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Synthesis of All-Conjugated Diblock Copolymers by Quasi-Living Polymerization and Observation of Their Microphase Separation

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To develop high-performance polymer electronic devices, such as organic field-effect transistors (OFETs)¹ or photovoltaic devices (OPVs),² it is of crucial importance to control the nanostructures of semiconducting polymers.³ One of the interesting strategies is to develop diblock copolymers (BCPs) containing semiconducting polymer segments. BCPs composed of two different units are well-known to self-organize and spontaneously form 3-D microphase-separated patterns,⁴ driven by factors such as immiscibility or the crystallinity difference between two segments. The control of molecular orientation and the pattern of such microphase separations have also been reported.⁵ A combination of these techniques with the use of BCPs based on semiconducting blocks such as poly(3-hexylthiophene) (P3HT) can lead to the bottom-up construction of high-performance polymer electronic circuits. There have been several reports on the synthesis and observation of the microphase separation of P3HT-based BCPs.⁶ However, all such BCPs are combined with insulating polymers, which limits the electronic conductivity of the materials. In addition, from the synthetic viewpoint, all synthetic routes involve the use of functionalized P3HT as a macroinitiator in the second polymerization step. As a result, the obtained BCPs tend to have large polydispersity indices (PDIs) and the removal of the macroinitiator polymer by further fractionations is often necessary.

Here we demonstrate the synthesis of a novel all-conjugated BCP via modified Grignard metathesis (GRIM) polymerization. GRIM is a synthesis method for regioregular aromatic polymers recently developed by McCullough et al.⁷ and further modified by Yokozawa et al.⁸ One interesting feature of GRIM is its quasi-living chain growth mechanism,⁹ which could lead to the possibility of developing a regioregular BCP with a narrow PDI in one pot. In this study, highly regioregular poly[(3-hexylthiophene)-*block*-(3-(2-ethylhexyl)thiophene)]s (P(3HT-*b*-3EHT)s) were synthesized via GRIM polymerization by sequentially adding two monomers. It was also found that the crystallinity of the poly(3-alkylthiophene) was drastically decreased from P3HT to P3EHT by only substituting the linear alkyl chains with a branched one, resulting in the microphase separation of the polymer blocks. This is the first report on the nanostructure formation of all-conjugated BCPs synthesized via a chain growth polymerization.

The synthetic route for the P(3HT-*b*-3EHT)s is shown in Scheme 1. We used the modified GRIM method reported by Yokozawa et al. to synthesize the monomers. The key steps in the monomer synthesis are bromination and iodination at the 2- and 5-positions of 3-alkylthiophenes, respectively. This enables the selective synthesis of a product with magnesium halides at the 5-position (step *i*). The polymerization of the 3-hexylthiophene derivative proceeded via quasi-living polymerization with the addition of Ni catalyst, together with monomer conversion of 80–87% after 2 h (step *ii*). Living P3HT

Scheme 1. Synthetic Route for Poly[(3-hexylthiophene)-*block*-(3-(2-Ethylhexyl)thiophene)] (P3HT-*b*-P3EHT): (i) Isopropyl Magnesium Chloride, THF, 0 °C, 30 min; (ii) Ni(dppp)Cl₂, 35 °C, 2 h; (iii) 35 °C, 7 h

