Unravelling the Correlation between Microphase Separation and CocrySTALLization in Thiophene-Selenophene Block Copolymers for Organic Field-Effect Transistors

Xin Shang, Yue Yin, Shuwen Chen, Mingjing Zhu, Dalong Zhai, Xiaofeng Liu, and Juan Peng*

ABSTRACT: Despite significant advances in double-crystalline coil−coil block copolymers (BCPs), investigations into double-crystalline all-conjugated rod−rod BCPs have been comparatively fewer and are limited in scope. Moreover, the ability to control the crystalline structures of all-conjugated BCPs may endow the materials and devices with enhanced optoelectronic properties over the two respective constituents. Herein, we report the synthesis of a series of poly(3-hexylthiophene)-block-poly(3-butylselenophene) (P3HT-b-P3BS) BCPs with tunable block ratios and investigate the effects of block ratio and thermal annealing process on their crystallization and microphase-separated structures. These rod−rod BCPs exhibit a sole P3HT crystallization (P3HT/P3BS = 63:37) or individual P3HT and P3BS crystallization (P3HT/P3BS = 55:45 and 42:58) in as-cast thin films, influenced by the block ratio of P3HT/P3BS. Interestingly, upon 200 °C-annealing (i.e., annealed at the temperature below the melting points of P3HT and P3BS form I blocks), P3HT-b-P3BS (P3HT/P3BS = 63:37) remains the sole P3HT crystallization, while P3HT-b-P3BS (P3HT/P3BS = 55:45 and 42:58) transforms from two individual P3HT and P3BS crystal domains into cocrystals, accompanied by the phase transition of P3BS block from form II to I. Remarkably, after a higher thermal annealing at 230 °C (i.e., close to the melting point of P3HT block yet below the melting point of P3BS form I block), the cocrystalline structures originally existing in P3HT-b-P3BS (P3HT/P3BS = 55:45 and 42:58) at the 200 °C-annealing process do not form, and they reverse back to individual P3HT and P3BS form I crystals. Finally, the relationship between various structures of P3HT-b-P3BS and the resulting charge mobilities is clarified. This study provides an insight into the interplay between microphase separation of P3HT-b-P3BS and crystallization of both P3HT and P3BS blocks tailored by the block ratio and thermal annealing temperature and correlates their different structures with the charge transport properties.

INTRODUCTION

Block copolymers (BCPs) can microphase-separate into well-defined nanoscale structures due to the thermodynamic incompatibility between different blocks.1 When one or more blocks in the BCPs can crystallize, the crystalline behavior usually induces their final structure and morphology more complicated owing to the competition between microphase separation and crystallization.2 As crystallization and microphase separation are two kinds of fundamental phase transitions in polymers, the subject of crystallization in BCPs has attracted much attention in the past decades.3−6 In the case of BCPs containing one crystalline block, the microphase structure can be either retained or destroyed after “confined crystallization” or “breakout crystallization”, respectively, influenced by the BCP separation strength, the crystallization temperature (Tc) of the crystalline block, the glass transition temperature (Tg) of the amorphous block, and the order−disorder transition temperature (ToDT) of BCPs. Compared
with the crystalline–amorphous BCPs, double-crystalline BCPs can be even more complex as the crystallization of the respective block may influence the crystalline process and morphology of each other. Much work on double-crystalline BCPs has focused on biomaterials that are coil–coil type, such as poly(l-lactide)-block-poly(ε-caprolactone) (PLLA-b-PCL), poly(ethylene oxide)-block-poly(ε-caprolactone) (PEO-b-PCL), and poly(l-lactide)-block-poly(ethylene glycol) (PLLA-b-PEG), etc. However, studies on double-crystalline rod–rod BCPs with more rigid characteristics such as DNA, liquid crystalline polymers, conjugated polymers, etc., have been comparatively few and limited in scope.10 As semirigid polymers usually possess special physical properties and greatly impact the condensed structures and properties of materials, research on the double-crystalline rod–rod BCPs is important for not only academic interest but also practical significance.

Among rod–rod BCPs, all-conjugated BCPs comprising two dissimilar conjugated polymers (CPs) have garnered considerable attention as they have the fascinating microphase-separated properties of BCPs and the optoelectronic properties of the respective conjugated component.11–13 Introducing CPs into BCP systems has been demonstrated to be effective in controlling the crystalline structures and nanoscale morphologies of CPs, which is recognized as the key to high-performance optoelectronic devices.14 Poly(3-alkylthiophene)s (P3ATs), particularly poly(3-hexylthiophene) (P3HT) as a model system, have been widely studied due to their high charge carrier mobility and excellent solution processability.15,16 Recent advances in polymerization techniques realize the synthesis of a variety of P3AT-based rod–rod BCPs,17–22 such as poly(p-phenylene)-block-(3-hexylthiophene) (PPP-b-P3HT), poly(3-dodecylselenophene)-block-poly(3-dodecylthiophene) (P3DDS-b-P3DDT),18 poly(3-hexylthiophene)-block-poly[(9,9-dioctylfluorene)-2,7-diy-alt-[4,7-bis-(thiophen-5-yl)-2,1,3-benzothiadiazole]-2’,2’-diyl] (P3HT-b-PFTBT),19 and poly(3-hexylthiophene)-block-poly(3-hexylthiophene hexylacetate) (P3HT-b-P3THA).20 Notably, compared with the most studied P3ATs, their close analogue poly(3-alkylthiophene)s (P3ASs) are much less investigated. Selenium atom substitution has some advantages over P3ATs, such as narrower bandgap and improved interchain charge transport, etc.23,24 A pioneering work on poly(3-hexylthiophene) (P3HS) has shown that P3HS has different crystalline polymorphs of forms I and II, in which their main difference is the shorter a-axis repeat distance (i.e., interlayer spacing between the conjugated backbones) of form II than that of form I.25 Recently, we have reported reversible phase transition between forms I and II in P3HS thin films treated by alternating thermal and solvent vapor annealing and the cocrysals of poly(3-butylhexylthiophene)-block-poly(3-hexylthiophene) (P3BT-b-P3HS) for high-performance organic field-effect transistors (OFETs). Furthermore, we have extended the cocrysals to triblock copoly(3-alkylthiophene) and explored the effect of block sequence on their crystalline and charge transport behavior.26 However, as an important member in the P3AS family, the relation between crystalline structures of poly(3-butyleneselenophene) (P3BS) and their charge transport properties has not yet been reported due to its synthesis difficulty and poor solubility in common organic solvents. Thus, it is challenging to do film deposition for the fabrication of thin film devices.

