Polymer Chemistry

Accepted Manuscript

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Controlling micro-phase separation in semi-crystalline/amorphous conjugated block copolymers

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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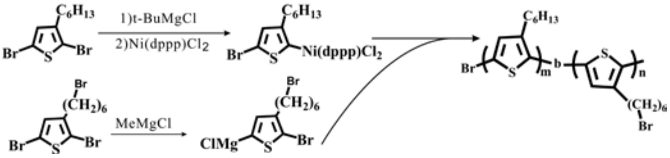
Bromine-functionalized polythiophene (P3BrHT) block copolymers with different block ratios were synthesized and their micro-phase separation features in solid state that allows for retaining molecular packing identities of the unmodified polythiophene (P3HT) were experimentally confirmed.

Controlling self-organization of conjugated polymer is of crucial importance because both optical and electronic properties are sensitive to the molecular packing.[1] It is believed that ordered self-organization of conjugated polymer significantly increase hole mobility and balance charge transport in photovoltaic devices. [2] Recently, there is increasing interest in controlling micro-phase separation in non-conjugated or conjugated/non-conjugated block copolymers because it is a spontaneous process that offers significant control over nanoscale structure.[3] Thus, the phase behavior of coil-coil and rod-coil block copolymers has been widely investigated. While the micro-phase separation strategy has been demonstrated for a variety of non-conjugated or conjugated/non-conjugated block copolymers,[4] it is still challenging for all-conjugated block copolymers because of (i) lack of methods and monomers that lead to controlled polymerization, (ii) the strong driving force for conjugated polymers to crystallize. The synthesis of block copolymers that incorporates polythiophene motifs has been explored by several studies,[5] which take advantage of the quasi-living Grignard metathesis[6] polymerization method to prepare "all-conjugated" block copolymers. Fully conjugated block polythiophenes incorporating blocks with different alkyl side chains[7] or backbones[8] have been synthesized. Jenekhe et al. reported the synthesis and self-assembly of crystalline-crystalline diblock copoly(3-alkylthiophene)s with different side chains,[7b] while Seferos et al. reported a new type of block copolymer that consists of blocks of distinct polyheterocycles.[8c] However, these polymers are still focused on inert blocks without any reactive sites, which limits further functionalization.

Modification of side chain has been proven to be a powerful method for achieving functionalized or reactive P3HT-based polymers with different packing behaviors or electronic and photonic properties.[9] Br-functionalized P3HT (P3BrHT) homopolymers were previously synthesized and their salient features allowing for post-polymerization derivation of various functionalities was confirmed.[10] Moreover, random copolymers containing 3-hexylthiophene (3HT) and 3-(6-bromohexyl) thiophene (3BrHT) were synthesized and used for increasing the thermal stability of photovoltaic devices owing to their structural features enabling photocrosslinking via the reactive bromine sites.[2b,11] However, It deserves mentioning that, randomly introducing of bromine sites dramatically disturbs the polymer packing, which is critical for both charge transport and light absorption.[11] Nevertheless, to the best of our knowledge, there is still no research focused on the self-organization and micro-phase separation of bromine functionalized P3HT block copolymers.

Here we demonstrate the synthesis of a regioregular poly(3-hexylthiophene)-block-poly(3-bromohexylthiophene) ((P3HT-b-P3BrHT)) block copolymer via modified Grignard metathesis (GRIM) polymerization, (Scheme 1) and the discovery of the micro-phase separation driven by the crystallinity difference between P3HT (crystalline) and P3BrHT (amorphous) segments. In addition, the crystallinity of the block copolymers can be controlled by micro-phase separation in block copolymers with different crystalline/amorphous block ratios. Furthermore, post-polymerization reaction was successfully carried out to functionalize the Br sites on the P3BrHT segments.



Scheme 1 Synthetic route for poly(3-hexylthiophene)-block-poly(3-bromohexyl thiophene) (P3HT-b-P3BrHT).

The NMR spectra were initially used to determine the chemical structures and quantify the block ratios since the 3HT and 3BrHT units have distinct ^1H NMR resonances. Namely, the 3BrHT units have a new resonance peak at 3.4 ppm because of the introduction of bromine atom (Fig. 1 left). Thus, the block ratios can be confirmed by integrating peaks at 2.8 and 3.4 ppm. In addition, the peaks around 0.9 ppm corresponding to the terminal methyl group of 3HT also decrease as the 3BrHT block increases. A series of block copolymers with approximate block ratios (3HT: 3BrHT) of 70:30, 50:50 and 30:70 and regioregularity of 95% were synthesized. Polystyrene equivalent molecular weight was determined by gel permeation chromatography (GPC) in THF. The copolymers with block ratios of 70:30, 50:50 and 30:70 have number average molecular weights (M_n) of 17 600 , 17 800 and 15 400 g mol^{-1} with PDIs of 1.40, 1.49 and 1.52, respectively. These results indicate the successful synthesis of block copolymers with different block ratios by quasi-living GRIM polymerization. For comparison, two homopolymers of P3HT and P3BrHT and one statistical copolymer with monomer ratio of 50:50 were also synthesized(Fig. S4).

