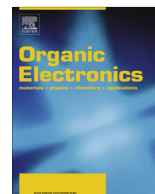




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# Synergism of molecular weight, crystallization and morphology of poly(3-butylthiophene) for photovoltaic applications

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## ABSTRACT

A series of poly(3-butylthiophene) (P3BTs) with molecular weights (MWs) ranged from 7 kDa to 50 kDa is synthesized and characterized. The DSC studies show that the thermal property and crystallinity of P3BT increase with MWs within the range from 7 kDa to 25 kDa, then decrease with further higher MW. The characteristic morphologies of discontinuous crystalline nanofibrils, interconnected nanofibrillar networks, and relative large clusters associate to low, medium and high MW P3BTs, respectively, demonstrate the strong correlation between MW, crystallinity and morphology of P3BT. It is found that the P3BT could be re-considered as the promising candidate for applications in organic optoelectronics if synergism of the crystallinity and morphology could be precisely controlled via tuning molecular weight. The polymer solar cells (PSCs) device based on P3BT with medium MW achieves an attractive power conversion efficiency of 3.5%, which is, to the best of our knowledge, the record for P3BT/PC<sub>61</sub>BM PSCs and comparable to the well-studied P3HT devices.

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## 1. Introduction

With a wide range of promising applications in organic electronics,  $\pi$ -conjugated polymers have evolved as one of the keystone materials for the next generation of economical and efficient electronic devices due to their light weight, easy fabrication, low cost, and scalable dimension [1–3]. As an important class of  $\pi$ -conjugated polymers, regioregular poly(3-alkylthiophene)s (rrP3ATs), exemplified by poly(3-hexylthiophene) (P3HT), have been extensively studied as p-type semiconductors in organic light

emitting diodes (OLEDs) [4], organic field-effect transistors (OFETs) [5,6], and polymer solar cells (PSCs) [7–11], due to their advantages in, e.g. high charge carrier mobilities [12,13], solution processabilities [14], self-assembly capacities [15,16], and environmental stabilities [17]. In particular, the tremendous success of P3HT in overcoming the barriers of charge carrier mobility of 0.1 cm<sup>2</sup>/V s [18] for OFETs and power conversion efficiency (PCE) [19] of 5% for PSCs, makes P3ATs the benchmark materials for various device optimization methodologies such as thermal or solvent annealing [20,21], controlled solvent vapor treatment [22], additive [23] and “whisker method” [24,25].

Besides omnifarious processing parameters, numerous works have corroborated the critical dependence of the properties and optoelectronic performance of P3HT on its molecular weight (MW) [26–40], polydispersity (PDI) [31], regioregularity [41–43] and ending groups [44,45].

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73 These macromolecular characteristics directly induce  
74 changes in crystallinity, microstructure and charge trans-  
75 portation properties of P3HT (blend) thin films. In the case  
76 of PSCs, a consensus has been reached that P3HT with high  
77 regioregularity (>95%) does benefit device performance  
78 [41], whereas the correlation of MW and PCE remains  
79 somewhat subtle despite extensive studies in the past decade  
80 [5,9,10]. It is reported that high MW helps improving  
81 the PCE of P3HT/PCBM ([6,6]-phenyl C<sub>61</sub> butyric acid  
82 methyl ester) device due to high charge carrier mobility  
83 of P3HT [30,38]. Another study subsequently found that  
84 intermediate MW might lead to better device performance  
85 due to poor solubility of high MW P3HT in solution and its  
86 bad miscibility with PCBM [34]. Further investigations re-  
87 vealed that the ideal P3HT should be with an appropriate  
88 sufficient PDI, e.g. ca. 2.0 [31]. This constraint could be  
89 overcome via an alternative strategy of mixing the high  
90 and low MW P3HTs. The poor reproducibility and the con-  
91 flicting MW criteria for the optimal PSCs performance hint  
92 that the influence of MW on the most-studied P3HT is still  
93 not fully understood. Further investigations on P3HT as  
94 well as other P3ATs are necessary to establish a more com-  
95 plete and systematic model in order to provide conclusive  
96 guideline, so as to design novel polymeric materials (e.g.  
97 low band gap conjugated polymers) for organic electronics.

98 Poly(3-butylthiophene) (P3BT), with the shortest side  
99 chains on thiophene backbone, has been considered as  
100 the most ideal model to study crystallization of P3ATs  
101 due to a large palette of polymorphism [46–48]. However,  
102 the low solubility and thus poor processability result in an  
103 overall unfavorable device performance [31,49,50], which  
104 impedes its further studies. Until recently, Xin et al.  
105 [24,25,51] and Gadisa et al. [52] demonstrated that P3BT  
106 based PSCs could achieve comparable PCE to P3HT by  
107 “whisker method” and solvent annealing, respectively.  
108 Nevertheless, it is worthwhile to note that there is no rel-  
109 evant research reported on the effect of MW on P3BT prop-  
110 erties to date. Furthermore, all the previous studies were  
111 only focused on the commercially available P3BTs without  
112 any delicate MW control.

