

# Design, Synthesis and Micro-phase Separation of All-conjugated Diblock Copolymer Towards Organic Solar Cell

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The control of the surface morphology and nanostructure in electronic materials is recently an essential subject in organic electronic devices. [1-2] 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 [3-4] such as spherical, cylindrical, gyroid and lamella phases at nanometer scale, driven by factors such as immiscibility or the crystallinity difference between two segments. 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. However, all the reports combined P3HT with non-conjugated, insulating polymers to induce the micro-phase separation structures, which is generally disadvantageous for the electronic device performance. 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.

In this research, we designed and synthesized a novel p-type all-conjugated diblock copolymer with poly(3-hexylthiophene) (P3HT) and poly(3-ethylhexylthiophene) (P3EHT). It was found that the substitution of the linear alkyl chains with the branched ones totally changed the polymer property from crystalline (P3HT) to amorphous (P3EHT). The different properties of the two blocks are expected to induce the formation of self-organized micro-phase separation in the thermodynamically stable state.

P(3HT-b-3EHT) diblock copolymers were synthesized by a modified Grignard metathesis (GRIM), a 'quasi'-living polymerization previously reported by McCullough et al [5] and later modified by Yokozawa et al [6]. We synthesized the series of diblock copolymers with the average molecular weight of around 20000 and the various P3HT/P3EHT block ratios. <sup>1</sup>H NMR and GPC analysis at each stage of the reaction showed the well-controlled, living manner of the polymerization. In the AFM phase image, uniform micro-phase separated structures with the scale of several tens of nanometer were clearly observed in the samples from the P(3HT-b-3EHT) with 20%-80% P3HT blocks (Fig. 1a). Surprisingly, in P(3HT-b-3EHT) diblock copolymer with P3HT ratio of 80%, the absorption spectrum showed a strong shoulder around 620 nm which indicates the highly ordered P3HT packing in P(3HT-b-3EHT) block copolymer, despite the fact that P3HT fraction was smaller in the block copolymer (Fig 1b). This is considered that the relatively unconstrained P3EHT segment enhance the ordered structure of P3HT packing, thus resulted in a well-defined micro-phase separated structure in the AFM phase images. This nanostructure control by self-assembly in the diblock copolymers could be applicable to the high-performance organic solar cell.

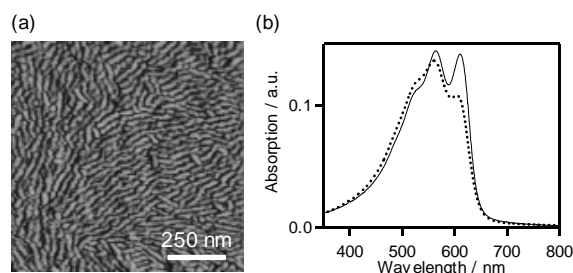


Fig. (a) AFM phase image (scale: 1  $\mu\text{m} \times 1 \mu\text{m}$ ) and (b) UV-vis spectrum (black line) of the thin films of P(3HT-b-3EHT) with a block ratio of 83:17 after annealing at 240  $^{\circ}\text{C}$ . The UV-vis spectrum of the P3HT homopolymer film annealed at 250  $^{\circ}\text{C}$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

- [1] Yang, X.-N.; Loos, J.; Veenstra, S. C.; Verhees, W. J. H.; Wienk, M. M.; Kroon, J. M.; Michels, M. A. J.; Janssen, R. A. J. *Nano. Lett.* 2005, 5, 579.
- [2] Reyes-Reyes, M.; Kim, K.; Dewald, J.; López-Sandoval, R.; Avadhanula, A.; Curran, S.; Corroll, D. L. *Org. Lett.* 2005, 7, 5749.
- [3] Hamley, I. W. *Nanotechnology* 2003, 14, R39.
- [4] Mao, G.; Ober, C. K. *Acta Polymerica* 1997, 48, 405.
- [5] McCullough, R. D. *Adv. Mater.* 1998, 10, 93.
- [6] Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* 2004, 37, 1169.

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