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Rod–coil and all-conjugated block copolymers for photovoltaic applications

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ABSTRACT

Control, understanding and manipulation of the morphology and nanostructure of the active layer of bulk heterojunction solar cells are crucial for the development of polymeric solar cells. Rod–coil and all-conjugated block copolymers can self-assemble into well-ordered morphologies and provide an exciting approach to rationally design and control the nanoscale organization of these materials in organic photovoltaic devices. This article reviews the highlights of the synthesis, morphology, and properties of block copolymers for application in organic photovoltaics. Combination of the precise living polycondensation and controlled polymerization through the grafting-from or grafting-onto approaches produce various architectures of rod–coil and all conjugated block copolymers. The relationships between copolymer morphologies, physical properties and device performance are analyzed.

Contents

Abbreviations: 3EHT, 3-(2-ethylhexyl)thiophene; AFM, atomic force microscopy; ATRP, atom transfer radical polymerization; BCP, block copolymer; BHJSC, bulk heterojunction solar cell; BTT, benzo-[1,2-b:3,4-b′:5,6-d″]trithiophene; BT, 2,1,3-benzothiadiazole; CPE, conjugated polyelectrolytes; DBC, diblock copolymer; DCB, 1,2-dichlorobenzene; DEH-PPV, poly(2,5-di(2-ethylhexyloxy)-1,4-phenylenevinylene); DPP, diketopyrrolopyrrole; FF, fill factor; FTIR, Fourier transform infrared spectroscopy; GIXRD, grazing incidence X-ray diffraction; GRIM, grignard metathesis; HOMO, highest occupied molecular orbital; ITO, indium tin oxide; J_{sc}, short circuit current density; LUMO, lowest unoccupied molecular orbital; MALDI-TOF, matrix-assisted laser desorption/ionization-time of flight; MDMO-PPV, poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene; MEH-PPV, poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene]; NMRP, nitroxide mediated radical polymerization; OFET, organic field effect transistor; OPV, organic photovoltaic; OSC, organic solar cell; P(2,7F-DTBT), poly[9′,9′-dioctyl-2,7-fluorene-*alt*-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)]; P3AT, poly(3-alkylthiophene); P3BT, poly-(3-butylthiophene); P3EHT, poly[3-(2-ethylhexyl)thiophene]; P3HT, poly(3-hexylthiophene); P3OT, poly(3-octylthiophene); P3TODT, poly[3-(2,5,8,11-tetraoxadodecane)thiophene; P4VP, poly(4-vinylpyridine); PCBA, [6,6]-phenyl-C_{61}-butyric acid; $PC_{61}BM$, phenyl-C_{61}-butyric acid methyl ester; $PC_{71}BM$, phenyl-C_{71}-butyric acid methyl ester; PCE, power conversion efficiency; PDI, polydispersity index; PEDOT:PSS, poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate); PFO, poly(9,9-dioctylfluorene); PFBT, poly(9,9-dioctylfluorene-co-benzothiadiazole); PFTBTT, poly(9,9-dioctyl-fluorene-*alt*-4,7-di-thiophen-2-yl-benzothiadiazole); PLA, polylactic acid or polylactide; PPV, poly(*p*-phenylenevinylene); PTCDI, 3,4,9,10-perylene tetracarboxyl diimide; RAFT, reversible addition-fragmentation chain transfer; ROMP, ring opening metathesis polymerization; SAXS, small-angle X-ray scattering; SCLC, space-charge limited current; TEM, transmission electron microscopy; TEMPO, tetramethylpiperidine-*N*-oxide; TPD, thienopyrroledione; V_{oc}, open circuit voltage; XRD, X-ray diffraction.

