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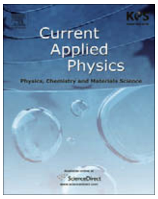

Effects of molecular weight and polydispersity of poly (3-hexylthiophene) in bulk heterojunction polymer solar cells

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ABSTRACT

This paper reports the effect of the molecular weight (MW) and polydispersity (PD) of poly (3-hexylthiophene) (P3HT) in bulk heterojunction polymer solar cells (BHJ-SCs). The P3HT with low MW and broad PD exhibited higher crystallinity compared to that with high MW and narrow PD. Due to the improved crystallinity, the BHJ-SCs based on P3HT with low MW and broad PD showed performance with a power conversion efficiency of 3.8% with short-circuit currents of -9.90 mA/cm^2.

1. Introduction

Bulk heterojunction polymer solar cells (BHJ-SCs) have been considered a possible alternative to the current, silicon-based p–n junction photovoltaic devices due to their advantages of high photoconversion efficiency (>5%) [4], simple fabrication process and low production cost [1–4]. BHJ-SCs consist of hole transporting materials on an electrode, organic semiconductor layers with a three-dimensional, bicontinuous network, and a metal layer as the counter electrode [1,2]. The active layer of conventional BHJ-SCs consists of poly (3-hexylthiophene) (P3HT) and [(6,6)-phenyl-C61 butyric acid methyl ester (PCBM)] [1,5,6]. After the absorption of a photon, excited electrons are generated by the p-type P3HT polymer, and the consequent electrons and holes can be quickly dissociated into separate phases of P3HT and PCBM [3]. The performance in BHJ-SCs is mainly influenced by the morphology of the active layer [7], recombination rate at the interfaces [8], light harvesting ability of the p-type polymer [4], hole transfer mobility of the polymer on the electrode [9], and interfacial contact between the counter electrode and active layer [10]. In addition to these properties, the molecular weight (MW) of the p-type polymer also strongly influences the performance of BHJ-SCs because MW is directly related to the nanostructure of the P3HT films which affects its charge carrier mobility [11,12].

Heeger et al. recently reported that MW affects the performance of BHJ-SCs (Ed – this acronym has already been defined above) and that the best conversion efficiency was achieved in the device using P3HT with an optimum ratio between high MW and low MW components (high/low ratio = 1:4) [12]. Considering only the charge carrier (hole) mobility of P3HT, BHJ-SCs made of high MW P3HT possess high charge carrier mobility that exhibits a high performance due to the long conjugation length of the polymer chain and the excellent interconnections within the bicontinuous network [3]. However, the solubility problems induced by the high MW P3HT cause processing difficulties and an uneven PCBM distribution [11,12]. This adversely affects the performance of the nano-interpenetrating network (IPN) structure consisting of an electron donor (P3HT) and an electron acceptor (PCBM). In order to fabricate an ideal IPN structure to maximize device performance, PCBM

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should diffuse out of the polymer matrix to form a percolated network with improved electron transport properties. Molecular diffusion of PCBM out of the polymer matrix, which can easily occur in the low MW P3HT, increases the chain ordering and crystallinity of the P3HT.

Despite the recent research on the MW of P3HT, no reports have appeared in the literature on the effect of polydispersity (PD). PD is the ratio of low and high MW of polymers and can also affect the nanomorphology of polymers. By considering the carrier mobility, solubility, and crystallinity of the P3HT, it is necessary to determine the optimum MW and PD of the P3HT in order to enhance the solar cell performance. Based on the previous research on BHJ-SCs [9,13], we demonstrated the effect of the MW and PD of P3HT on the solar cell performance. BHJ-SCs were fabricated with two kinds of P3HT, one with relatively low MW and broad PD (LB-P3HT) and the other with high MW and narrow PD (HN-P3HT), prepared through a series of column and extraction methods. The effects on the device performances of the MWs and PDs of the two different P3HTs were studied.

2. Experimental

2.1. Materials

The LB-P3HT and PCBM were purchased from Rieke Metals and Nano-C Co., respectively. Poly(3,4-ethylenedioxythiophene):poly-(styrene sulfonic acid) (PEDOT:PSS) in aqueous solution was obtained from Bayer AG (Baytron Al 4083) and indium tin-oxide (ITO, $10\ \Omega$ cm) glass from Samsung Corning Co. (Korea). The HN-P3HT was prepared by the following method. The LB-P3HT was dissolved in toluene and passed through a column filled with Celite 545 (20 cm, Aldrich)/florisil (20 cm, mesh 60, Aldrich). After the solution was dried by rotary evaporation, the solidified-P3HT was extracted by Soxhlet with methanol and acetone for 24 h.