Herein, we synthesize a series of poly(3-hexylthiophene)-block-poly(3-butyleneselenophene) (P3HT-b-P3BS) BCPs with tunable block ratios via Grignard metathesis (GRIM) polymerization. The copolymerization of P3BS with P3HT greatly improves the solubility of P3BS, thereby facilitating its potential applications in various thin-film devices. The interplay between the microphase separation of P3HT-b-P3BS and the crystallization of both P3HT and P3BS blocks is scrutinized via modulating the block ratio and annealing temperature. As P3HT and P3BS have similar molecular structures and carry respective optoelectronic properties, the P3HT-b-P3BS rod–rod BCPs may exhibit enhanced optoelectronic properties over the two individual constituents. These as-cast P3HT-b-P3BS thin films with varied P3HT/P3BS block ratios are shown to form a sole P3HT crystallization (P3HT/P3BS = 63:37) or individual P3HT and P3BS crystal domains (P3HT/P3BS = 55:45 and 42:58). After 200 °C-annealing, P3HT-b-P3BS (P3HT/P3BS = 63:37) retains singular P3HT crystal domains with improved crystallinity. In contrast, P3HT-b-P3BS (P3HT/P3BS = 55:45 and 42:58) yield cocrystals, accompanied by the phase transition from P3BS form II to form I during the formation of cocrystals. Quite intriguingly, when thermal treatment is conducted at a higher temperature (230 °C), the crystalline structures do not appear in P3HT-b-P3BS (P3HT/P3BS = 55:45 and 42:58) and instead reverse back to individual P3HT and P3BS form I crystals. Finally, the relation between various structures of P3HT-b-P3BS and the resulting mobilities is explored. This work may strengthen the fundamental understanding on the crystallization and microphase separation of rod–rod all-conjugated BCPs, and in turn facilitate the development of both P3AT and P3AS-based materials for use in optoelectronic devices.

### EXPERIMENTAL SECTION

#### Materials

Monomers 2-bromo-5-iodo-3-hexylthiophene and 2,5-dibromo-3-butylselenophene were prepared according to the literature.29 Isopropylmagnesium chloride ([i-PrMgCl, 2.0 M in tetrahydrofuran) and (1,3-bis(diphenylphosphino)-propane)-dichlorinonickel(II) ([Ni(dppp)Cl] were purchased from Aldrich and used as received. Tetrahydrofuran (THF) was freshly dried over sodium benzenophene ketyl. Other solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (SRC) and used as received.

**Synthesis of Poly(3-hexylthiophene)-block-poly(3-butyleneselenophene) (P3HT-b-P3BS).** P3HT-b-P3BS BCPs with various P3HT/P3BS block ratios were synthesized by Grignard metathesis (GRIM) polymerization based on our previous report.10–12 As a representative, the procedure for the synthesis of P3HT-b-P3BS with a feed molar ratio of 60:60 was given as follows: 2-bromo-5-iodo-3-hexylthiophene (0.895 g, 2.4 mmol) was dissolved in THF (60 mL) in a three-neck flask and stirred under N2. After cooling the solution to 0 °C, i-PrMgCl in THF (1.2 mL, 2.4 mmol) was added via a syringe, and the mixture was stirred for 30 min. The solution was then heated up to 35 °C, followed by the addition of [Ni(dppp)Cl] catalyst (0.0217 g, 0.04 mmol). The mixed solution was stirred at 35 °C for 2 h to ensure the completely consumed 2-bromo-5-iodo-3-hexylthiophene monomers before the addition of the second monomers.13,33 Meanwhile, in another three-neck flask, 2,5-dibromo-3-butylselenophene (0.828 g, 2.4 mmol) was reacted with i-PrMgCl (1.2 mL, 2.4 mmol) at 0 °C for 30 min. After the 30 min reaction, the solution in the second flask was added to the first one, and the mixture was reacted at 35 °C for 8 h. Subsequently, the reaction was quenched by adding HCl (aq) (50 wt %), and the product was precipitated in methanol and hexane, and dried under vacuum to obtain a purple solid (0.57 g, 69%). P3HT-b-P3BS BCPs with the feed molar ratios of 50:70 (0.66 g, 77%) and 40:80 (0.69 g, 80%) were synthesized in the same way, so did poly(3-butyleneselenophene) (P3BS) and poly(3-hexylthiophene)
(P3HT) homopolymers without adding the second monomer. On the basis of the ratio of the integration areas of the two peaks at 6.98 and 7.13 ppm due to the proton resonances on the thiophene and selenophene rings, respectively, the actual molar ratios of P3HT to P3BS are 63:37, 55:45, and 42:58, denoted as HT63BS37, HT55BS45, and HT42BS58, respectively.

**OFET Device Fabrication.** To characterize the charge transport properties of P3HT-b-P3BS BCPs, bottom-gate top-contact OFET devices were crafted using highly n-doped silicon wafers with 300 nm SiO2 layer. The wafers were cleaned by acetone, methanol, and isopropanol, then treated by plasma for 10 min and modified by n-octadecyltrichlorosilane (ODTS). The polymer solution (10 mg/mL in toluene) was then spin-coated on silicon wafers or followed by thermal annealing. Subsequently, 30 nm thick gold was evaporated onto the polymer films acting as the source and drain electrodes through a shadow mask with a channel length and width of 30 and 300 μm, respectively.

