Tailoring Cocrystallization and Microphase Separation in Rod–Rod Block Copolymers for Field-Effect Transistors

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ABSTRACT: Conjugated rod–rod block copolymers (BCPs) are important semiconducting materials because they combine the unique microphase-separation characteristics of BCPs with the remarkable optoelectronic properties of conjugated polymers. The ability to tailor the two fundamental phase transitions (microphase separation and crystallization) in BCPs could enable efficient control over their physical and optoelectronic properties. Herein, a set of poly(3-butylthiophene)-block-poly(3-dodecylthiophene) (P3BT-b-P3DDT) BCPs with controlled block ratios are synthesized and the interplay between their microphase separation and cocrystallization is explored by tuning both the intrinsic (i.e., block ratios) and extrinsic factors (i.e., solvent and thermal annealing temperatures). An increased P3BT content, slower solvent evaporation, and higher thermal annealing temperatures favor microphase separation in P3BT-b-P3DDT. Furthermore, the relationship between various P3BT-b-P3DDT crystalline structures and their charge-transport properties is scrutinized. This work elucidates how P3BT-b-P3DDT BCPs undergo microphase separation and crystallization and how these processes can be tailored, strengthening our fundamental understanding of conjugated rod–rod BCP systems.
butylthiophene)-block-poly(3-octylthiophene) (P3BT-b-P3OT), with varying side-chain lengths, self-assembled and crystallized into nanowires in solution and microphase-separated into lamellae during the melt phase. With carboxylate-bearing side chains differing in length by only three atoms, poly(3-butythiophene)-block-poly(3-thiophene hexylacetae) (P3HT-b-P3THA) can form various microphase-separated crystalline-amorphous, crystalline-crystalline, and cocrystalline structures through compositional changes. For poly(2,5-dihexyloxy-p-phenylene)-block-(3-hexylthiophene) (PPP-b-P3HT), which possesses a distinct conjugated backbone, three different molecular orientation transitions could be observed in self-epitaxial crystallization circles upon changing the heating process, displaying the edge-on or face-on orientations in the P3HT and PPP blocks. Due to the similar chemical structure and crystallization kinetics of the two blocks, poly(3-butythiophene)-block-poly(3-hexylthiophene) (P3BT-b-P3HS) can also form cocrystals, which displayed markedly enhanced charge mobilities over their microphase-separated P3BT and P3HS crystal domains. It is worth noting that most studies regarding tailoring the crystalline structure of conjugated rod–rod BCPs are based on post-treatment strategies such as thermal annealing. However, their crystalline structures can also be efficiently and directly tuned in the solution state by controlling the selectivity of the solvent, which has relatively few investigations.

Herein, we report the crystallization and microphase-separation behavior of a poly(3-butythiophene)-block-poly(3-dodecylthiophene) (P3BT-b-P3DDT) BCP by controlling both the solvents in the solution state and the subsequent thermal annealing processes in the film state. P3BT-b-P3DDT was selected due to the lengths of its alkyl side chains (P3BT and P3DDT) being very different, which we believed could enable the tunability of the sub-balance between crystallization and microphase separation upon changing the solvents. Interestingly, P3BT-b-P3DDT BCPs of various block ratios (P3BT/P3DDT = 35:65, 48:52, and 67:33) formed cocrystalline structures when processed from chloroform (CHCl3), while different cocrystalline or microphase-separated structures were obtained with much slower evaporation rates when casting from dichlorobenzene (ODCB) and 1,2,3-trichlorobenzene (TCB). Notably, the crystal types of the P3ATs in this work remained orthorhombic, and the changes in their crystalline structures indicate changes in their cocrystalline structures as well as in their lattice parameters. It was found that P3BT-b-P3DDT BCPs with a greater P3BT content are more likely to undergo microphase separation during the solvent evaporation process than P3BT-b-P3DDT BCPs with a greater P3DDT content. After annealing at 150 °C, these P3BT-b-P3DDT cocrystals cast from CHCl3 retained cocrystalline structures with improved crystallinity. When the annealing temperature was raised to 220 °C, which is between the melting points of P3DDT and P3BT, the chain mobilities were very different and microphase separation that formed individual P3BT and P3DDT crystal domains was observed for all P3BT-b-P3DDT BCPs tested. Finally, the linkages between the different crystalline structures in the P3BT-b-P3DDT BCPs and their charge mobilities were studied. Overall, this study elucidated that both intrinsic factors, including the block ratio, and extrinsic factors, including the solvent and thermal annealing temperature, have profound effects on the cocrystallization and microphase separation of conjugated BCPs, which consequently influence their resulting charge mobilities.

