



Amphiphilic *N*-methylimidazole-functionalized diblock copolythiophenes

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ARTICLE INFO

Article history:

Received 14 November 2013

Received in revised form 22 January 2014

Accepted 23 January 2014

Available online 31 January 2014

Keywords:

Diblock copolymers

Ionic polythiophenes

Solution properties

Dynamic light scattering

Thermal properties

Organic photovoltaics

ABSTRACT

Amphiphilic diblock copolythiophenes are synthesized by an efficient two-step synthetic strategy. The block architecture is created via the quasi-living Grignard metathesis reaction, after which ionic imidazolium moieties are introduced by substitution on the bromohexyl side chains of one of the monomer constituents. The compositional influence on the solution behavior and thermal properties of both the precursor and ionic block copolythiophenes is investigated. The novel materials are of particular appeal for integration in organic solar cell stacks, either as active layer or interlayer materials.

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1. Introduction

Poly(3-alkylthiophenes) (P3ATs) are widely studied in organic electronics due to their easy production and appealing optoelectronic and charge transport properties. In recent years, they have mostly been applied as light-harvesting electron donor materials in organic photovoltaics (OPV), the most prominent example being poly(3-hexylthiophene)

(P3HT) [1–4]. Organic solar cells show a number of beneficial features compared to traditional crystalline Si-based devices, such as low cost large area fabrication by solution-processing techniques, reduced weight, flexibility, more appealing looks, and improved diffuse light operation, which render them a topic of high current interest [5–10]. Main issues to be solved before successful market entry can be envisaged are OPV device efficiency and stability, and most current research efforts are hence directed toward these parameters. Another important aspect to be considered is the environmental impact of the OPV production process [11,12]. At present, the active layer of the state of the art bulk heterojunction (BHJ) organic solar cells, an intimately mixed blend of a low bandgap donor polymer (or

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small molecule) and a fullerene acceptor, is generally deposited from solutions in high-boiling chlorinated solvents such as (di)chlorobenzene. To reduce the ecological footprint, solution processing from less harmful solvents is highly desirable. For that purpose, more polar polymers and fullerenes are pursued, allowing solubility in alcohols (and ultimately water). As an additional benefit, the increased polarity may also result in a higher dielectric constant, which has been considered as a potential pathway to a new efficiency regime for OPV [13,14].

We have recently prepared a series of imidazolium-substituted ionic polythiophenes, both in homopolymer and (statistical) copolymer configurations [15–17]. The homopolymers were applied as active materials in efficient bi-layer solar cells [15] and as highly effective electron transport (ETL) materials improving photovoltaic performance [16], outperforming the state of the art analogous ETLs such as PFN. In the latter study, a clear effect of molecular structure on ETL performance was observed, which seems to be related with the active layer coverage and molecular orientation within the interlayer. Aiming at deeper fundamental understanding of the underlying structure-performance relationships, a series of ionic random copolymers was synthesized [17]. On the other hand, analogous block copolythiophenes are also of particular interest as the block structure may impose a well-defined nanoscale morphology. More in general, (all-) conjugated block copolymers may have several specific applications in OPV. They have already been used as active layer materials and compatibilizers in BHJ blends, increasing the efficiency and/or stabilizing the blend nanomorphology, and as self-organizing hole transport layers [18–23]. Their exceptional solubility properties also enable these materials to be used as surfactants, for example for inorganic nanocrystals to be added to the active layer blend [24,25].