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1. Introduction

The need for low cost, renewable energy sources and the recent increase in power efficiency of organic solar cells (OSCs) have fostered the development of new polymeric materials for bulk heterojunction solar cells (BHJSCs) [1], among the most promising solutions for the realization of low-cost, printable, and flexible renewable energy sources. The use of BHJSCs can facilitate the exploitation of the advantages of printed electronics (such as the cost-effective production over large areas using solution-processing techniques), together with the advantages of organic materials, (versatility in organic material design, lightweight, mechanical flexibility, abundant sources of raw materials) for the realization of competitive PV technologies. The reference materials for BHJSCs are regioregular poly(3-hexylthiophene) (rrP3HT) and its derivatives, blended with fullerene or its soluble derivatives, mainly phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) even though a number of new polymers has been presented in the last years [2]. A key parameter to evaluate the performance of a photovoltaic device is power conversion efficiency (PCE), defined as the ratio between the maximum power produced by the photovoltaic cell and the power of incident light. Currently, OSCs achieve PCEs over 8% [1,3] and values close to 10% are now being announced. Projections and preliminary results indicate that PCE could soon reach 15–20% [4].

1.1. A brief history of OPV

The organic photovoltaic history [5] goes back to 1959 when the first pioneer work was carried out by Kallmann and Pope, who observed a photovoltaic effect in a single crystal of anthracene, sandwiched between two identical electrodes and illuminated from one side [6]. The PCEs in this early phase were generally low, in the range of 10^{-3} to 10^{-2}%, except for merocyanine dyes that reached 0.7% [7,8]. A significant advance was made with the introduction of bilayer heterojunction concept, in which two organic layers with specific electron or hole transporting properties were sandwiched between the electrodes, by analogy with classical p–n junctions. In 1986 Tang reported a PCE of about 1% in a bilayer solar cell made of two different dyes [9]. The main drawback of this strategy is that for complete absorption of the incident light, the layer thickness of the absorbing material must be of the order of the absorption length, i.e., approximately 100 nm. This is much more than the diffusion length of the excitons, which is about a few tens of nanometers in organic semiconductors. To overcome the low exciton diffusion length in organic semiconductors, a new concept, the so-called bulk heterojunction architecture, was introduced. The basic idea behind the BHJ concept is to bring the interface to the exciton instead the exciton to the interface. In 1992, Sariciftci et al. demonstrated a photo-induced electron transfer from poly[2-methoxy-5-(2′-ethyl-hexyloxy)-*p*-phenylenevinylene] (MEH-PPV) to a fullerene blend [10], followed in 1995 by the first dispersed polymer heterojunction photovoltaic cell, prepared by spin coating on an indium-tin oxide (ITO) substrate a solution of MEH-PPV and C_{60} [11]. Blends of MEH-PPV and fullerenes exhibited a charge photogeneration efficiency of electrons per photon (η_c) of 29% and a PCE of 2.9%. The efficient charge separation is due to photoinduced electron transfer from the MEH-PPV to C_{60} and the high value of charge collection efficiency comes from the bicontinuous network of the internal donor–acceptor heterojunction (Fig. 1).

To overcome the mismatch between the solar spectrum and the absorption spectrum of MEH-PPV, mainly due to its large band gap, this polymer was replaced by regioregular P3HT, having a lower band gap (1.9 eV) (Fig. 1) and ensuring a higher hole mobility, thanks to its high crystallinity. Nowadays, the most-widespread donor–acceptor combination for BHJSCs is a blend of P3HT and $PC_{61}BM$. Even though P3HT is still the reference materials for BHJSC, its high HOMO (highest occupied molecular occupied) level (−5.1 eV) and its relatively high band gap limit the PCE attainable with combination of materials. To overcome this limits, an increasing number of new functional polymers have been proposed, leading to a spectacular increase of PCEs, from about 5% in 2005 to 10% in 2012 [3,12].

From this picture is clear that in less than 20 years, since the seminal work of Sariciftci et al. [10], polymer solar cells have undergone an impressive evolution, with energy conversion efficiencies close to 10%, and now offer a promising approach for a low-cost and flexible photovoltaic technology [3]. The possibility to produce light, flexible and even