## EXPERIMENTAL SECTION

### Materials

Two monomers, 2-bromo-5-iodo-3-butythiophene and 2-bromo-5-iodo-3-dodecylthiophene, were synthesized according to previous report.[35] [1,3-Bis(diphenylphosphino)propane]dichloronickel(II) (Ni(dppp)Cl2) and isopropylammonium chloride (iPrMgCl), 2.0 M solution in tetrahydrofuran (THF) were purchased from Sigma-Aldrich. P3BT-b-P3DDT BCPs with various block ratios (P3BT/P3DDT = 35:65, 48:52, and 67:33), comparable molecular weights (Mw = 31 200–33 800), narrow polydispersity indices (PDI; 1.04–1.09), and high regioregularity (RR; 96–97%) were prepared by GRIM polymerization (Scheme S1, Figures S1 and S2).[36,37] The actual block ratios of P3BT/P3DDT in the three BCPs were determined to be 35:65, 48:52, and 67:33 and are denoted as B35DD65, B48DD52, and B67DD33, respectively. These ratios were determined according to the integration area ratio of the proton resonances at 0.98 and 0.87 ppm, which are from the terminal methyl groups belonging to the butyl and dodecyl chains, respectively. Two P3BT (Mw = 27 100, PDI = 1.03) and P3DDT (Mw = 35 400, PDI = 1.08) homopolymers were also synthesized for comparison (Figures S1 and S2). Compositions and molecular weights of the three P3BT-b-P3DDT, P3BT, and P3DDT homopolymers are summarized in Table 1.

### Table 1. Summary of Compositions, Molecular Weights (Mw), Polydispersity Indices (PDI), and Regioregularity (RR) of P3BT-b-P3DDT with Different Block Ratios

<table>
<thead>
<tr>
<th>P3BT</th>
<th>P3DDT</th>
<th>B35DD65</th>
<th>B48DD52</th>
<th>B67DD33</th>
</tr>
</thead>
<tbody>
<tr>
<td>n/m</td>
<td>100:0</td>
<td>0:100</td>
<td>1:2</td>
<td>2:1</td>
</tr>
<tr>
<td>Mw (K)</td>
<td>27 100</td>
<td>35 400</td>
<td>35 65</td>
<td>67 33</td>
</tr>
<tr>
<td>PDI</td>
<td>1.03</td>
<td>1.08</td>
<td>1.05</td>
<td>1.04</td>
</tr>
<tr>
<td>RR (%)</td>
<td>97</td>
<td>97</td>
<td>100</td>
<td>96</td>
</tr>
</tbody>
</table>

*Measured by ^1^H NMR. **n/m:** the block ratio of P3BT/P3DDT. Measured by GPC. Measured by ^1^H NMR.

### Sample Preparation and Treatment

P3BT-b-P3DDT BCPs were dissolved in three different solvents, i.e., CHCl3, ODCB, and TCB (10 mg/mL). Subsequently, the P3BT-b-P3DDT solutions were dropped cast or spin-coated onto silicon wafers with a native oxide layer or a 300 nm SiO2 layer in thickness. Two annealing temperatures were chosen to treat the polymer films. A common procedure involving annealing at 150 °C for 10 min was employed for the 1P3ATs, along with another method involving annealing at a much higher 220 °C for 10 min, followed by slow cooling to room temperature. For organic field-effect transistor (OFET) measurements, the silicon wafers with a 300 nm SiO2 layer were cleaned using acetone and ethyl alcohol. They were then cleaned by plasma for 20 min and treated using octadecyltrichlorosilane (ODTS). A layer of gold (40 nm) was evaporated onto the as-cast or thermally annealed polymer films via a shadow mask that acted as the source/drain electrode and had a channel length of 30 μm and width of 300 μm.

### Characterization

1H NMR spectra were obtained on a DMX 500 MHz spectrometer using tetramethylsilane (TMS) as the internal standard in CDCl3. Gel permeation chromatography (GPC) measurements were performed using an Agilent 1260 system with THF as the eluent. Grazing-incidence X-ray diffraction (GIXRD) measurements were carried out at the Shanghai Synchrotron Radiation Facility (SSRF) on the beamline BL14B1 (wavelength: 1.24 Å). The incidence angle of the X-ray beam was 0.15°. The energy of the X-ray was 10 keV and the critical angle for this energy was 0.13°. Small-angle X-ray scattering (SAXS) experiments were conducted with a Xeuss 2.0 (Xenocs, France) instrument using Cu Kα1 X-ray beam.
Figure 1. (a, c, e) 2D grazing-incidence X-ray diffraction (GIXRD) images and (b, d, f) 1D-GIXRD images of thin films of poly(3-butylthiophene)-block-poly(3-dodecylthiophene) (P3BT-b-P3DDT) with various block ratios (P3BT/P3DDT = 35:65, 48:52, and 67:33) cast from (a, b) chloroform (CHCl₃), (c, d) dichlorobenzene (ODCB), and (e, f) 1,2,3-trichlorobenzene (TCB). The \( q_x \) and \( q_y \) parameters indicate the out-of-plane and in-plane directions, respectively.

Kevin radiation (wavelength: 1.54 Å). Differential scanning calorimetry (DSC) was performed with a Q2000 calorimeter (TA Instruments). Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris instrument at a heating rate of 20 °C/min in a N₂ atmosphere. Atomic force microscopy (AFM) was performed in the tapping mode of the Bruker FastScan system. The OFET performances were measured with a Keithley 4200-SCS parameter analyzer in a glovebox under argon.