**Characterizations.** Gel permeation chromatography (GPC) measurement was performed on an Agilent 1260 system equipped with a G1314F UV detectors (eluent: THF; calibration: polystyrene standards). 1H NMR spectra were obtained on a DMX500 MHz spectrometer in CDCl3 with tetramethylsilane (TMS) as the internal standard. Grazing-incidence X-ray diffraction (GIXRD) experiments were carried out at the BL14B1 beamline of Shanghai Synchrotron Radiation Facility (SSRF), with a fixed wavelength of 1.24 Å. The samples for the GIXRD were prepared by drop-casting the 10 mg/mL polymer toluene solution onto silicon wafers. Small-angle X-ray scattering (SAXS) measurements were performed at Xeus 2.0 (Xenocs, France) using Cu Kα X-ray source (λ = 0.154 nm). The sample-to-detector distance was 2310 mm. The exposure time was set to 30 min for high-resolution pattern. Differential scanning calorimetry (DSC) was measured using a TA DSC Q2000 at a heating rate of 10 °C/min under N2 flow. UV–vis absorption spectra were recorded on PerkinElmer Lambda 750 UV–vis spectrophotometers. Cyclic Voltammetry (CV) curves were obtained using a CHI 660 Electrochemical Analyzer with a degassed acetonitrile solution of tetraethylammonium hexafluorophosphate (Bu4NPF6, 0.1 M). Atomic force microscopy (AFM) images were obtained using a Bruker Dimension FastScan in the tapping mode. The samples for AFM measurement were prepared by spin-coating the polymer solutions (10 mg/mL) on silicon wafers at 2000 r/min for 20 s. The charge transport properties of OFETs were measured using a Keithley 4200-SCS in an argon-filled glovebox.

**RESULTS AND DISCUSSION**

As shown in Scheme 1, P3HT-b-P3BS BCPs with different block ratios (P3HT/P3BS = 63:37, 55:45, and 42:58) were synthesized using the modified GRIM method. The 2-bromo-5-iodo-3-hexylthiophene monomer was polymerized first to obtain the end-living P3HT polymers. Then the activated 2,5-dibromo-3-butylselenophene monomer was added to the reacting P3HT solution to prepare the final P3HT-b-P3BS BCPs. Notably, the P3HT block should be polymerized first because the second P3BS block has poor solubility. For comparison, P3BS block was also polymerized first followed by the polymerization of the second P3HT block. However, their GPC data often display two peaks coming from the BCP and the P3BS contaminant. Since the reactivity of 2,5-dibromo-3-butylselenophene monomer is lower than that of 2-bromo-5-iodo-3-hexylthiophene monomer and the solubility of P3BS block was poor, some P3BS active centers were terminated and formed P3BS homopolymer during the block copolymer polymerization. While in this order with P3HT synthesized in the first step, the GPC profiles of all P3HT-b-P3BS BCPs can remain single peaks, and their peaks all shift to higher molecular weights, indicating little P3HT contaminant in BCPs (Figure 1). Table 1 summarizes the molecular weights of the P3HT-b-P3BS BCPs ranging from 23 700 to 29 500 with a narrow polydispersity index (PDI) of 1.10–1.14, and the block ratios of P3HT/P3BS calculated according to 1H NMR spectra (Figure S1 of the Supporting Information, SI). According to the ratio of the integration areas of the two peaks at 6.98 and 7.13 ppm from the proton resonances on the thiophene and selenophene rings, respectively, the actual molar ratios of P3HT to P3BS are calculated to be 63:37, 55:45, and 42:58, denoted as HT63BS37, HT55BS45, and HT42BS58, respectively. To compare their crystalline behavior, P3HT (Mn = 14 500, PDI = 1.05) and P3BS (Mn = 12 000, PDI = 1.09) were also synthesized and characterized by GPC (Figures S2).

To investigate the molecular structure and frontier orbital distributions of thiophene and selenophene and their effects on the electronic properties of P3HT-b-P3BS BCPs, density functional theory (DFT) calculations were performed based on dodecamers using the B3LYP/6-31G(d) basis set. As shown in Scheme 1, P3HT-b-P3BS Block Copolymers by Grignard Metathesis (GRIM) Polymerization
that selenophene block occupies more distribution contours in the highest occupied molecular orbital (HOMO) and LUMO than the thiophene block. The theoretical bandgap \( E_g \) can be calculated by the following equation:

\[
E_g = 0.68 \times (\text{LUMO}_{\text{DFT/B3LYP}} - \text{HOMO}_{\text{DFT/B3LYP}}) + 0.33 \text{ eV}
\]

The theoretical bandgap of thiophene-selenophene BCP is 1.78 eV, which is between that of thiophene (1.90 eV) and selenophene oligomers (1.70 eV) (Table S1). By cyclic voltammetry (CV)

### Table 1. Summary of Molecular Weights and Compositions of P3HT-b-P3BS BCPs

<table>
<thead>
<tr>
<th>polymers</th>
<th>designations</th>
<th>( n/m )^a</th>
<th>( M_n ), first step</th>
<th>( M_n ), second step</th>
<th>PDI^b</th>
</tr>
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<tbody>
<tr>
<td>P3HT-b-P3BS</td>
<td>HT63BS37</td>
<td>63:37</td>
<td>16 300</td>
<td>29 500</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>HT55BS45</td>
<td>55:45</td>
<td>11 500</td>
<td>25 400</td>
<td>1.14</td>
</tr>
<tr>
<td></td>
<td>HT42BS58</td>
<td>42:58</td>
<td>8 500</td>
<td>23 700</td>
<td>1.10</td>
</tr>
</tbody>
</table>

^a Determined by \(^1\)H NMR. \( n \) and \( m \): the molar amount of the P3HT and P3BS blocks in the synthesized P3HT-b-P3BS BCPs, respectively. ^bPDI of P3HT-b-P3BS BCPs.

