Crystallization and Microphase Morphology of Side-Chain Cross-Linkable Poly(3-hexylthiophene)-block-poly[3-(6-hydroxy)hexylthiophene] Diblock Copolymers

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ABSTRACT: A series of thermal cross-linkable poly(3-hexylthiophene)-b-poly[3-(6-hydroxy)hexylthiophene] (P3HT-b-P3HHT) diblock copolymers (BCPs) with different block ratios were synthesized to explore the effect of cross-linking on crystallization and microphase morphology of polymer films. The obtained BCPs formed microphase separation structure with a lamellar packing due to the different polarity of the two blocks. Though, after thermal annealing at 200 °C, the cross-linking of P3HHT block damaged the microphase separation structure and the roughness of films increased, the crystalline structure still remained “edge on”, and the degree of crystallization greatly improved due to the rearrangement of the un-cross-linked parts. Based on the weight loss of the cross-linking reaction, the degree of cross-linking was calculated, and the ductility of film was characterized by the crack onset strain. Then a quantitative correlation between the ductility of film and the degree of cross-linking was established. It proved that cross-linking during thermal annealing at 200 °C can both improve the ductility of film and the degree of crystallization, which is a promising way to develop flexible electronic devices.

INTRODUCTION

Crystallization in BCPs has attracted considerable attention,1–3 since the crystallization is an important process to affect the solid state structure and morphology in BCPs. Meanwhile, BCPs can form well-defined one-, two-, or three-dimensional microphase-separated nanostructures driven by the thermodynamic incompatibility between the different blocks.4,5 As a result, when one or more blocks in the BCPs can crystallize, the final structure and morphology are the result of the competition between phase separation and crystallization. For the case of BCPs with one crystalline block, which is the simplest case of crystallizable BCPs, it has been fully investigated.6 The resulting structure is dependent on the order-disorder transition temperature (T_{ODT}) of the BCP, the crystallization temperature (T_c) of the crystalline block, and the glass transition temperature (T_g) of the amorphous block.

Compared with the crystalline-amorphous BCPs, the crystallization of one block may affect the crystallization and morphology of the second block in double-crustalline BCPs, in which the crystallization and microphase separation become more complicated.7 In most double-crustalline BCP systems, the melting temperature (T_m) of one block is far from the other. During cooling, the block with higher T_m crystallizes first and results in a specific structure. Then the microphase separation and the crystallization of the block with lower T_m may be changed. When the melting temperatures of the two blocks are close enough, the two blocks can crystallize at the same time, and the crystallization behavior become more complicated. Of the research on double-crustalline BCPs, a large focus has been put on the biomaterials, such as poly(ethylene oxide)-b-poly(ε-caprolactone) (PEO-b-PCL),7,8 poly(ε-lactide)-b-poly(ε-caprolactone) (PLLA-b-PCL),6,9 and poly(ε-lactide)-b-poly(ethylene oxide) (PLLA-b-PEO),10,11 etc. These double-crustalline BCPs belong to coil–coil type, which are composed of two flexible blocks. In contrast, rod–rod BCPs (such as DNA, polypeptide, and conjugated polymers) with two different rigid blocks have different phenomenon. Because of the rigid-rod structure of the rod-like blocks, rod–rod diblock copolymers preferably form low-curvature vesicular in dilute solution and lamellar nanostructures in concentrated solution and solid state.12

Among the rod–rod BCPs, all-conjugated polymers, especially the poly(3-alkylthiophene)s (P3ATs)-based BCPs, have attracted considerable attention because of their potential for the development of low cost, large area, and flexible electronic devices, since they have remarkable electronic activity and can form well-controlled nanostructures.13 Generally, the final nanostructures are determined by the microphase separation and the crystallization of the P3AT-based BCPs,14–17 which is important to improve the performance.