RESULTS AND DISCUSSION

The crystalline structures of P3BT-b-P3DDT cast from three different solutions, CHCl₃, ODCB, and TCB, were analyzed by 2D-GIXRD (Figure 1). Figure S3 schematically illustrates the 2D-GIXRD measurements. For comparison, homopolymers of P3BT and P3DDT (Figure S4) and a P3BT/P3DDT blend (Figure S5) cast from CHCl₃ solutions were also analyzed by 2D-GIXRD. Their interlayer spacing \( d_{100} \) and \( \pi-\pi \) stacking distances \( d_{010} \) are summarized in Table 2. The P3BT and P3DDT homopolymers exhibited the (100) diffraction in the out-of-plane direction at \( q_z = 5.1 \) and 2.5 nm\(^{-1}\), respectively. The weak (100) diffraction in the in-plane direction can be detected as well (Figure S4). It indicates the dominant edge-on orientation accompanied by the existence of a minor flat-on orientation. In addition, P3DDT has a more flat-on orientation than P3BT. According to the Bragg equation,\(^{16} \) the \( d_{100} \) values of P3BT and P3DDT along the \( q_x \) direction are 12.3 and 25.1 Å, respectively. The (010) diffractions of P3BT and P3DDT in the in-plane direction were observed at \( q_y \) values of 16.0 and 16.4 nm\(^{-1}\), respectively, which correspond to \( d_{010} \) values of 3.9 and 3.8 Å, respectively. A detailed analysis indicated that the (100) diffraction peak of the P3BT homopolymer had a full width at half-maximum (FWHM) of 0.97 nm\(^{-1}\) that was wider than that of the P3DDT homopolymer (100) diffraction peak (0.53 nm\(^{-1}\)). Contrastingly, the FWHM for its (010) diffraction peak (1.36 nm\(^{-1}\)) was narrower than that of the P3DDT (010) diffraction peak (1.55 nm\(^{-1}\)) (Figure S6). As the FWHM reflects the crystallite sizes and disorder within the crystal, an increased ordering as well as the growth of crystallites will lead to a decrease in FWHM.\(^{40-42} \) Thus, the narrower FWHM of the (100) diffraction peak of P3DDT indicates that it possesses a more ordered crystalline structure and a larger crystal size along the (100) direction. Meanwhile, P3DDT has a less ordered crystalline structure along the (010) direction, which may be due to its interlaced, long alkyl side chains.

Among the three P3BT-b-P3DDT BCPs cast from CHCl₃, B35DD65 and B48DD52 exhibited one (100) peak at \( q_z \) values of 3.1 nm\(^{-1}\) (\( d_{100} = 20.3 \) Å) and 3.2 nm\(^{-1}\) (\( d_{100} = 19.6 \) Å), respectively (Figure 1a,b and Table 2). Their \( d_{100} \) values lie between those of the P3BT (\( d_{100} = 12.3 \) Å) and P3DDT (\( d_{100} = 25.1 \) Å) homopolymers, indicating that these two P3BT-b-P3DDT BCPs cocrystallize in a dominant edge-on orientation, in which the \( \pi-\pi \) stacking and the main backbone are parallel to the substrate while the side alkyl chains are normal to the substrate. Their \( d_{010} \) is 3.7 Å with \( q_y \) values of 17.0-17.1  nm\(^{-1}\). In addition, a small fraction of the face-on orientation can also be detected in these BCPs, deducing from the appearance of the very weak (100) diffraction in the in-plane direction. The P3BT-b-P3DDT containing more P3DDT (i.e., B35DD65) showed more fractions of the face-on orientation than that with less P3DDT. In contrast, the P3BT/P3DDT blend displayed two obvious (100) peaks at \( q_z \) values of 5.1 and 2.5 nm\(^{-1}\), corresponding to the individual P3BT and P3DDT crystal domains, respectively (Figure S5). Moreover, the (100) peak of P3DDT has a higher intensity than that of the (100) peak of P3BT, implying a higher crystallinity of
Table 2. Summary of the GIXRD Measurement of P3BT-b-P3DDT with Various Block Ratios (P3BT/P3DDT = 35:65, 48:52, and 67:33), and P3BT and P3DDT Homopolymers in Different States

<table>
<thead>
<tr>
<th>polymer</th>
<th>solvent</th>
<th>Tx 130 °C</th>
<th>Tx 220 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3BT</td>
<td>CHCl3</td>
<td>12.3</td>
<td>16.6/17.4</td>
</tr>
<tr>
<td>P3DDT</td>
<td>CHCl3</td>
<td>25.1</td>
<td>16.6/17.4</td>
</tr>
<tr>
<td>P3BT/P3DDT</td>
<td>CHCl3</td>
<td>20.3</td>
<td>17.0/17.2</td>
</tr>
<tr>
<td>B35DD65</td>
<td>ODCB</td>
<td>19.6</td>
<td>16.5/16.8</td>
</tr>
<tr>
<td>B48DD52</td>
<td>TCB</td>
<td>24.2/17.5</td>
<td>16.8/17.2</td>
</tr>
<tr>
<td>B67DD33</td>
<td>TCB</td>
<td>23.3/12.3</td>
<td>16.8/17.4</td>
</tr>
<tr>
<td>B48DD52</td>
<td>ODCB</td>
<td>24.2/14.1</td>
<td>16.8/17.4</td>
</tr>
<tr>
<td>B67DD33</td>
<td>ODCB</td>
<td>24.2/14.1</td>
<td>16.8/17.4</td>
</tr>
</tbody>
</table>