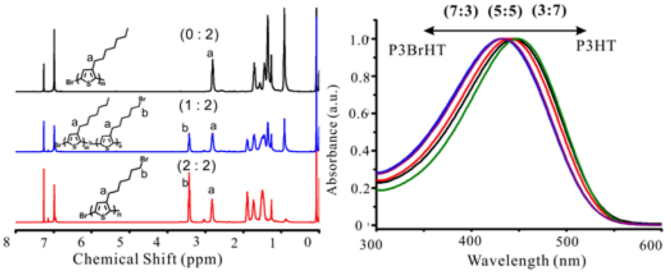


Fig. 1 ^{1}H-NMR spectra (left) and UV-Vis absorption spectra (right) of P3HT, P3BrHT homopolymers and block copolymers with different block ratios in chloroform.

The absorption properties of polymers with different block ratios in solution were first investigated. For reference, the absorption of P3HT and P3BrHT homopolymers in chloroform solution positioned at 448 and 433 nm, respectively. While the absorptions of block polymers shift to higher energy gradually as the 3BrHT content increases, indicating the presence of the P3BrHT chromophore in the block structures (Fig. 1, right). Based on the ^{1}H NMR and solution absorption measurements, block polymers with controlled 3HT to 3BrHT ratios were successfully synthesized.

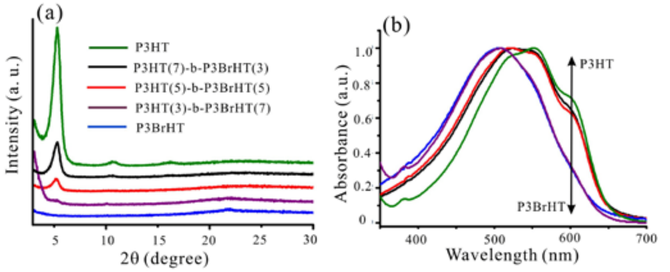


Fig. 2 The XRD (a) and absorption spectra (b) of annealed polymer films.

With these polymers in hand, we next investigated their solid state properties in films. X-ray scattering was first used to investigate the crystallization behaviors of different polymers. To make the films, two homopolymers and three block copolymers were first dissolved in chloroform with concentration of 5.0 mg mL^{-1} and then spin casted on glass substrates followed by annealing at 120 ºC under N_2 for 0.5 hour. The analysis results demonstrates that the P3HT film is crystalline with a characteristic peak at 2θ = 5.28º corresponding to a 16.7 Å spacing while the P3BrHT homopolymer is totally amorphous (Fig. 2a blue line). Taking the slight discrepancy in the structural features between P3HT and P3BrHT and the striking crystallinity difference, it is believed that the introduction of the bromine on the side chains greatly affect the organization of the homopolymer, which is consistent with the previous report.[2b,11] As the P3HT block increased to 30%, the diffraction peak at 2θ = 5.28º is still very weak. However, upon further increasing the 3HT block to 50% and 70%, a clear diffraction peak coincide with the crystallization peak of P3HT appears, indicating crystallization of P3HT block in the block copolymers. Taking the amorphous feature of P3BrHT, it is therefore reasonable to speculate that the P3HT block undergoes orderly organization processes in the block copolymers. It is worthy of noting that the observed intensity of diffraction peak of the block copolymer is obviously weaker than that of P3HT homopolymer even in the case of block copolymer with 70% of 3HT units, due to the dilution effect and the possible negative effect that the amorphous P3BrHT block exerts on the organization of the P3HT block. However, when compared with the statistical copolymer, which is almost amorphous with very weak diffraction peak (Fig. S6), the crystallization in the block copolymer is quite distinct.