2.2. Photovoltaic devices fabrication

BHJ-SCs were fabricated in the configuration of ITO/PEDOT:PSS/active layer (P3HT:PCBM)/Al with an active area of 14 mm^2. The patterned ITO substrates were washed with acetone, *i*-propanol and deionized water in an ultrasonication bath for 15 min each, and finally treated with O$_2$-plasma. The PEDOT:PSS was spin-coated to a thickness of 40 nm on ITO glass. The PEDOT:PSS/ITO was then dried at 120 °C for 10 min under a N$_2$ atmosphere. An active layer was prepared on the PEDOT:PSS/ITO by spin-coating from P3HT:PCBM (1:0.8 w/w%) solutions, which were prepared by different MWs of P3HT in chlorobenzene. The film thickness of the active layer was about 110 nm. The active layer was then dried at 120 °C for 10 min under a N$_2$ atmosphere as pre-annealing before Al deposition. An Al cathode of 150 nm was deposited by thermal evaporation in vacuum (10^{-6} Torr). Finally, thermal annealing was carried out by directly placing the devices on a hotplate in a glove-box filled with N$_2$ at 150 °C for 30 min as post annealing.

2.3. Measurements

The MWs of P3HT were measured by gel permeation chromatography (GPC, Shodex column). The polymer films were characterized by UV–vis absorption spectra (Hewlett Packard 8452A Diode Array spectrophotometer) and X-ray diffraction (XRD, RIGAKU). The current–voltage (*I*–*V*) measurements of the BHJ-SCs were performed by 100 mW/cm^2 white light with air mass (AM) 0 and 1.5 filters as a solar simulator in the presence of a water filter (450 W xenon lamp, Oriel Instruments), and the photocurrent was measured with a Keithley 2400 source meter.

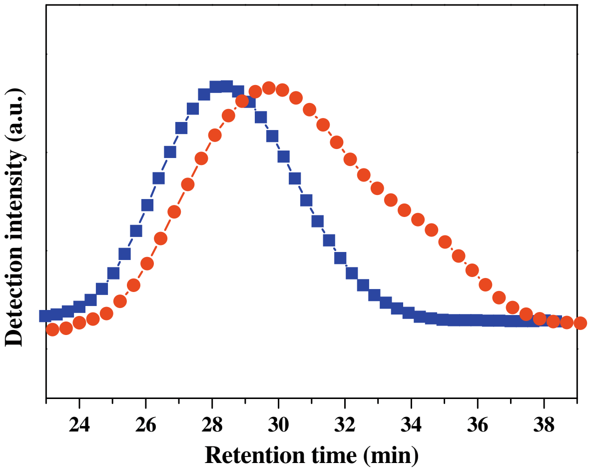

Fig. 1. GPC data of (a) LB-P3HT (-●-) and (b) HN-P3HT (-■-).

3. Results and discussion

3.1. Preparation of pristine and purified P3HTs

By GPC measurement, we monitored MW and PD of LB-P3HT and HN-P3HT. GPC was accomplished by passing the sample through porous media and retention time was measured. Fig. 1 shows the GPC data of LB-P3HT and HN-P3HT with different retention times. Shorter retention time represents that the molecule has a larger MW because it can pass quickly through GPC media without accessing into small pores. MW and PD of LB-P3HT and HN-P3HT were calculated with calibration by measuring the retention times of standard samples. LB-P3HT presented a low MW of Mn = 26,000 and Mw = 76,000 with a broad PD = 2.85. On the other hand, the HN-P3HT had a MW of Mn = 78,000 and Mw = 136,000 with PD = 1.72. This indicates that the low MW portion of the LB-

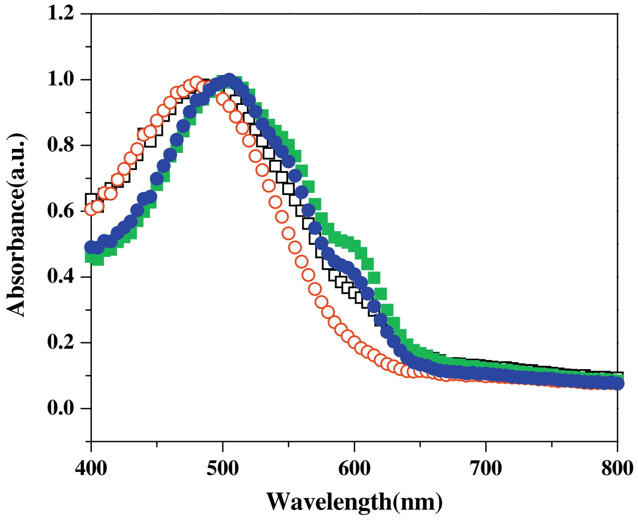

Fig. 2. Absorption spectra of active layer (P3HT:PCBM = 1:0.8 w/w) LB-P3HT (-□-) and HN-P3HT (-○-) prepared onto the surface of PEDOT:PSS on ITO before annealing and active layer using LB-P3HT (-■-) and HN-P3HT (-●-) after annealing at 150 °C for 30 min.