



All-conjugated block copolymers for efficient and stable organic solar cells with low temperature processing

Priyanka Tyagi^a, Sun-Chen Hua^b, Daniel Roger Amorim^{a,c}, R.M. Faria^c, Jeff Kettle^{a,*}, Masaki Horie^{b,**}

^a School of Electronic Engineering, University of Bangor, Dean St, Gwynedd, Bangor, LL57 1UT, UK

^b Department of Chemical Engineering, National Tsing Hua University, 101, Sec. 2, Kuang-Fu Road, Hsinchu, Hsinchu City 30013, Taiwan

^c Instituto de Física de São Carlos, Universidade de São Paulo, 13560-970 São Carlos, SP, Brazil

ARTICLE INFO

Keywords:

Conjugated block copolymer
Organic photovoltaic
Energy payback time
Stability

ABSTRACT

The low embodied energy within Organic Photovoltaics (OPVs) provides the technology with a characteristic that surpasses all other PV materials. In this work, all-conjugated block copolymers comprising of P3HT and PTB7-Th have been synthesized which enable even lower temperature processibility, thus reducing the embodied energy further. The all-conjugated block copolymers comprise of P3HT and poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*;4,5-*b'*]dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothiopheno[3,4-*b*]thiophene-)-2-carboxylate-2,6-diyl)] (PTB7-Th). To synthesis these, a narrow-distributed, monobrominated P3HT ($M_n = 7000$, $M_w/M_n = 1.31$) is synthesized by Grignard metathesis polymerisation. This is further reacted with distannyl and dibromo monomers of PTB7-Th by Stille step-growth polycondensation to provide the block copolymers of P3HT-*b*-PTB7-Th. In these reactions, block ratios are adjusted to 1 to 2 and 1 to 10 based on the numbers of the repeating units of the monomers (i.e. 3-hexylthiophene unit: two monomers of PTB7-Th = 1:2 and 1:10). The block copolymer showed hole mobility of $5.9 \times 10^{-5} \text{ cm}^2/\text{Vs}$. The highest power conversion efficiency of 3.6%, which was achieved with the photoactive layer processed at 60 °C, which is substantially lower than the annealing temperature needed for standard P3HT-based solar cells. Furthermore, the stabilised lifetime of encapsulated devices is enhanced compared to P3HT and PTB7-Th devices, with no drop in efficiency noted for 7 days after initial burn in process.

1. Introduction

Organic photovoltaics (OPVs) are categorised as a third generation solar cell technology and remain of commercial interest due to their unique attributes such as low-temperature solution processability, flexibility, light weight and low energy payback time [1–9]. The development of new synthetic routes and types of conjugated polymers has been the key reason for the rise of OPV efficiency to 13% in the past few years [1–9]. To achieve high efficiencies, the main focus of research has been on developing low band gap conjugated polymers [10–13]. Although several new materials have been developed during past decade, poly (3-hexylthiophene) (P3HT) has remained the most studied conjugated polymer for photovoltaic applications and there are numerous papers studying the effects of chemical, photo and thermal processes on device performance [14,15].

One of the reasons for continuing research on P3HT based solar cells is the relatively stable operation and low cost synthetic procedure when

compared to many more complex co-polymer material systems. Furthermore, it is available in > 1 kg quantities and has been demonstrated several times in the roll-to-roll manufacturing. However, P3HT based solar cells do suffer from two disadvantages; firstly, the power conversion efficiency (PCE) is lower than state of the art polymers and secondly, P3HT-based OPVs are only realised by processing the photoactive layer at high temperatures (typically more than 120 °C) [5]. By reducing the annealing temperature, the cost could be further reduced in addition to a reduction in the embodied energy that is needed for processing that the active layer possesses suitable crystallinity, homogeneous internal phase composition, and an optimal phase separation [5]. One of the important parameter for PV modules is the energy payback time (EPBT). EPBT is the time required for the module to generate the amount of energy invested in order to fabricate it. The values of EPBT for crystalline silicon solar cell is about 2.4–4.1 years [16–18] while for the OPVs, the current value stands at 0.2–4 years [19]. It has also been predicted that EPBT can be reduced to even 1 day

* Corresponding author.