aComparison of the FWHM values of cocrystals B35DD65, B48DD52, and B67DD33 implies the occurrence of a very weak segregation. By comparing the FWHM values of cocrystals B35DD65, B48DD52, and B67DD33, an increase in the FWHM values with increasing P3BT contents can be observed; specifically, their FWHM values of the (100) diffraction peaks were noted at 0.95 nm⁻¹, 1.03 nm⁻¹ (B48DD52), and 1.54 nm⁻¹ (B67DD33) and their FWHM values of the (010) diffraction peaks were observed at 1.85 nm⁻¹ (B35DD65), 1.98 nm⁻¹ (B67DD33), and 2.09 nm⁻¹ (B67DD33) (Figure S6). Since the FWHM value reflects the crystallite size and disorder within the crystal, the values we obtained imply that reduced ordering and crystallite sizes occur along the (100) and (010) directions in P3BT-b-P3DDT BCPS with an increase in the P3BT block content.

Compared to the CHCl3 solutions, P3BT-b-P3DDT thin films cast from ODCB solutions exhibited some differences. B35DD65 retained a single (100) diffraction peak with increased intensity compared to that of the (100) diffraction peak of the same BCP in CHCl3, suggesting the retention of a crystalline structure with increased crystallinity (Figure 1c,d and Table 2). However, for B48DD52, in addition to the diffraction peak of the cocrystal at a qz of 3.6 nm⁻¹, another peak appeared at a qz of 2.6 nm⁻¹, which is attributed to the P3DDT crystallization (Figure 1c,d and Table 2). This indicates the appearance of microphase separation in B48DD52 cast from ODCB, which was not seen for the cocrystals formed in the same BCP cast from CHCl3. Such microphase separation was intensified in B67DD33, which contains more P3BT than P3DDT. Specifically, it demonstrated two peaks at qz values of 5.1 and 2.7 nm⁻¹, representing individual P3BT and P3DDT crystal domains, respectively (Figure 1c,d and Table 2). The microphase-separated degree of B67DD33 cast from ODCB was also higher than the same BCP cast from CHCl3.

When these three P3BT-b-P3DDT BCPS were cast from TCB, the tendency of microphase separation between the P3BT and P3DDT blocks is more obvious. Even B35DD65 exhibited two (100) diffraction peaks at qz = 3.4 and 2.5 nm⁻¹, corresponding to the P3BT-b-P3DDT cocrystals and P3DDT crystals, respectively (Figure 1e,f and Table 2). For the other two BCPS, B48DD52 retained the coexistence of a P3BT-b-P3DDT cocrystal and P3DDT crystal domains (Figure 1e,f and Table 2). B67DD33 exhibited three (100) diffraction peaks at qz = 2.6, 3.9, and 5.1 nm⁻¹, corresponding to the P3DDT crystal, P3BT-b-P3DDT cocrystal, and P3BT crystal, respectively (Figure 1e,f and Table 2). In addition to the three (100) diffraction peaks, B67DD33 also exhibited one more peak at a qz of 6.0 nm⁻¹, which was assigned to the (200) diffraction peak of the P3DDT crystal.

From the above results, it is clear that both the block ratio and solvent have significant effects on the microphase-
Separated and cocrystalline behavior of P3BT-b-P3DDT. It is reported that three requirements need to be met to form polymer cocrystals: similar chemical structures, similar crystallization kinetics, and comparable potential energies. Due to the largely different side-chain lengths of P3BT and P3DDT, the two blocks possess greatly different crystallization rates. They tend to microphase separate from each other during the crystallization process with the P3BT block crystallizing first due to its lower solubility, followed by the crystallization of the P3DDT block. However, when the three P3BT-b-P3DDT BCPs are cast from different solvents, the crystalline structure of the BCPs is predominantly influenced by the solvent evaporation process. As CHCl$_3$ evaporates very fast, P3BT and P3DDT have no time to microphase separate from each other and crystallize individually. As a result, these BCPs with varied block ratios crystallize together to form cocrystals, with the exception of B67DD33, which also displayed very weak P3BT cocrystals when cast from TCB. Figure 2 depicts the formation of the P3BT-b-P3DDT cocrystalline structure during solvent evaporation. P3AT is crystallization includes two steps, i.e., coil-to-rod conformational transition and subsequent crystallization between rods. P3BT-b-P3DDT chains are semiflexible in CHCl$_3$, which is a good solvent for both blocks. During the continuous solvent evaporation, the concentration of the BCP solution increased and their chains gradually changed to planar and rigid due to the reduced solubility. Subsequently, π-π stacking between these rigid BCP chains occurred, resulting in P3BT-b-P3DDT cocrystals.