### Table 2. Summary of 2D-GIXRD Measurement of Thin Films of P3HT-b-P3BS BCPs, P3HT and P3BS Homopolymers, and P3HT/P3BS Blend

<table>
<thead>
<tr>
<th>polymers</th>
<th>( d_{100} ) (nm)^a</th>
<th>( d_{010} ) (nm)^a</th>
<th>( d_{100} ) (nm)^b</th>
<th>( d_{010} ) (nm)^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>1.63</td>
<td>0.38</td>
<td>1.65</td>
<td>0.38</td>
</tr>
<tr>
<td>P3BS</td>
<td>0.99</td>
<td>0.42</td>
<td>1.29</td>
<td>0.38</td>
</tr>
<tr>
<td>P3HT/P3BS blend</td>
<td>1.65/0.99</td>
<td>0.39/0.42</td>
<td>1.67/1.28</td>
<td>0.39</td>
</tr>
<tr>
<td>HT63BS37</td>
<td>1.56</td>
<td>0.38</td>
<td>1.57</td>
<td>0.38</td>
</tr>
<tr>
<td>HT55BS45</td>
<td>1.59/0.98</td>
<td>0.38/0.42</td>
<td>1.51</td>
<td>0.38</td>
</tr>
<tr>
<td>HT42BS58</td>
<td>1.56/0.99</td>
<td>0.38/0.42</td>
<td>1.42</td>
<td>0.38</td>
</tr>
</tbody>
</table>

^aLamellar distance. ^b\( \pi-\pi \) stacking distance.

Figure 1. (a-c) GPC profiles of P3HT-b-P3BS BCPs. The black dashed curves are the GPC profiles of the P3HT block in the first-step polymerization, and the red solid curves are the GPC profiles of the resulting (a) HT63BS37, (b) HT55BS45, and (c) HT42BS58 BCPs.

Figure 2. (a) Schematic diagram of 2D-GIXRD measurement on P3HT-b-P3BS thin films. (b) 2D-GIXRD images and the resulting (c) 1D-GIXRD images along the out-of-plane \( (q_z) \) and in-plane \( (q_{xy}) \) directions of three as-cast P3HT-b-P3BS thin films with various block ratios (P3HT/P3BS = 63:37, 55:45, and 42:58, respectively). (d) Schematic diagram of chain packing in as-cast P3HT-b-P3BS thin films. HT63BS37 exhibits the sole P3HT crystallization with an amorphous P3BS state, while HT55BS45 and HT42BS58 display individual P3HT and P3BS form II crystallization.
(Figure S4) and UV-vis absorption spectroscopy (Figure S5), the actual bandgaps of three P3HT-b-P3BS BCPs were measured to be 1.78–1.84 eV, which are between the bandgap of P3HT (1.86 eV) and P3BS (1.65 eV) (Figure S6 and Table S1). This result is consistent with the theoretical bandgaps, indicating the effect of both thiophene and selenophene on the BCP bandgap.

To study the crystalline structures of as-cast P3HT-b-P3BS BCPs, 2D-GIXRD measurements were performed (Figure 2) together with P3HT homopolymer (Figure S7), P3BS homopolymer (Figure S8) and P3HT/P3BS blend (Figure S9) for comparison. The obtained interlayer spacing (d_{100}) and π–π stacking distance (d_{001}) of three P3HT-b-P3BS BCPs and control samples are summarized in Table 2. The schematic diagram of the synchrotron GIXRD measurement is described in Figure 2a. P3HT and P3BS display (100) diffraction patterns along the out-of-plane (q_{z}) direction, representing the edge-on orientation with the directions of alkyi side chains and π–π stacking vertical and parallel to the substrate, respectively (Figures S7a and S8a). Their (100) diffraction patterns were also observed along in-plane direction, indicating some crystalline domains in face-on orientation as well. Their 1D-GIXRD images show the P3HT and P3BS (100) diffractions at the scattering vector (q_{y}) of 3.85 and 6.37 nm\(^{-1}\), respectively, corresponding to d_{100} of 16.3 and 9.9 Å, respectively (Figures S7b and S8b; Table 2). The d_{100} of P3HT and P3BS are 3.8 and 4.2 Å, according to the scattering vectors (q_{x,y}) of 16.7 and 14.9 nm\(^{-1}\), respectively (Figures S7c and S8c; Table 2). The diffraction peaks with the d_{100} of 16.3 and 9.9 Å can be assumed as P3HT form I crystal and P3BS form II crystal\(^{32}\) respectively. As the diffraction peak intensity is approximately proportional to the materials crystallinity, the stronger intensity of (100) diffraction of P3HT indicates it has a higher crystallinity than P3BS form II (Figures S7a and S8a).

For as-cast three P3HT-b-P3BS thin films, their crystalline structures are found to be greatly influenced by the block ratio of the two P3BT and P3BS constituents. For HT63BS37 (P3HT/P3BS = 63:37), only one (100) and (010) diffraction peaks at q_{z} of 4.03 nm\(^{-1}\) (d_{100} = 15.6 Å) and q_{x,y} of 16.56 nm\(^{-1}\) (d_{001} = 3.8 Å), respectively, are observed, which are ascribed to the P3HT crystals in edge-on orientation (Figure 2b and Table 2). The (100) and (010) diffraction peaks of the other P3BS block are not observed. For the other two BCPs, P3HT-b-P3BS exhibits two (100) diffraction peaks at q_{z} of 3.94 and 6.40 nm\(^{-1}\) (d_{100} = 15.9 and 9.8 Å, respectively) for HT55BS45 and at q_{z} of 4.03 and 6.35 nm\(^{-1}\) (d_{001} = 15.6 and 9.9 Å, respectively) for HT42BS58, which can be ascribed to the crystallization of individual P3HT block and P3BS form II block in the edge-on orientation (Figure 2b and Table 2). Their π–π stacking distances are 3.8 and 4.2 Å for HT55BS45 and HT42BS58 with d_{001} of 16.67 and 18.45 nm\(^{-1}\), respectively for HT55BS45, and q_{x,y} of 16.54 and 18.46 nm\(^{-1}\), respectively for HT42BS58. (Figure 2b and Table 2). The d_{100} and d_{001} of P3HT block are comparable to previous theoretic and experimental studies.\(^{57-59}\) The 1D-GIXRD images of three as-cast P3HT-b-P3BS thin films through the q_{x} and q_{x,y} directions are shown in Figure 2c. For the three P3HT-b-P3BS BCPs cast from the toluene solution, the solvent evaporation process would influence the microphase separation and crystallization of BCPs during the film deposition. As toluene dissolves P3HT much better than P3BS and P3HT has much stronger crystallizability than P3BS (Figures S7a and S8a), P3BS crystallizes or precipitates from the solution first during the solvent evaporation, followed by the crystallization of P3HT. As a result, all three P3HT-b-P3BS BCPs microphase-separate during the solvent-casting process. For HT63BS37, the major P3HT block dominates the crystalline structure while the crystallization of the minor P3BS block is greatly depressed. As the content of P3BS increases in the other two copolymers (HT55BS45 and HT42BS58), the crystallizability of P3BS is enhanced and thus both P3HT and P3BS blocks crystallize to form individual crystal domains. On the basis of the above analysis, the possible chain packing in three P3HT-b-P3BS BCPs at the as-cast state is described in Figure 2d. The alkyl side chains are packed in a tilted mode, which is drawn based on the literature.\(^{40-42}\) It has been reported that at low temperatures, the alkyl side chains experience an order–disorder transition rapidly at temperatures just above 300 K, and the tilted angle was found to increase with increased temperature in the range of 280–300 K.\(^{42}\) As in our work, the P3HT-b-P3BS thin films were crafted at room temperature followed by high temperature annealing, and no side-chain ordering peak was found.

