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Well-defined rod coil diblock copolymers based on poly(3-hexylthiophene) and poly(methyl methacrylate) via metal-free atom transfer radical polymerization

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ABSTRACT

We have successfully demonstrated a facile synthetic route for well-defined three poly(3-hexylthiophene)-*block*-poly(methyl methacrylate) rod-coil diblock copolymers (P3HT-*b*-PMMA), $P3HT_{50}$-*b*-$PMMA_{16}$, $P3HT_{50}$-*b*-$PMMA_{21}$, and $P3HT_{50}$-*b*-$PMMA_{63}$ by metal-free atom transfer radical polymerization using pyrene as an organic photocatalyst. Polymerization of methyl methacrylate is efficiently activated with light leading to excellent control over the molecular weight, polydispersity, and compositions of the resulting diblock copolymers. The structure and properties of the resulting P3HT-*b*-PMMA diblock copolymers were characterized by proton nuclear magnetic resonance, gel permeation chromatography, fourier transform infrared.

Introduction

The self-assembly of rod-coil block copolymers based on π-conjugated rod segment as regioregular poly(3-hexylthiophene) (P3HT) has attracted significant interest owing to its potential in a variety of applications such as chemical and optical sensors, light-emitting diodes (OLED's), field-effect transistors (OFET's), smart windows and organic photovoltaic (OPV) devices [1–7]. The preparation of these block copolymers typically involves either elaborating an end-functionalized polythiophene into an appropriate macroinitiator for the chain extension of a second block via a polymerization process that is mechanistically distinct from that of P3HT or coupling preformed homopolymers with complementary end-functionalities [8, 9]. Atom transfer radical polymerization (ATRP) is one of the most used controlled radical polymerization (CRP) for the synthesis of diblock copolymers with controlled molecular weight low polydispersity, well-defined architecture, and their compositions. The rod-coil diblock copolymers containing regioregular P3HT have already been reported by a number of research groups, such as the synthesis of P3HT-*b*-poly(methyl methacrylate), P3HT-*b*-polystyrene, and P3HT-*b*-poly(isobornyl methacrylate) by traditional ATRP with a transition metal catalyst (i.e., Cu(I), Ru(II), Fe(II)) [10-12]. However, the metal catalysts have been used in traditional ATRP process that lead to a contamination of metal in electronic devices [13, 14].

In recent years, metal-free ATRP using organic photoredox catalysts to generate the radicals between