirred at 120 °C for 72 h. After cooled down to room temperature, the mixture was poured into hexane. The precipitate was filtered, washed with hexane, and dried. A dark-purple polymer was obtained. The yield was 0.245 g (84%).

### 2.5. Photovoltaic device fabrication

All the devices were manufactured with a configuration of ITO/PEDOT:PSS (30 nm)/active layer (85 nm)/LiF (0.5 nm)/Al (100 nm).

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