Thermal annealing is an efficient method to control and enhance the ordering of chain packing of conjugated polymers.\(^{43}\) BCP chains can move and reconstruct themselves to a more thermodynamically stable state during thermal annealing process. In this context, thin films of P3HT-b-P3BS were treated by thermal annealing at 200 °C (which is lower than the melting point of P3HT (T_{m} = 237 °C for M_{w} = 14.7K) while close to the melting point of P3BS block in form II (T_{m} = 196 °C for M_{w} = 12K) (Table S2) for 30 min and then examined by 2D-GIXRD (Figure 3 and Table 2).

![Figure 3](https://dx.doi.org/10.1021/acs.macromol.0c01395)

**Figure 3.** (a) 2D-GIXRD images and their (b) 1D-GIXRD images along the out-of-plane (q_{z}) and in-plane (q_{x,y}) directions of three P3HT-b-P3BS thin films with varied block ratios (P3HT/P3BS = 63:37, 55:45, and 42:58, respectively) after 200 °C-annealing. (c) Schematic diagram of chain packing in HT55BS45 and HT42BS58 cocryystals. The hexyl and butyl side chains compromise to achieve a balanced d_{001}-spacing.

Compared with as-cast samples, HT63BS37 (P3HT/P3BS = 63:37) remains the sole P3HT crystallization in edge-on orientation with improved crystallinity together with amorphous P3BS block (Figure 3a and Table 2). For HT55BS45 and HT42BS58, the previous two (100) diffraction peaks at q_{z} of 3.94 and 6.40 nm\(^{-1}\) for HT55BS45 and at q_{z} of 4.03 and 6.35 nm\(^{-1}\) for HT42BS58, respectively, disappeared. The two
BCPs exhibit new single (100) diffraction peak at \( q_x \) of 4.15 nm\(^{-1} \) (\( d_{100} = 15.1 \) Å) for HT55BS45 and at \( q_x \) of 4.42 nm\(^{-1} \) (\( d_{100} = 14.2 \) Å) for HT42BS58, respectively (Figure 3a and Table 2). Similarly, the previous two (010) diffraction peaks existed in as-cast HT55BS45 and HT42BS58 samples changed to one (010) diffraction peak at \( q_{yy} \) of 16.43 nm\(^{-1} \) (\( d_{010} = 3.8 \) Å). Their 1D GIXRD images of three BCPs along the \( q_y \) and \( q_z \) directions are shown in Figure 3b, indicating the formation of cocry stalline structures in the edge-on orientation in both HT55BS45 and HT42BS58 BCPs. Their \( d_{100} \) spacings are between that of P3HT and P3BS homopolymers, and HT42BS58 with more P3BS content has smaller \( d_{100} \) compared with HT55BS45 as the P3BS block has smaller \( d_{100} \) value. On the contrary, the P3HT/P3BS (1:1) blend displays two (100) diffraction peaks at \( q_y \) of 3.81 and 6.35 nm\(^{-1} \) at as-cast state and \( q_y \) of 3.76 and 4.89 nm\(^{-1} \) after 200 °C-annealing. It implies that P3HT and P3BS in the blend crystallize individually at both as-cast and 200 °C-annealed states (Figure S9 and Table 2). Remarkably, the change of \( q_y \) of 6.35 and 4.89 nm\(^{-1} \) for P3BS block at as-cast and 200 °C-annealed states, respectively, also indicates the change of interlayer spacing \( d_{100} \) during the thermal annealing for P3BS, which is due to the phase transition of P3BS block and will be discussed in the following. Figure 3c describes the possible chain packing for HT55BS45 and HT42BS58 cocry stallines, where their alkyl side chains compromise and adjust their conformations to achieve a balanced \( d_{100} \)-spacing.

Intriguingly, during the 200 °C-annealing process, the initial form II crystals of P3BS block in as-cast HT55BS45 and HT42BS58 thin films as well as in P3HT/P3BS (1:1) blend thin films transformed into form I crystals completely, and thus the HT55BS45 and HT42BS58 cocry stallines are constituted of P3BS form I and P3HT. For comparison, the as-cast P3BS homopolymer thin film was also annealed at 200 °C, in which the previous (100) diffraction peak at the \( q_y \) of 6.37 nm\(^{-1} \) (\( d_{100} = 9.9 \) Å) disappeared while a new intense (100) diffraction peak at the \( q_y \) of 4.87 nm\(^{-1} \) (\( d_{100} = 12.9 \) Å) appeared, corresponding to the (100) diffraction of P3BS form I (Figure 8 and Table 2). Due to the interdigitation of butyl side chains, P3BS form II has a shorter \( d_{100} \) between the conjugated backbones than form I. It indicates P3BS forms I and II are thermodynamically stable and kinetically controlled, respectively, similar to our previously report about P3HS forms I and II. We noticed such phase transition from P3BS form II to form I could not be achieved when it was annealed at a lower temperature of 150 °C (Figure S8). The structural models of P3BS form I and form II polymorphs are presented in Figure S10.