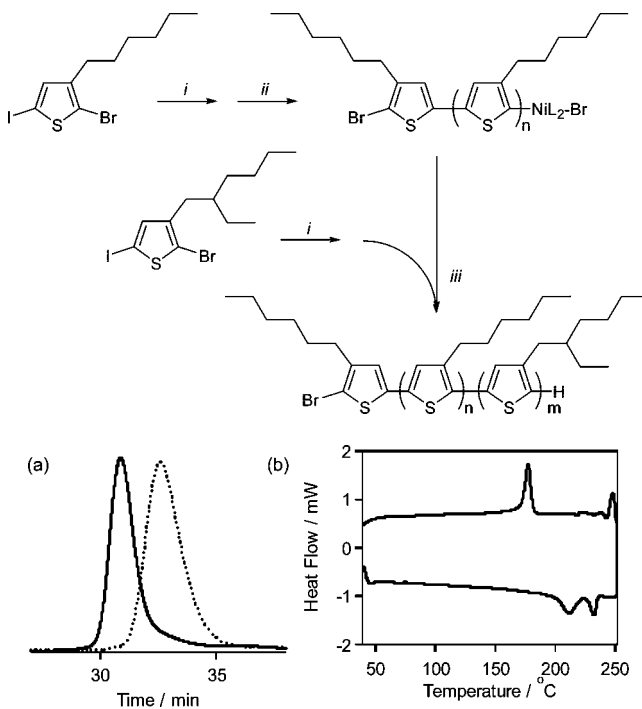


Figure 1. (a) GPC profiles of living P3HT (dashed line) and P(3HT-*b*-3EHT) (solid line), (b) DSC of P(3HT-*b*-3EHT) with a block ratio of 56:44 (see the text).

homopolymer chains subsequently reacted with the added GRIM product of 3-(2-ethylhexyl)thiophene to produce P(3HT-*b*-3EHT). The feed molar ratios of the two monomers were 50:50 and 75:25. Homopolymers and random copolymers of P3HT and P3EHT were also synthesized to serve as reference samples. The molecular weight of all the polymers was controlled by fixing the ratio of the amount of Ni catalyst to the total monomer amount at 1:100.

The ¹H NMR spectra of the P(3HT-*b*-3EHT)s are shown in Supporting Information (SI) with the assignments of the peaks. From the integration of the peaks for each alkyl chain, the molar ratios of the P3HT and P3EHT segments were 56:44 and 83:17, which were close to the feed molar ratios of 50:50 and 75:25, respectively. In the gel permeation chromatography (GPC) profiles (Figure 1a and SI), the broken and solid lines show the GPC traces of the P3HT living polymer and P(3HT-*b*-3EHT), respectively. Note that the reaction mixtures were quenched with 6 M aqueous HCl at each stage of polymerization and subjected to the measurements without fraction-

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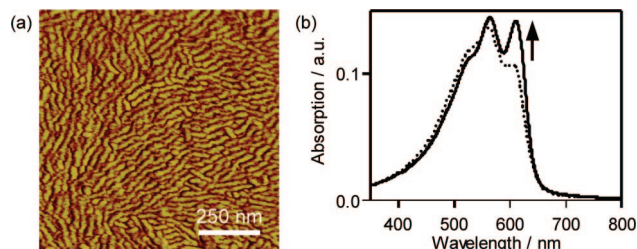


Figure 2. (a) AFM phase image (scale: $1\ \mu\text{m} \times 1\ \mu\text{m}$) and (b) UV-vis spectrum (black line) of the thin films of P(3HT-*b*-3EHT) with a block ratio of 83:17 after annealing at 240 °C. The UV-vis spectrum of the P3HT homopolymer film annealed at 250 °C (dotted line) is also presented for comparison.

ation. The peaks shift to higher molecular weights with the maintenance of the one-peak shapes, indicating the production of the P(3HT-*b*-3EHT)s with little P3HT homopolymer contamination in the reaction solutions. The copolymers with block ratios of 56:44 and 83:17 have number average molecular weights (M_n) of 21 600 and 20 400 with narrow PDIs of 1.10 and 1.17, respectively. These results indicate the successful synthesis of the regioregular P(3HT-*b*-3EHT)s by quasi-living GRIM polymerization.