** Copresponding author.

E-mail addresses: p.tyagi@bangor.ac.uk (P. Tyagi), j.kettle@bangor.ac.uk (J. Kettle), mhorie@mx.nthu.edu.tw (M. Horie).

for OPVs by reducing the process energy. The proportion of process energy devoted to annealing of the active area in P3HT:PC₇₁BM solar cell is ~26% [19]. By reducing the annealing temperature, the EPBT of modules based on OPVs can be significantly reduced.

Recently block copolymers have been developed as the promising photovoltaic materials enabling better nanoscale control of blend interfaces within thin films without additional annealing or processing with additives [20–23]. All-conjugated block copolymers contain two or more chemically different monomer units and are synthesized using one or more condensation polymerisation steps [24]. It is possible to copolymerise two donor units to enhance their properties or one donor with an acceptor unit to lower the bandgap [25,26]. Block copolymers are used in OFETs and OLEDs, but most commonly reported as a donor or acceptor material in OPV active layers to improve the morphology and also the electronic properties of the active layer [27]. Although the block copolymer represents a huge potential for OPVs, the reported PCEs are very low around 1–3% [28] because the research has been focused on limited material systems due to difficulties in the synthesis and purification methods. Synthesizing block copolymers of two different donors can pave a route to enhance the donor properties.

In this paper, the synthesis of block copolymers consisting of P3HT and Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl-*alt*-(4-(2-ethylhexyl)-3-fluorothieno[3,4-*b*]thiophene-2-carboxylate-2,6-diyl)] (PTB7-Th) units is reported. The results show that by including even a low relative concentration of PTB7-Th block into the P3HT polymer chain, it is possible to create a P3HT-based polymer that can be annealed at low temperature (60 °C) by the inclusion of the processing additive 1,8-diiodooctane (DIO). This opens the possibility of lowering the embodied energy needed in OPV manufacture. Here we present the synthesis and photovoltaic studies of all-conjugated block copolymers P3HT-*b*-PTB7-Th.

2. Methods

2.1. Materials and general methods

All the chemicals used for synthesis were purchased from Sigma-Aldrich and used without further purification. P3HT and PTB7-Th were synthesized according to the reported method [29]. ¹H NMR spectra were recorded at room temperature by using a Varian-Unity INVA-500 spectrometer. Matrix-assisted laser desorption ionisation-time-of-flight (MALDI-TOF) mass spectra were obtained by using a Bruker Autoflex III TOF/TOF equipped with a nitrogen laser (337 nm) in positive-ion mode. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a JASCO 870 UV detector, a 880 pump, and American Polymer Standards Corporation ultrastryragel columns (Serial 2-15-89 A, B, and C) eluted with tetrahydrofuran (THF) as the solvent and polystyrene was used as the standard. UV–vis absorption spectra were measured at room temperature by using a JASCO V-630 UV–Vis spectrophotometer. Thermogravimetric analysis (TGA) was performed with a SDTQ600 thermogravimetric analyzer. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer Diamond DSC. AFM images were obtained using a Park XE-70 AFM.

2.2. Synthesis of P3HT-*b*-PTB7-Th

Monomers (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) (BDT-T) (41.9 mg, 0.046 mmol) and 2-ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-*b*]thiophene-2-carboxylate (TT-F) (19.6 mg, 0.042 mmol) and P3HT (72.0 mg) were dissolved in a mixture of 2 mL of toluene and 0.2 mL of DMF. Pd(PPh₃)₄ (1.7 mg, 1.5 μmol) was first purged with nitrogen for 15 min and then added as the catalyst. The mixture was then purged with nitrogen for 5 min. The reaction mixture was stirred and heated to reflux for 4 h. It was then cooled to room temperature and poured into methanol. The precipitate was dried under vacuum. P3HT-*b*-PTB7-Th was

obtained as dark blue solid (yield 87%). This was then purified using a preparative GPC JAI LC-9204 with a column JAIGEL-3H-40 eluted with chloroform.