It is important to note that the specific annealing temperature may influence the crystalline structure of P3HT-b-P3BS BCPs. Therefore, a higher annealing temperature at 230 °C was carried out subsequently, which is near the melting point of P3HT block (\( T_m = 237 \) °C for \( M_w = 14.7 \) K) while below the melting point of P3BS form I block (\( T_m = 263 \) °C for \( M_w = 12 \) K) (Table S2). This annealing temperature is chosen based on the consideration that if two blocks in BCPs which can cocry stallize together have very different mobilities, they may crystallize individually and occur microphase separation. After 230 °C-annealing, naturally, HT63BS37 remained the structure of crystalline P3HT block with amorphous P3BS block (Figure 4a). Its (100) diffraction peak was well pronounced through both out-of-plane and in-plane directions, indicating the coexistence of edge-on and face-on orientations. While for HT55BS45 and HT42BS58, interestingly, they did not form cocry stalline structures compared to the 200 °C-annealed samples. Instead, two (100) diffraction peaks emerged at \( q_y \) of 3.97 and 4.64 nm\(^{-1} \) (\( d_{100} = 15.8 \) and 13.5 Å, respectively) for HT55BS45 and \( q_y \) of 4.01 and 4.72 nm\(^{-1} \) (\( d_{100} = 15.7 \) and 13.3 Å, respectively) for HT42BS58, which indicate the crystallization of individual P3HT block and P3BS form I block (Figure 4a and Table 2). The schematic diagram of the possible chain packing in HT55BS45 and HT42BS58, displaying individual P3HT and P3BS form I crystallization.

To further elaborate the microstructure of P3HT-b-P3BS BCPs, the small-angle X-ray scattering (SAXS) measurements were performed to analyze HT55BS45 and HT42BS58 after thermal annealing at 200 or 230 °C (Figure S11). The SAXs profiles exhibit a very weak and broad signal at the scattering vector of \( \sim 0.21-0.37 \) nm\(^{-1} \) and 0.19–0.43 nm\(^{-1} \) for HT55BS45 and HT42BS58 copolymers after 200 °C-annealing, corresponding to a domain size of \( \sim 16.9-29.9 \) nm and 14.6–33.1 nm, respectively. From GIXRD results, P3HT and P3BS form cocry stallines at this state. The domain size is assumed as the size of the cocry stalline domains. After thermal annealing at 230 °C, an obvious scattering peak was identified at the scattering vector of \( \sim 0.20-0.21 \) nm\(^{-1} \) for these two BCPs, indicating the existence of microphase separation with the domain size of \( \sim 29.9-30.5 \) nm. It is in accordance with their GIXRD results that HT55BS45 and HT42BS58 microphase-separated into individual P3HT and P3BS crystals after 230 °C-annealing. Due to the less ordered structure of these two BCPs in a large scale, higher order peak was not observed in the SAXs. Notably, a series of P3BT-b-P3HS BCPs have been obtained and treated by one-step or two-step thermal annealing. As different alkyl side chains in all-conjugated diblock copoly(3-alkylthiophene)s influence their physical properties, such as solubility, melting point, and crystalline nature greatly, P3HT-b-P3BS BCPs in the present study
exhibit different crystalline structures at both as-cast and thermal-annealed states from P3BT-b-P3HS BCPs.

To further investigate the crystalline behavior of the P3HT-b-P3BS BCPs, DSC measurements were performed. Figure 5 and Table S2 compare the endothermic traces of the first heating cycle of P3HT-b-P3BS BCP samples scraped off from the as-cast (Figure 5a), 200 °C (Figure 5b), and 230 °C-annealed samples (Figure 5c), respectively. Under the same condition, DSC measurements of as-cast and 200 °C-annealed P3HT and P3BS homopolymers were also performed (Figure 5a and 5b, Table S2). HT63BS37 displays one endothermic peak in the range of 227 to 234 °C at three different conditions. This is in accordance with the GIXRD results that sole P3HT crystallization with amorphous P3BS domains existed in HT63BS37 at three different conditions. For the copolymer HT42BS58, three endothermic peaks around 182 °C, 222 °C, and 257 °C are observed in the as-cast state. During the heating process, the P3BS block II crystal melt around 182 °C and recrystallize to form I crystal. Subsequently, the P3HT block melts around 222 °C. The third endothermic peak around 257 °C is the melting of the newly formed P3BS block I crystal. The as-cast HT55BS45 sample shows two endothermic peaks around 226 and 253 °C, which can be ascribed to the melting of P3HT and P3BS form I crystals, respectively. The absence of the endothermic peak of P3BS block II crystal in as-cast HT55BS45 as compared with as-cast HT42BS58 sample is due to the lower content of P3BS block in the former. Interestingly, two endothermic peaks are observed in the 200 °C-annealed cocrystal samples of HT55BS45 and HT42BS58 in the DSC heating curves, i.e., 224 °C and 250 °C for HT55BS45 cocrystal and 223 °C and 258 °C for HT42BS58 cocrystal. Such result seems contradictory to GIXRD data (Figure 3) and unusual as single endothermic peak in DSC is usually considered as the first endothermic peak in HT55BS45 and HT42BS58 cocrystals. The melting of the remaining P3BS crystals accounts for the second endothermic peak. Similar phenomenon has been found in P3HT/P3BT cocrystals, which exhibit two endothermic peaks as well. The 230 °C-annealed HT55BS45 and HT42BS58 samples show two endothermic peaks at 221 and 248 °C for HT55BS45 and 220 and 258 °C for HT42BS58, which are ascribed to the P3HT and P3BS form I crystals, respectively.