When these BCPs were cast from ODCB and TCB with much slower evaporation rates, both the P3BT and P3DDT chains had more time to restructure themselves to microphase separate from each other and crystallize more sufficiently. Therefore, microphase separation of P3BT-b-P3DDT occurred in different degrees and was influenced by the block ratio. Comparing the three BCPs cast from the same ODCB or TCB solvent, the increase of the P3BT content in the BCPs favors the microphase separation of P3BT-b-P3DDT, i.e., the BCP containing a higher P3BT content has a higher microphase-separated degree than the BCP with a lower P3BT content. For the two BCPs cast from ODCB or TCB, B35DD65 and B48DD52, they contained P3BT-b-P3DDT cocrystals or were accompanied with P3DDT crystal domains; whereas, B67DD33 formed individual P3BT and P3DDT crystal domains when cast from ODCB or coexisted with P3BT-b-P3DDT cocrystals when cast from TCB. Thermal annealing is a commonly used strategy to control the crystalline ordering and size of conjugated polymers. In this context, P3BT-b-P3DDT thin films cast from a CHCl$_3$ solution were chosen for the following thermal annealing. Considering the effect of annealing temperature on the crystalline structure of conjugated polymers, two different temperatures were used. One was 150 °C, which is commonly used for P3ATs. This temperature is close to the melting point of the P3DDT component ($T_m = 144$ °C for $M_{n,P3DDT} = 11.6$ K) but is much lower than that of the P3BT component ($T_m = 271$ °C for $M_{n,P3BT} = 12.5$ K) (Figure S7). The other annealing temperature used was 220 °C, which is much higher than the melting point of the P3DDT block and lower than the melting point of the P3BT block. TGA measurements indicated that these P3BT-b-P3DDT BCPs exhibited excellent thermal stability during the 220 °C annealing process and their degradation with 5% weight loss occurred in the range of 450−477 °C (Figure S8). Annealing at higher temperatures (220 vs 150 °C) can endow the P3BT and P3DDT blocks in BCPs with higher chain mobilities and may yield different crystalline structures in the BCPs. After thermal annealing at 150 °C, the three P3BT-b-P3DDT BCPs cast from CHCl$_3$ retained their crystalline
structures with increased crystallinity deduced from the increased intensity of their (100) diffractions (Figure 3a,b). The FWHM values of both their (100) and (010) diffraction peaks became narrower, implying improved ordering and crystallite sizes along both directions after annealing at 150 °C (Figure S6). Similar to their as-cast samples, B35DD65, B48DD52, and B67DD33 after annealing exhibited increased FWHM values of their (100) and (010) diffraction peaks with an increase in the P3BT content; specifically, 0.69 nm\(^{-1}\) (B35DD65), 0.77 nm\(^{-1}\) (B48DD52), and 1.37 nm\(^{-1}\) (B67DD33) for their (100) diffraction peaks and 1.42 nm\(^{-1}\) (B35DD65), 1.45 nm\(^{-1}\) (B48DD52), and 1.51 nm\(^{-1}\) (B67DD33) for their (010) diffraction peaks (Figure S6).

Control samples of the P3BT and P3DDT homopolymers also exhibited increased ordering and crystallite sizes with narrower FWHM values after annealing at 150 °C, namely, which are 0.56 nm\(^{-1}\) (P3BT) and 0.17 nm\(^{-1}\) (P3DDT) for their (100) peaks and 0.95 nm\(^{-1}\) (P3BT) and 1.23 nm\(^{-1}\) (P3DDT) for their (010) peaks (Figure S6).

Upon high heating at 220 °C, all three P3BT-b-P3DDT BCPs displayed different crystalline structures. The previously observed (100) peaks of the corecrysals at qz values of 3.1–3.4 nm\(^{-1}\) for the P3BT-b-P3DDT BCPs disappeared completely.

Two new separate (100) peaks were shown at qz values of 2.5–2.6 and 4.9–5.0 nm\(^{-1}\) for these three BCPs, corresponding to the individual crystal domains of P3DDT and P3BT blocks, respectively (Figure 3c,d). This suggests that the P3BT-b-P3DDT corecrysals were damaged by the heating at 220 °C and microphase separation between P3BT and P3DDT occurred.

Naturally, the intensity of the (100) peak of the P3DDT component is stronger in B35DD65 and B48DD52 because it is the main component, while the P3BT (100) peak is more intense in B67DD33 where it is the main component (Figure 3d). It is noted that a series of P3BT-b-P3HT BCPs were reported to retain corecrysals upon high-temperature treatment at 220–250 °C and microphase separation could only occur after a two-step thermal treatment, which is quite different from P3BT-b-P3DDT in this report. Due to their alkyl side-chain lengths being similar, the chain mobilities of P3BT and P3HT are also similar when annealed at 220–250 °C. Therefore, they could not separate from each other and remained corecrysals. The P3BT-b-P3HT BCPs underwent a two-step thermal treatment comprising heating around their melting point, followed by heating at 150 °C for the second round. This endowed the P3BT and P3HT chains with varying chain mobilities. As such, they underwent microphase separation to form their respective P3BT and P3HT crystal domains. It is known that for polythiophene-based BCPs, only the differences in their alkyl chain length or topology (e.g., linear or branched) can endow them with different physical properties (e.g., solubility, melting point, crystalline behavior, and self-assembled behavior). Due to their greatly different

Figure 3. (a, c) 2D-GIXRD and (b, d) D-GIXRD images of the thin films of P3BT-b-P3DDT with various block ratios (P3BT/P3DDT = 35:65, 48:52, and 67:33) after annealing at (a, b) 150 °C and (c, d) 220 °C, respectively. The qz and qx,y parameters indicate the out-of-plane and in-plane directions, respectively.