113 To address the questions discussed above, a series of well-  
114 defined P3BTs with different MWs was synthesized in this  
115 work. It was found that the properties of bulk P3BTs, espe-  
116 cially crystallization and nanostructure, greatly depend on  
117 the MW. By adjusting MW, the photovoltaic devices based  
118 on the blend of P3BT and PCBM could reach a PCE of 3.5%,  
119 which is the highest one to the best of our knowledge, making  
120 a comparable number to the P3HT device. Moreover, the  
121 mechanism of MW effect on P3BT device performance was  
122 explored and elucidated. These findings not only deepen  
123 our understanding on the well-known P3ATs, but also reveal  
124 that P3ATs other than well-known P3HT, could be potential  
125 candidates for high-performance PSCs.

## 126 2. Experimental section

### 127 2.1. Materials

128 Tetrahydrofuran (THF) was purchased from Sinopharm  
129 Chemical Reagent and distilled from sodium/benzophe-

none before use. Ortho-dichlorobenzene (ODCB), 1,3-bis-  
(diphenylphosphino) propane nickel (II) dichloride  
(Ni(dppp)Cl<sub>2</sub>) and t-butyl magnesium chloride (2 M in  
THF) were obtained from Sigma–Aldrich. PCBM (99.5%  
pure) was obtained from American Dye Source Inc.  
Poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate)  
(PEDOT:PSS) Al4083 was provided by H.C. Starck. GmbH.  
Other reagents were used as supplied without further puri-  
fication. The synthesis of the monomer, 2,5-dibromo-3-  
butylthiophene, was carried out following the route similar  
to that described elsewhere [58].

### 2.2. Synthesis of P3BT

A dry 250 ml three-neck flask was purged with argon  
followed by loading 2,5-dibromo-3-butylthiophene  
(4.47 g, 15 mmol) and anhydrous THF (30 ml). 7.5 ml  
(15 mmol) of t-butyl magnesium chloride in THF solution  
were then added through a syringe, and the reaction mix-  
ture was gently stirred for 24 h. Afterward, the solution  
was diluted with 150 mL of anhydrous THF and the reac-  
tion was initiated with Ni(dppp)Cl<sub>2</sub> suspended in THF.  
The polymerization was allowed to proceed for another  
10 h at ambient temperature and then terminated by add-  
ing 5 ml of 5 N HCl. The reaction mixture was precipitated  
in methanol, and the obtained filtered polymer (raw P3BT)  
was purified by sequential Soxhlet extractions with meth-  
anol, hexane, and chloroform. Finally, the polymer was  
dried overnight in vacuum. In order to fine-tune the MW  
of P3BT, molar ratio between monomer and initiator was  
adjusted to 30, 60, 120, 150, 180, 230 and 400, which were  
correspondingly denoted as P3BT1 to P3BT7 in the context.

### 2.3. Instrument and measurement

<sup>1</sup>H NMR spectra were obtained from Bruker AV400 at  
400 MHz operated at 120 °C using ODCB-d<sub>4</sub> as the solvent.  
Matrix-assisted laser desorption/ionization-time of flight  
(MALDI-TOF) mass spectra were recorded on a Bruker/  
AutoflexIII Smartbeam MALDI Mass Spectrometer using  
dithranol as the matrix. Gel permeation chromatograph  
(GPC) analysis was conducted using Agilent PL-GPC 220  
against polystyrene standards in eluent of 1,2,4-trichloro-  
benzene at 150 °C. Differential scanning calorimetry  
(DSC) curves were obtained on TA Q100 DSC, all the sam-  
ples were firstly heated to 300 °C for 10 min to eliminate  
the thermal history, and then cooled down to room tem-  
perature. The rate of the heating and cooling scan was  
10 °C/min. The UV–Vis absorption spectrum was recorded  
on a Lambda 750 spectrophotometer (Perkin–Elmer,  
Wellesley, MA) with 1.0 slit width. Powder XRD experi-  
ments were carried out on Bruker D8 Advance using Cu  
Kα1 radiation with X-ray generation power of 40 kV tube  
voltage and 200 mA tube current. The scan was performed  
at 2θ/θ scanning mode, and the scanning speed was 1° (2θ)  
per minute with 0.02° (2θ) step size. X-ray diffraction  
(XRD) profiles of thin films were obtained by using a Bru-  
ker D8 Discover Reflector with X-ray generation power of  
40 kV tube voltage and 40 mA tube current. The diffraction  
was acquired at a θ–2θ symmetry within the range of  
2θ = 3–30°. Transmission electron microscopy (TEM) was

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