At this point, it is interesting to deduce the effects of the P3HT/P3BS block ratio and thermal annealing temperature on the microphase-separated or cocrystalline structures of these P3HT-b-P3BS BCPs. It is reported that polymers possess similar structures, potential energies, and crystallization kinetics may form cocrystals and only several examples of polymer cocrystals have ever been reported to date. For the three P3HT-b-P3BS BCPs casting from toluene solution, they exhibit microphase-separated structures composed of sole P3HT crystalline domains or individual P3HT and P3BS crystalline domains depending on the block ratio of P3HT/P3BS (Figure 2d). After 200 °C-annealing these BCP samples, P3BS form II changed to form I of higher crystallinity and larger d_{100}-spacing in HT55BS45 and HT42BS58. Due to their similar molecular structure and close bondings between P3HT and P3BS blocks, they form cocrystals in HT55BS45 and HT42BS58 (Figure 3c). Notably, the covalent bonding between P3HT and P3BS blocks is key to form cocrystallization in HT55BS45 and HT42BS58 as well. For comparison, P3HT/P3BS (1:1) blend thin films could not form cocrystals even it experienced 200 °C-annealed process and P3BS occurred phase transition from form II to form I (Figure S9). During 230 °C-annealing which is quite close to the melting point of P3HT block but below that of P3BS form I block, HT55BS45 and HT42BS58 are actually in a partial melting state in which the P3HT chains are much more flexible than P3BS chains. Thus, the P3HT chains escape from the cocrystals, while P3BS form I blocks remain rod-like and crystallize solely, followed by the crystallization of P3HT chains during the cooling process (Figure 4c).

To gain insight into the relation between the crystalline structures of P3HT-b-P3BS BCPs at various states (i.e., as-cast, 200 °C, and 230 °C-annealed states) and their charge transport properties, OFET devices in the bottom-gate top-contact configuration were crafted. It is important to note that although the drop-cast films for 2D-GIXRD are much thicker than the spin-coated films for OFETs, they exhibit the same crystalline structures with much weaker crystalline signal from the spin-coated samples, except (100) diffraction of P3BS form II was not observed in the as-cast HT55BS45 due to weaker signal (Figure S12). It is believed that the film thickness will not influence the crystalline structures (i.e., cocrystallization or microphase-separated structures) of these P3HT-b-P3BS films. Taken HT42BS58 as an example, Figure 6 compares their...
transfer and output curves at three different states. These curves of HT63BS37 and HT55BS45 are given in Figures S13 and S14, respectively. The field-effect mobility ($\mu_{\text{FET}}$) was calculated from the transfer curves in the saturation regime ($V_{\text{DS}} = -60$ V) according to the following equation:\cite{50}

$$I_{\text{DS}} = \frac{W}{2L}\mu_{\text{FET}}C_{\text{s}}(V_{\text{G}} - V_{\text{T}})^{2}$$

where $I_{\text{DS}}$ is the drain current, $V_{\text{G}}$ and $V_{\text{T}}$ are the gate-source voltage and the threshold voltage, respectively, $C_{\text{s}}$ is the capacitance of the gate dielectric, and $W$ (300 μm) and $L$ (30 μm) are the width and length of the transistor channel, respectively. The OFET performances of three P3HT-b-P3BS thin films are summarized in Table 3. As-cast P3HT-b-P3BS films exhibited the average charge mobilities of $5.40 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ for HT63BS37, $5.01 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ for HT55BS45, and $2.54 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ for HT42BS58, respectively. The highest charge mobility of $1.65 \times 10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$ was observed in HT63BS37. These charge mobilities of P3HT-b-P3BS obtained here are comparable to other reported polythiophene or polyselenophene-based systems (Figure S15).\cite{24,26,27,51–56} It is widely recognized that high crystallinity facilitates the charge transport as charge carriers usually travel faster in the ordered domain than in the disordered domain.\cite{57} Thus, it is not surprising that HT63BS37 with major P3HT block exhibited higher charge mobilities as P3HT block has much higher crystallinity than P3BS block.

After 200 °C-annealing, the crystallinity of three P3HT-b-P3BS thin films all increased. Moreover, HT55BS45 and HT42BS58 formed cocrystalline structures. Therefore, we initially considered that all BCPs would exhibit higher charge mobilities than their as-cast states. By comparison, the average charge mobilities of HT42BS58 increased to $3.37 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$, while unexpectedly HT63BS37 and HT55BS45 showed decreased charge mobilities of $2.13 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ and $2.43 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$, respectively (Table 3). This inconsistent effect on charge mobilities of three P3HT-b-P3BS by 200 °C-annealing may be rationalized as follows. On the one hand, P3HT-b-P3BS containing more P3BS shows a lower crystallinity compared to the BCP with more P3HT, resulting in an unfavorable effect on the charge transport. On the other hand, more P3BS in P3HT-b-P3BS renders the BCP with better heat-resisting properties. Both factors contribute and influence the charge transport in the three BCP thin films together. As a result, their charge mobilities are determined by which factor dominates. For HT42BS58, the heat-resisting factor dominated, leading to the increase of charge mobilities after 200 °C-annealing, while the lower-crystallinity-factor dominated in HT63BS37 and HT55BS45, which led to decreased mobilities.

For charge transport properties of 230 °C-annealed P3HT-b-P3BS thin films, they all demonstrated decreased charge mobilities in the range of $3.42 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ to $1.17 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$. As discussed above, conjugated polymers are readily degraded after long-time high temperature treatment and it is hard to obtain stable charge mobilities, which is assumed as the main reason for their decreased charge mobilities. Besides, for HT55BS45 and HT42BS58, due to the cooperative effect of two blocks since P3BS block has the higher planarity and facilitates intrachain charge transport and the P3HT block has more closed molecular packing and favors interchain charge transport, their cocrystals formed after 200 °C-annealing are considered to more favor the charge transport than their individual crystals after 230 °C-annealing.

To further analyze the film microstructure and quality, the surface morphology of P3HT-b-P3BS thin films at the as-cast state and after annealing at 200 and 230 °C were examined by

![Figure 6](https://example.com/figure6)

**Figure 6.** (a, c, e) Transfer curves and (b, d, f) output curves of OFETs prepared with HT42BS58 thin films at (a, b) as-cast state and after (c, d) 200 °C and (e, f) 230 °C-annealing. $V_{\text{DS}} = -60$ V. Schematic diagram of OFET device configuration is given as an inset in (a).