Having determined the crystallization behaviors of these polymers, we next investigated the optical properties of these polymer films. Interestingly, unlike the absorption profile of P3HT possessing shoulders at 603 nm that coincide with the π-π stacking (Fig. 2b green curve),the P3BrHT homopolymer has a nearly featureless absorption profile (Fig. 2b blue curve). The shoulder peak in the polymer thin film is indicative of organization and π-π stacking in the solid state,[8c] and such lack of a well-defined shoulder definitely suggests the poor π-π stacking characteristics in the P3BrHT homopolymer as previously reported.[12] Although the shoulder peak is still missing in the block copolymer containing 30% of P3HT block(Fig. 2b purple line),it becomes very pronounced upon increasing the ratio of P3HT up to 50% and 70%, indicating the improved π-π stacking in the block copolymer with increased P3HT ratio. In sharp contrast, for the film sample of the statistical copolymer with the same block ratio, the shoulder peak is still inconspicuous(Fig. S7). Taken the X-ray scattering and absorption data together, as well as the poor π-π stacking and crystallinity feature of P3BrHT homopolymer, the π-π stacking and crystallization in block copolymers are ascribed to the organization of P3HT block, which demonstrates that the block copolymer undergoes a significant degree of micro-phase separation in the solid state between poor crystalline P3BrHT phase and good crystalline P3HT phase.

To further confirm the micro-phase separation in the block copolymers, the thermal properties of the polymers were investigated by differential scanning calorimetry (DSC). The P3HT homopolymer showed melting and recrystallization peaks at 223 and 194 °C, respectively, indicating its crystalline nature as previously reported (Fig. 3a). [7d] In contrast, the P3BrHT homopolymer showed no peak under the same conditions, suggesting its low crystallinity (Fig. 3e). These results are also consistent with X-ray and absorption data. The thermal properties of P3HT-b-P3BrHT with different block ratios of 70:30, 50:50 and 30:70 are then tested with the results shown in Fig. 3b, c and d. The melting and recrystallization peaks are still missing in P3HT(3)-b-P3BrHT(7) with 30% of P3HT (Fig. 3d),which is also consistent with the poor π-π stacking and crystallinity of this polymer observed in absorption and X-ray data. Interestingly, two endothermic peaks at 229 and 244 °C during the heating process, and an exothermic peak at 199 °C during the cooling process were observed in the 50:50 block copolymer. Similar results, i.e. two endothermic peaks at 223 and 239 °C and an exothermic peak at 194 °C, were also observed for the block copolymer with a block ratio of 70:30 (Fig. 3b), indicating the recrystallization of this block copolymer. Additionally, it was found that the melting and recrystallization temperature of the 50:50 block copolymer are a little higher as compared to those of the P3HT homopolymer, which is attributable to the bromine-mediated crosslinking that facilitates increase in the stability of the block polymer.[2b] Such stabilization effect arising from the bromine-mediated crosslinking is expected to fade away upon further decreasing the percentage of P3BrHT block to 30% in the block copolymer. Moreover, it was found that the melting and recrystallization temperatures of the block polymer containing 30% P3BrHT are nearly the same as those of the P3HT homopolymer, indicating the formation of the crystalline phase of P3HT block in the block copolymer. In contrast, P3HT-s-PBrHT random copolymers with monomer ratios of 50:50 showed neither endothermic nor exothermic peaks, indicating the lack of crystalline phase in the random polymer. These results further confirm the phase segregation of the crystalline P3HT block in the P3HT-b-P3BrHT block copolymers.

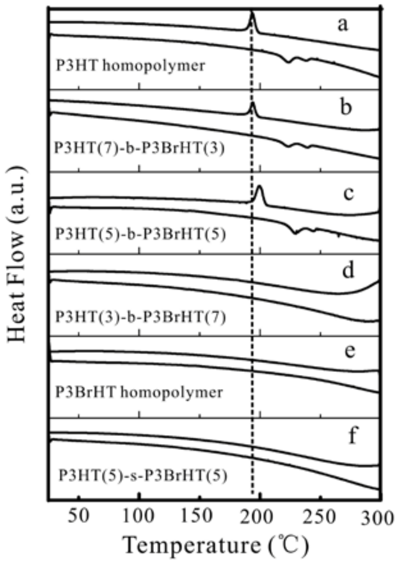


Fig. 3 DSC profiles of the P3HT (a), P3BrHT (e) homopolymers, P3HT-b-P3BrHT block copolymers with different block ratios (b-d) and P3HT-s-P3BrHT statistical polymer with 50:50 monomer ratio (f).