Figure 4. Small-angle X-ray scattering (SAXS) curves of P3BT-b-P3DDT samples with different block ratios as-cast or after annealing at 150 and 220 °C: (a) B35DD65 (P3BT/P3DDT = 35:65), (b) B48DD52 (P3BT/P3DDT = 48:52), and (c) B67DD33 (P3BT/P3DDT = 67:33).
alkyl side-chain lengths, P3BT-b-P3DDT BCPs show much higher microphase-separation abilities than those of the P3BT-b-P3HT BCPs. All P3BT-b-P3DDT BCP samples of various P3BT/P3DDT block ratios could undergo microphase separation after heating at 220 °C without the need for a two-step thermal treatment to trigger the microphase separation.

To further elucidate the crystalline structure of BCPs, SAXS and DSC were conducted to analyze these BCP samples at different processing stages. For the SAXS measurement, no scattering peak was detected for B35DD65, B48DD52, or B67DD33 cast from CHCl₃ after annealing at 150 °C, indicating that they are in a miscible state (Figure 4).

Although very weak microphase separation was observed in B67DD33 by 2D-GIXRD, it did not exhibit a characteristic scattering peak in SAXS at a much larger scale. When B35DD65, B48DD52, and B67DD33 underwent annealing at 220 °C, they showed a clear scattering peak at ~0.20 nm⁻¹. This implies the presence of microphase-separated domains with a size of ~31.4 nm. This is consistent with the 2D-GIXRD results that microphase separation occurred for these three BCPs to form respective P3BT and P3DDT crystal domains after annealing at 220 °C.

Subsequently, the DSC results of B35DD65, B48DD52, and B67DD33 at different stages were elucidated. The three BCPs in their three different states (as-cast after preparation from CHCl₃ and after annealing at 150 and 220 °C) were scraped off and their first heating cycles were compared (Figure 5). DSC results of P3BT, P3DDT, and the P3BT/P3DDT blend were analyzed for comparison (Figure S7). Although the three P3BT-b-P3DDT BCPs formed cocrysalts in the as-cast state, the DSC heating melted the cocrysalts and induced their microphase separation. B67DD33 displayed an endothermic peak in the range of 271–277 °C for the three different states that were assigned to the melting of the P3BT crystal domains.

It also exhibited additional peaks at 190 and 154 °C for the samples annealed at 150 and 220 °C, respectively, which were due to the melting of P3DDT. Due to the lower crystallinity of the minor P3DDT block, the as-cast sample of B67DD33 did not exhibit an endothermic peak of P3DDT. B48DD52 exhibited two endothermic peaks in the ranges of 156–198 and 266–270 °C in the three different states, which corresponded to the melting of the P3DDT and P3BT crystal domains, respectively. Notably, the B48DD52 sample after annealing at 220 °C had a much lower melting point for P3DDT (i.e., 156 °C) than those of the other two states (195 °C for the as-cast state and 198 °C for the 150 °C-annealed state). This is because the microphase-separated degree of B48DD52 in the two samples during the DSC heating process was lower than the already formed, microphase-separated 220 °C-annealed sample. Therefore, the covalently connected P3BT block increased the melting point of the P3DDT in the former case. This can also be proven from the DSC results of the P3DDT homopolymer and the P3BT/P3DDT blend without the covalent bond. In these two systems, P3DDT exhibited an even lower melting point, 144 °C for the homopolymer and 146 °C for the blend (Figure S7). Similarly, B35DD65 displayed two peaks in all three states and the melting point of 220 °C-annealed P3DDT (i.e., 160 °C) was much lower than those of the other two states (193 °C for the as-cast state and 196 °C for the 150 °C-annealed state).

The reason for P3BT-b-P3DDT retaining a cocrysal structure after annealing at 150 °C while microphase-separating after annealing at 220 °C is discussed. During heating to 150 °C, the chain mobilities of P3BT and P3DDT increased. This allowed for more effective crystallization, leading to more ordered crystalline structures with narrower FWHM values for both the (100) and (010) diffraction peaks compared to those of their as-cast states. However, this annealing temperature is below the melting points of both blocks. As a result, the P3BT and P3DDT blocks have comparable chain mobility, which is insufficient to render the microphase separation of P3BT-b-P3DDT, even though these two blocks are thermodynamically immiscible. In contrast, under annealing at a higher temperature (220 °C), the chain mobility of both P3BT and P3DDT is increased, with that of P3DDT being much higher than that of P3BT. Therefore, they tend to reorganize themselves to a more thermodynamically stable state. The P3DDT chains with lower melting temperatures in the cocrysalts were melted and escaped from the cocrysalts, while the P3BT chains retained their rigid characteristics owing to their higher melting temperature.