The thermal properties of the polymers were investigated by differential scanning calorimetry (DSC). The P3HT homopolymer showed melting and recrystallization peaks at 239 and 208 °C, respectively, indicating its crystalline nature as previously reported (cf. SI). In contrast, the P3EHT homopolymer showed no peak under the same conditions, suggesting its low crystallinity (cf. SI). Considering the fact that the difference between P3HT and P3EHT is only the branch at the alkyl chain, this large difference in crystallinity is quite striking. The thermal property of P(3HT-*b*-3EHT) with a block ratio of 56:44 is shown in Figure 1b. Interestingly, two endothermic peaks were observed at 211 and 232 °C during the heating process. An exothermic peak at 177 °C was also observed, indicating the recrystallization of the block copolymer but at a temperature significantly lower than that in the case of the P3HT homopolymer. Similar results (two endothermic peaks at 228 and 239 °C and an exothermic peak at 197 °C) were also observed for the P(3HT-*b*-3EHT) copolymer with a block ratio of 83:17 (cf. SI). In contrast, P(3HT-*co*-3EHT) random copolymers with similar monomer ratios of 75:25 and 56:44 simply showed lower melting of 187 and 144 °C and recrystallization temperatures of 158 and 107 °C, respectively, which showed totally different thermal behaviors from those of diblock copolymers' (cf. SI). These results indicate the segregation of the crystalline P3HT block in the P(3HT-*b*-3EHT)s.

To investigate their morphology, thin films of the regioregular P(3HT-*b*-3EHT)s were prepared by spin coating from a chlorobenzene solution on glass substrates at room temperature, then annealed at 240 °C. The surface morphology of thin films of P(3HT-*b*-3EHT) with a block ratio of 83:17 was observed by atomic force microscopy (AFM). Before the thermal annealing, a flat surface without any phase pattern was observed in the AFM images. After the annealing, the height images remained very flat (cf. SI). The phase image (Figure 2a), however, showed a partly aligned worm-like structure with a width of approximately 15 nm. Considering the large difference in crystallinity between the blocks, this nanostructure can be attributed to the microphase separation of the crystalline (P3HT) and amorphous (P3EHT) blocks. To investigate the optical properties, the UV-vis spectra of P(3HT-*b*-3EHT) and the P3HT homopolymer were measured on the films after annealing (Figure 2b). The absorption shoulder at around 610 nm has been reported to be indicative of the strong intermolecular π - π interaction and therefore the high crystallinity of

the P3HT homopolymer.¹⁰ Interestingly, the intensity of the absorption shoulder was much higher for P(3HT-*b*-3EHT) than for the P3HT homopolymer. This indicates the highly ordered P3HT domain in the P(3HT-*b*-3EHT) films, despite the fact that the amount of crystalline P3HT fraction is reduced to 83% of the total polymer chain. It is suggested that the relatively unconstrained P3EHT segments attached to the P3HT homopolymer can enhance the formation of the ordered self-organization of P3HT segments, resulting in the microphase-separated structure observed by AFM. A similar nanostructure and an absorption shoulder were also observed in P(3HT-*b*-3EHT) with a block ratio of 56:44 (cf. SI). A fiber-like structure with a width of approximately 10 nm and a length of several hundreds of nanometers was observed in P(3HT-*b*-3EHT) after the annealing, which is thinner but much longer than the pattern in Figure 2a. This difference suggests that the larger amounts of P3EHT blocks in the copolymer facilitate the self-organization of P3HT blocks to form longer continuous fibrous domains. In contrast, thin films of the corresponding random copolymers showed ill-defined, partially crystallized structures upon thermal annealing (cf. SI), indicating the importance of block copolymerization for nanostructure formation.

In conclusion, all-conjugated P(3HT-*b*-3EHT)s were synthesized by quasi-living GRIM polymerization in a well-controlled manner. The introduction of an amorphous P3EHT unit into P3HT induced the formation of a microphase-separated nanostructure and enhanced the interchain interactions of P3HT blocks. A systematic study of semiconducting BCPs with different block ratios is underway. Further investigation of the relationship between electronic properties and nanostructures will provide insights into the design of polymers suitable for high-performance electronic devices.

Supporting Information Available: Experimental, ¹H NMR, GPC AFM, UV-vis, and DSC of the block and the random copolymers, and complete ref 6b. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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