2.3. Device fabrication

Hole-only and the photovoltaic devices were fabricated on pre-patterned indium tin oxide (ITO) coated glass substrates ($R_s = 15\Omega/\text{square}$, transparency = 84% purchased from Xinyan Ltd.). All the device processing has been undertaken in a cleanroom environment. For both sets of devices, the substrates were cleaned sequentially in deionised water, acetone and isopropanol each for 20 min in an ultrasonic cleaner and subsequently treated with an oxygen plasma for 5 min. Hole-only devices were fabricated with a structure ITO/PEDOT:PSS/Polymer/Au (40 nm). Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was spin coated at 5000 rpm for 60 s in ambient conditions and annealed at 140 °C for 20 min. Substrates were then transferred into the glove box and the polymer layer was deposited in inert environment. The polymer layers were annealed at two different temperatures 100 °C and 140 °C to study the effect of annealing on hole mobility. Afterwards the top gold contacts were evaporated under high vacuum at deposition rate of 6 nm/min.

OPV devices were fabricated in an inverted structure ITO/ZnO (40 nm)/Photoactive layer/MoO₃ (13 nm)/Ag (70 nm). Zinc oxide was used as electron transport layer and was prepared by spin coating zinc acetate dehydrate (109 mg) dissolved in 2-methoxyethanol (1 mL) and ethanolamine (0.03 mL) at 3500 rpm for 30 s on ITO substrate. The substrates were then annealed at 150 °C for 1 h for the zinc acetate to calcinate into ZnO. Photoactive layer was composed of a 1:1 (weight ratio) blend of block copolymer and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as an acceptor. P3HT based solar cell were prepared with 1:1 (weight ratio) with PC₇₁BM and PTB7-Th with 1:1.5. The blend solution was prepared in a 3 wt% concentration in chlorobenzene by stirring at 60 °C for 24 h. The effect of 1,8-diiodooctane (DIO) was also studied by including a 2.5 wt% of DIO into the chlorobenzene solution. Same concentration of DIO was mixed for PTB7-Th based solar cell in the blend. P3HT based solar cell was prepared without adding DIO in the active layer. The solution was then filtered using a 0.45 μm PTFE filter and spin coated at 1500 rpm for 60s in inert atmosphere. Photoactive layers were annealed at 60 °C, 100 °C and 140 °C for 30 min. The P3HT solar cell was fabricated by annealing the blend layer at 120 °C for 30 min while the PTB7-Th blend was not annealed. Afterwards the MoO₃ and Ag layers were evaporated under high vacuum at deposition rates of 0.6 nm/min and 6 nm/min, respectively. Devices were encapsulated inside the glove box using UV curable epoxy and glass coverslips. Current-Voltage (*J*-*V*) characteristics of these PV devices were measured under white light illumination (AM1.5) using an Oriel Newport AM1.5G solar simulator at an output intensity of 100 mW/cm². Lifetime test of devices was performed following ISOS-L-2 light soaking standards at 1 sun of irradiance (calibrated by the silicon reference cell). Devices were kept under open-circuit condition in between the I-V measurements. No additional cooling was applied to the devices during the lifetime test. Morphological characterisation was performed using a Veeco dimension 3100 atomic force microscope (AFM). X-ray diffraction (XRD) measurements were performed using a Philips X-PERT 3040/60 instrument at 40 kV voltage and 30 mA current with Cu Kα radiation.

3. Results and discussion

3.1. Polymer synthesis

Scheme 1 shows the synthesis of P3HT-*b*-PTB7-Th. Initially, regioregular P3HT with a Br terminal group (P3HT-Br) was synthesized by Grignard metathesis polymerisation using 2-bromo-3-hexyl-5-iodothiophene or 2,5-dibromo-3-hexylthiophene monomer. The optimum

Download English Version:

<https://daneshyari.com/en/article/7700452>

Download Persian Version:

<https://daneshyari.com/article/7700452>

[Daneshyari.com](https://daneshyari.com)