Then, P3BT crystallized first to form P3BT crystal domains. Subsequently, P3DDT chains crystallized during the cooling stage. This led to the formation of the respective P3BT and P3DDT crystal domains. It can be expected that microphase separation of P3BT-b-P3DDT can occur when annealing above the melting points of both blocks. However, high-temperature annealing is unfavorable to the device performance. The possible transition from P3BT-b-P3DDT cocrysalization to microphase-separated individual P3BT and P3DDT crystal domains...
domains after 220 °C-annealing is described schematically in Figure 6.

To correlate the P3BT-b-P3DDT BCPs with different structures and their charge mobilities, OFETs in a top-contact bottom-gate configuration were crafted. Although the spin-coated BCP thin films for the OFETs are much thinner than the solvent-cast thin films for 2D-GIXRD, they possessed similar crystalline structures. However, a weaker signal was obtained for the spin-coated thin films (Figure S9). It is known that P3ATs can pack into edge-on, face-on, and end-on lamellar orientations. As charge carriers transport from the source to the drain in OFETs, the edge-on orientation is favorable. Usually, charge mobilities increase with an increase in the molecular weight of P3HT. This is because charge carriers can transport farther along longer chains, and they provide charge carriers with more chances to hop to other chains. In this work, all three P3BT-b-P3DDT BCPs were packed into dominant edge-on orientations, which favors the charge transport. First, the charge-transport properties of various P3BT-b-P3DDT BCPs spin-coated from CHCl3 and ODCB solutions were compared, with their transfer and output curves given in Figures 7, S10, and S11. According to the formula, the three P3BT-b-P3DDT BCPs prepared from CHCl3 solutions displayed average charge mobilities of 2.44 × $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ (B35DD65), 3.91 × $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ (B48DD52), and 5.56 × $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ (B67DD33) (Table 3). It is known that in ordered crystalline domains, charge carriers can transport along the three directions, the directions of the main backbone, π-π stacking, and alkyl side chains. Since P3BT has smaller $d_{100}$ and $d_{010}$ values than those of P3DDT, the former (3.60 × $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$) possesses higher charge mobilities than the latter (3.75 × $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$) (Table 3). Naturally, for P3BT-b-P3DDT BCPs, the BCP with a higher P3BT content exhibited higher charge mobility, among which B67DD33 exhibited the highest value of 4.36 × $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$. When the three BCPs were prepared from ODCB, they all exhibited higher mobilities of 1.76 × $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ (B35DD65), 2.54 × $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ (B48DD52), and 3.12 × $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ (B67DD33) (Table 3). Generally, conjugated polymers with higher crystallinity are assumed to facilitate charge transport. As the P3BT-b-P3DDT BCPs processed from ODCB have higher crystallinity, it is not surprising that they exhibited higher charge mobilities than the BCPs processed from CHCl3. The charge mobilities of P3BT-b-P3DDT processed from ODCB are comparable to the mobilities of other polythiophene and polyselenophene thin films (Figure S12). The AFM study shows the three P3BT-b-P3DDT BCPs processed from both CHCl3 and ODCB solutions, exhibiting a featureless and flat surface (Figure S13). The root-mean-square (RMS) roughness values of B35DD65, B48DD52, and B67DD33 prepared from CHCl3 are 1.05, 0.92, and 1.75 nm, respectively, which are slightly smaller than those of the same BCPs prepared from ODCB, i.e., 1.26, 1.04, and 1.79 nm, respectively. The OFET performances of the three P3BT-b-P3DDT BCPs prepared from CHCl3 solutions were analyzed after heating, with their transfer and output curves given in Figures 8, S14, and S15. After 150 °C-annealing, B35DD65, B48DD52, and B67DD33 all displayed slightly increased charge mobilities of

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Figure 6. Schematic of the transition from the cocrystals of P3BT-b-P3DDT to the respective P3BT and P3DDT crystals during 220 °C-annealing. First, the P3DDT blocks melt and escape from the cocrystalline structure. Simultaneously, the P3BT blocks with a higher melting point remain rigid and crystallize to form P3BT crystal domains (top right). Subsequently, P3DDT only crystallizes during the cooling process to form P3DDT crystal domains (bottom). a-axis: the alkyl side-chain direction ((100) direction) and c-axis: the main backbone direction ((001) direction).