When prepared through the Ni(dppp)Cl-initiated chain growth process [26–29], it is possible to control the polymerization process toward regioregular P3ATs. As such, the method is also suitable for the synthesis of all-conjugated block copolythiophenes by consecutive monomer addition [30–39]. This has been explored by a number of research groups focusing on the synthesis of different types of diblock copolythiophenes. For example, the groups of Hayward and Park synthesized a series of amphiphilic diblock copolythiophenes containing a hydrophobic 3-alkylthiophene block and a hydrophilic poly(ethylene glycol-thiophene) block [34,36]. In chloroform/methanol or THF/methanol solvent mixtures, they observed the formation of superstructures with a hydrophobic core and the hydrophilic part exposed toward the polar environment. Ionic polythiophene derivatives were initially made by oxidative polymerization of charged thiophene monomers [40–44], resulting in regiorandom materials. Later on, they were also produced by the introduction of charged moieties on the side chains of regioregular P3ATs by post-polymerization procedures (or by end-capping) [45–51]. Until very recently, mostly homopolymers and statistical copolymers were synthesized, and only a few reports focus on conjugated ionic block copolymers [49,50].

In this work, we report on the synthesis of amphiphilic *N*-methylimidazole-functionalized diblock copolythiophenes

toward applications in organic photovoltaics. The influence of the structural composition on the solution behavior and thermal properties of both the precursor and ionic block copolythiophenes is investigated.

2. Experimental

2.1. General experimental methods

Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Diethyl ether and THF were dried using a MBraun MB-SPS 800 solvent purification system, operating under N₂ according to the principles described by Pangborn et al. [52]. Microwave synthesis was performed on a CEM Discover SP synthesis platform. NMR chemical shifts (δ , in ppm) were determined relative to the residual ¹H absorption of CHCl₃ (7.26 ppm) or DMSO-*d*₆ (2.50 ppm), or the ¹³C resonance shift of CDCl₃ (77.16 ppm) or DMSO-*d*₆ (39.52 ppm). UV–Vis measurements of the polymers in solution were performed with a scan rate of 600 nm/min in a continuous run from 200 to 800 nm. Molecular weights and molecular weight distributions were determined relative to polystyrene standards (Polymer Labs) by size exclusion chromatography (SEC). Analysis of the molecular weights and molecular weight distributions of the polymer samples was performed on a Tosoh EcoSEC System, comprising of an autosampler, a PSS guard column SDV (50 × 7.5 mm), followed by three PSS SDV analytical linear XL columns (5 μ m, 300 × 7.5 mm), and a UV detector using THF as the eluent at 40 °C with a flow rate of 1.0 mL/min. The SEC system was calibrated using linear narrow polystyrene standards ranging from 474 to 7.5 × 10⁶ g/mol ($K = 14.1 \times 10^{-5}$ dL/g and $\alpha = 0.70$). Polymer concentrations were in the range of 1 mg/mL. The energy levels of the different polymer materials were analyzed using cyclic voltammetry and (solid state) spectroscopic absorption data. Samples were prepared by dip-coating the platinum work electrode or drop-casting the polymer solutions, respectively. Chloroform was used as a solvent for all **P3BHT-*b*-P3HT** precursor copolymers and for **P3(MIM)HT-*b*-P3HT 30-70**, while **P3(MIM)HT-*b*-P3HT 50/50** and **70/30** were dissolved in DMSO for both dip-coating and drop-casting. Electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT 30 potentiostat/galvanostat using a three-electrode microcell with a Pt working electrode, a Pt counter electrode and a Ag/AgNO₃ reference electrode (silver wire/0.01 M AgNO₃/0.1 M NBu₄PF₆/MeCN). Freshly distilled anhydrous MeCN or CH₂Cl₂ with 0.1 M NBu₄PF₆ was used as the electrolyte. Cyclic voltammograms were recorded at a scan rate of 100 mV/s. All solutions were degassed with argon prior to each measurement and a curtain of argon was used to prevent air from entering the system during the experiments. The HOMO energy levels were calculated from the onset oxidation potentials, with the energy level of ferrocene/ferrocenium (Fc/Fc⁺) ($E_{\text{ox,onset}}$ at 0.01 and 0.13 eV in MeCN and CH₂Cl₂, respectively) set at a value of 4.98 eV below the vacuum level. The LUMO energy levels were calculated as the difference between

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