We expect that differences in micro-phase separation and molecular packing exert influence on the self-assembly features of the block copolymer. The self-assembly experiments were carried out in $CHCl_3$/CH_2Cl_2 mixture,[13] focusing on the nature of aggregates formed in solution by spontaneous self-assembly. The aggregates of different polymers were first investigated by atomic force microscopy (AFM) (Fig.4). Nanowire structures (NWs) were obtained in P3HT homopolymer and block copolymers with block ratio of 70:30 and 50:50. However, in the block copolymer with high P3BrHT block content (30:70) and P3BrHT homopolymer, the nanowire structure disappeared. Furthermore, no nanowire structures formed in statistical copolymer with block ratio of 50:50. Very similar results were obtained by transmission electron microscopy (TEM) (Fig. S8). The absorptions of these aggregates in solution were also tested. Results show that block copolymers with P3HT contents above 50% aggregated into order states with pronounced shoulder peaks corresponding to π-π stacking (Fig. S9). These results are perfectly consistent with the X-ray, absorption and DSC results showing that higher P3BrHT contents (more than 50%) greatly disturb the polymer chain packing and thus decrease the crystallization. Although the detailed molecular packing within the diblock copolymer NWs remains to be investigated, the fact that the ordered organization of P3HT section in the block copolymers is less affected than that in the statistical copolymer further confirms the phase separation in this bromine functionalized polythiophene block copolymer.

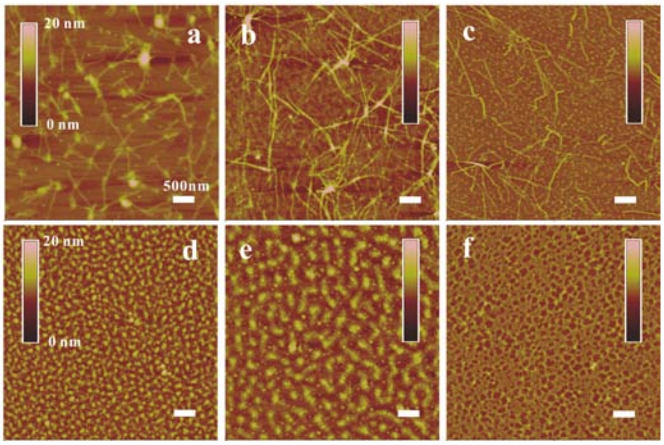


Fig. 4 Tapping-mode AFM height images of solution assembled nanostructures of P3HT (a), P3BrHT (e) P3HT-b-P3BrHT with different block ratios of 70:30 (b), 50:50 (c), 30:70 (d), and P3HT-s-P3BrHT with monomer ratio of 50:50(f).

The ultimate goal of synthesizing P3HT-b-P3BrHT block copolymer is to further functionalize the Br sites in the block copolymers. To test this hypothesis, the 50:50 block copolymer was reacted with lithiated 2,4,4-trimethyloxazoline and potassium thiolacetate to produce 2,4,4-trimethyl-2-oxazoline and thiolacetate substituted polymers, which can be readily transferred to carboxylic acid and thiol functionalized polymers,[10] respectively. The quantitative conversion of Br sites to 2,4,4-trimethyl-2-oxazoline and thiol acetate groups was confirmed by NMR specta (Fig. S10). The resonance peak at 3.4 ppm assigned as the terminal methylene group α to the bromine shifts to 3.88 and 2.88 ppm, (Fig. S10 a and b) which are consistent with 2,4,4-trimethyl-2-oxazoline and thiol acetate substitution, respectively.[10]

In conclusion, we synthesized bromine functionalized P3HT-b-P3BrHT block copolymers with different block ratios and demonstrated that micro-phase separation happened in these block copolymers because of crystallinity difference between the crystalline P3HT and amorphous P3BrHT blocks. Importantly, we demonstrate that the organization of the P3HT block can be much better preserved in the block copolymer than that in the statistical copolymer because of micro-phase separation. Upon introduction of different ratios of P3BrHT block, the self-assembly behavior of the block copolymers can be controlled systematically. We at last demonstrate that the active bromine sites on the P3BrHT block can be readily functionalized by other functional groups with quantitative yields, which represents a general method to synthesize various P3HT based block copolymers by post polymerization reactions.

This work was supported by the National Research Fund for Fundamental Key Project (2014 CB 931801, Z. Tang), the National Natural Science Foundation for Distinguished Youth Scholars of China (21025310, Z. Tang), the National Natural Science

Foundation of China (grant no. 20973047, 91027011, 21173262, 21373218), and the “Hundred-Talent Program” of CAS to Z. Tian.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental Details, ^{1}H-NMR, GPC, TEM, absorption and X-ray measurements. See DOI:10.1039/c000000x/

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Graphical Abstract

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