Figure 7. (a, c) OFET transfer and (b, d) output curves fabricated using B67DD33 thin films spin-coated from (a, b) CHCl3 and (c, d) ODCB, respectively. $V_{DS} = -60$ V. The inset in (a) is a schematic of the OFET device used for measurements.
Table 3. Summary of OFET Performance of the Three P3BT-b-P3DDT BCPs (P3BT/P3DDT = 35:65, 48:52, and 67:33), and P3BT and P3DDT Homopolymers under Different Conditions

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Solvent</th>
<th>Conditions</th>
<th>$\mu_{\text{on}}$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\mu_{\text{off}}$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$I_{\text{on}}/I_{\text{off}}$</th>
<th>$V_{\text{TH}}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3BT</td>
<td>CHCl$_3$</td>
<td>as-cast</td>
<td>$3.34 \times 10^{-2}$</td>
<td>$3.60 \times 10^{-2}$</td>
<td>$10^2$-$10^3$</td>
<td>21-28</td>
</tr>
<tr>
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<td>as-cast</td>
<td>$3.03 \times 10^{-3}$</td>
<td>$3.75 \times 10^{-3}$</td>
<td>$10^2$-$10^3$</td>
<td>25-33</td>
</tr>
<tr>
<td>B35DD65</td>
<td>CHCl$_3$</td>
<td>as-cast</td>
<td>$3.99 \times 10^{-3}$</td>
<td>$2.44 \times 10^{-3}$</td>
<td>$10^2$-$10^4$</td>
<td>25-34</td>
</tr>
<tr>
<td>B48DD52</td>
<td>CHCl$_3$</td>
<td>as-cast</td>
<td>$2.10 \times 10^{-2}$</td>
<td>$1.76 \times 10^{-2}$</td>
<td>$10^3$-$10^4$</td>
<td>10-14</td>
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<tr>
<td>B67DD33</td>
<td>CHCl$_3$</td>
<td>as-cast</td>
<td>$5.92 \times 10^{-3}$</td>
<td>$3.91 \times 10^{-3}$</td>
<td>$10^2$-$10^4$</td>
<td>22-35</td>
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<tr>
<td></td>
<td>ODCB</td>
<td>as-cast</td>
<td>$2.86 \times 10^{-3}$</td>
<td>$2.54 \times 10^{-2}$</td>
<td>$10^2$-$10^6$</td>
<td>4-8</td>
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<tr>
<td></td>
<td>ODCB</td>
<td>150 °C</td>
<td>$8.38 \times 10^{-3}$</td>
<td>$6.06 \times 10^{-3}$</td>
<td>$10^2$-$10^4$</td>
<td>27-36</td>
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<tr>
<td></td>
<td></td>
<td>220 °C</td>
<td>$1.36 \times 10^{-3}$</td>
<td>$1.12 \times 10^{-3}$</td>
<td>$10^3$-$10^5$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CHCl$_3$</td>
<td>as-cast</td>
<td>$7.30 \times 10^{-3}$</td>
<td>$5.56 \times 10^{-3}$</td>
<td>$10^2$-$10^4$</td>
<td>25-38</td>
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<tr>
<td></td>
<td>CHCl$_3$</td>
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<td>$4.36 \times 10^{-2}$</td>
<td>$3.12 \times 10^{-2}$</td>
<td>$10^2$-$10^4$</td>
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<tr>
<td></td>
<td>ODCB</td>
<td>150 °C</td>
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<td>$1.06 \times 10^{-3}$</td>
<td>$10^2$-$10^4$</td>
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</tbody>
</table>

$^a$Average charge carrier mobility measured from at least 12 devices. $^b$On/off ratio of current. $^c$Threshold voltage.

Figure 8. (a, c) OFET transfer and (b, d) output curves fabricated using B67DD33 thin films spin-coated from CHCl$_3$, followed by (a, b) 150 °C-annealing and (c, d) 220 °C-annealing, respectively. $V_{\text{GS}} = -60$ V.

In summary, the crystalline and microphase-separated behaviors of a set of P3BT-b-P3DDT BCPs have been tailored by modulating the block ratios, solvents, and heating processes. The as-cast BCPs processed from CHCl$_3$ show the formation of P3BT-b-P3DDT cocrystals in an edge-on orientation or the coexistence of P3BT-b-P3DDT cocrystals and P3BT crystals depending on the P3BT/P3DDT block ratio. The increase in the P3BT content in the BCPs and slower solvent evaporation when processed from ODCB and TCB favor microphase separation to different degrees. One of the merits of using P3BT-b-P3DDT BCPs is the subtle balance between their cocrystallization and microphase separation, which can be tuned, while the P3BT/P3DDT blend displays only phase separation and separated crystal domains. Upon 150 °C annealing, the crystalline structures of the P3BT-b-P3DDT BCPs are retained, with increased crystallinity. In contrast, high heating at 220 °C yields distinct microphase separation of P3BT-b-P3DDT to form individual P3BT and P3DDT crystal domains. The relationship between P3BT-b-P3DDT with varying crystalline structures and their charge-transport characteristics was studied, showing the synergistic effects of the block ratios, film crystallinity, and annealing temperature on the charge mobilities. Overall, this study enriches the fundamental knowledge of the interplay between cocrystallization and microphase separation in conjugated rod–rod BCPs. The knowledge achieved from this work may facilitate their applications in diverse optoelectronic devices.
ASSOCIATED CONTENT

Supporting Information

Detailed characterization of P3BT-b-P3DDT BCPs, P3BT, and P3DDT homopolymers; GIXRD and AFM images; TGA and DSC data; and charge mobility comparison and their transfer and output curves (PDF)

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Notes
The authors declare no competing financial interest.

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