Table 3. Summary of OFET Device Performances of P3HT-b-P3BS BCPs with Varied Block Ratios at Different Conditions

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Conditions</th>
<th>$\mu_{\text{max}}$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>$\mu_{\text{avg}}$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>$I_{\text{on}}/I_{\text{off}}$</th>
<th>$V_{\text{th}}$ (V)</th>
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<tr>
<td>HT63BS37</td>
<td>as-cast</td>
<td>$1.65 \times 10^{-2}$</td>
<td>$5.40 \times 10^{-3}$</td>
<td>$10^{7}$</td>
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<tr>
<td></td>
<td>200 °C</td>
<td>$7.17 \times 10^{-3}$</td>
<td>$2.13 \times 10^{-3}$</td>
<td>$10^{7}$</td>
<td>$-5$ to $-13$</td>
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<tr>
<td></td>
<td>230 °C</td>
<td>$4.67 \times 10^{-4}$</td>
<td>$3.42 \times 10^{-4}$</td>
<td>$10^{7}$</td>
<td>$-3$ to $-31$</td>
</tr>
<tr>
<td>HT55BS45</td>
<td>as-cast</td>
<td>$9.36 \times 10^{-3}$</td>
<td>$5.01 \times 10^{-3}$</td>
<td>$10^{7}$</td>
<td>$-7$ to $-8$</td>
</tr>
<tr>
<td></td>
<td>200 °C</td>
<td>$5.03 \times 10^{-3}$</td>
<td>$2.43 \times 10^{-3}$</td>
<td>$10^{7}$</td>
<td>$-8$ to $-9$</td>
</tr>
<tr>
<td></td>
<td>230 °C</td>
<td>$8.27 \times 10^{-3}$</td>
<td>$1.84 \times 10^{-3}$</td>
<td>$10^{7}$</td>
<td>$-9$ to $-31$</td>
</tr>
<tr>
<td>HT42BS58</td>
<td>as-cast</td>
<td>$4.29 \times 10^{-3}$</td>
<td>$2.54 \times 10^{-3}$</td>
<td>$10^{7}$</td>
<td>$-8$ to $-6$</td>
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<td>$3.37 \times 10^{-3}$</td>
<td>$10^{7}$</td>
<td>$-3$ to $-9$</td>
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<tr>
<td></td>
<td>230 °C</td>
<td>$2.89 \times 10^{-3}$</td>
<td>$1.17 \times 10^{-3}$</td>
<td>$10^{7}$</td>
<td>$-8$ to $-15$</td>
</tr>
</tbody>
</table>

**Table 3 Summary of OFET Device Performances of P3HT-b-P3BS BCPs with Varied Block Ratios at Different Conditions**

- **$\mu_{\text{max}}$**: Maximum charge mobility.
- **$\mu_{\text{avg}}$**: Average charge mobility obtained from at least 18 OFET devices.
- **$I_{\text{on}}/I_{\text{off}}$**: Current on/off ratio.
- **$V_{\text{th}}$**: Threshold voltage.
AFM (Figure S16). It shows nodule-like morphology in all as-cast P3HT-b-P3BS thin films. With the increased annealing temperature, nanowire morphology was observed in these samples. Since AFM images characterize the surface structure of P3HT-b-P3BS films in a large scale, the molecular packing modes of different samples seem poorly reflected by the AFM data. A detailed exploration using high-resolution transmission electron microscopy (HRTEM) to distinguish molecular packing modes and crystalline nanodomains of different samples is ongoing and will be reported elsewhere. The root-mean-square (RMS) roughness of as-cast HT63BS37, HT55BS45, and HT42BS58 is 6.24, 3.22, and 3.33 nm, respectively. After 200 °C-annealing, their RMS roughness decreases a little, which is 3.39, 2.67, and 2.32 nm for HT63BS37, HT55BS45, and HT42BS58, respectively. It indicates that thermal annealing yields a smoother surface for each P3HT-b-P3BS thin film. It is interesting to note that after 230 °C-annealing, the roughness of HT63BS37 decreases to 1.63 nm, while it increases a little to 3.15 and 2.68 nm for HT55BS45 and HT42BS58, respectively, due to the formation of individual P3HT and P3BS crystal domains.

**CONCLUSIONS**

In summary, we synthesized a family of P3HT-b-P3BS BCPs of various block ratios and unraveled their crystallization and microphase separation that are modulated by the block ratios and thermal annealing temperature. The BCPs at the as-cast state display a singular P3HT crystallization or individual P3HT and P3BS form II crystallization, depending on the block ratio of P3HT/P3BS. The 200 °C-annealing transforms as-cast HT55BS45 and HT42BS58 from microphase-separated structures with individual P3HT and P3BS crystal domains into cocrystalline structures. At the higher thermal annealing temperature of 230 °C, the cocrystals originally existing in 200 °C-annealed HT55BS45 and HT42BS58 do not form. Instead, they revert to individual P3HT and P3BS form I crystals. Moreover, the relation between their different crystalline structures and charge mobilities is also investigated, demonstrating synergy of the P3HT/P3BS block ratio, film crystallinity, heat-resisting property, film morphology, etc. on the charge transport properties. By optimizing the device parameters, further enhanced charge mobility can be expected, which will be the subject of future research. The understanding of the interplay between crystallization and microphase separation of all-conjugated BCPs gained in this study may make them potentially promising materials for applications in OFETs and other optoelectronic devices.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c01395.

Detailed characterization of P3HT-b-P3BS, P3HT, and P3BS homopolymers; DFT calculations for dodecamers of P3HT-b-P3BS; oligothiophene and oligoselenophene; electrochemical characterization of P3HS-b-P3BS, P3HT, and P3BS homopolymers; GIXRD images of P3HT and P3BS homopolymers and P3HT/P3BS blends; SAXS of P3HT-b-P3BS, transfer, and output curves of P3HT-b-P3BS; and AFM height images of P3HT-b-P3BS (PDF)

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