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of electronic devices. For example, poly(3-butylthiophene)-b-poly(3-hexylthiophene) (P3BT-b-P3HT) forms cocrystallization, while poly(3-butylthiophene)-b-poly(3-octylthiophene) (P3BT-b-P3OT), poly(3-butylthiophene)-b-poly(3-dodecylthiophene) (P3BT-b-P3DPT), and poly(3-hexylthiophene)-b-poly(3-dodecylthiophene) (P3HT-b-P3DDT) microphase separate into two crystal domains when the side chain length of the two blocks is different more than two carbon atoms. Poly[(3-hexylthiophene)-b-(3-(2-ethylhexyl)thiophene)] (P3HT-b-P3EH) with a branched side chain block can also obtain highly ordered molecular packing and small microphase separation structure because of the steric hindrance of side chain. Moreover, the morphology and crystallinity are various with different annealing processes due to the competition between the microphase separation and crystallization. Although it is convenient to form well-ordered morphology, the conjugated BCPs are unstable when exposed to solvent, air, and thermal treatment, and these problems limit their practical applications.

Thus, there are many methods that have been developed to improve the stability of the conjugated BCPs devices, such as the introduction of compatibilizers and the development of cross-linkable systems. Among these methods, the synthesis of cross-linkable polythiophenes is a convenient approach to get solvent resistance and thermal stability. There are mainly two methods to develop cross-linkable systems. One method is the development of thermal cross-linkable polythiophenes. For instance, vinyl-functionalized and acrylate-functionalized polythiophene can easily form network structure by cross-linking during thermal annealing to stabilize the morphology of bulk heterojunction solar cells because the formation of large aggregations of PCBM is prevented after thermal cross-linking. The other method is the synthesis of photo-cross-linkable polythiophenes. For example, bromine-functionalized and azide-functionalized polythiophenes can cross-link under UV treatment. Compared to thermal cross-linking, photo-cross-linking can develop the desired morphology by thermal annealing before cross-linking, which is helpful to tune the microstructure. Furthermore, cross-linkable conjugated polymers have good potential application in flexible devices. Generally, the methods to develop flexible devices are introducing buckling structure to the films and developing polymer nanofibrils. Obviously, cross-linking by thermal or photo is more convenient than these methods. However, the introduction of cross-linking bridges in conjugated polymers usually disturb their molecular packing, which will degrade their performance, and the effect of cross-linking on crystallization and microphase separation of conjugated polymers is relatively unknown. Therefore, the study of crystallization and microphase separation of cross-linkable conjugated BCPs remains a challenge.

In this study, we have chosen P3HT as a model system to introduce hydroxyl cross-linkable units because regioregular P3HT is the most widely investigated polymer semiconductor for organic electronics. Meanwhile, hydroxyl groups are cross-linked during thermal annealing with releasing water, which can be used as a parameter to calculate the degree of cross-linking. Herein, we synthesized the diblock copolymers, poly(3-hexylthiophene)-b-poly[3-(6-hydroxy)hexylthiophene] (P3HT-b-P3PHHT) with different block ratios via modified GRIM polymerization. Because of the difference of polarity between the two blocks, the P3HT-b-P3HHT BCPs preferred to microphase separate into two crystalline domains with “edge on” structure formed by the independent crystallization of each block. The AFM images revealed the formation of clear microphase-separated lamellar structure and nanofibers, and the size of these structures depended on their compositions. When the P3HHT block is cross-linked at melt state, its chains cannot further reorganize into well-ordered crystalline structure and the degree of crystallinity of the BCPs is decreased. When the P3HHT block is cross-linked at the temperature below its T, the crystalline structure still remains “edge on”, and the degree of crystallinity is improved. However, the roughness of their film surfaces increases, and the lamellar structure and nanofibers are damaged. As the performance of organic devices is affected by both the microstructure and the degree of crystallinity of the films, then this result can illuminate the performance of cross-linkable P3HT/phenyl-C, C2-butyric acid methyl ester (PCBM) systems after cross-linking is slightly lower than that of original P3HHT/PCBM system in many studies. Based on the weight loss of the cross-linking reaction, the conversion of the cross-linking reaction was calculated to detect the degree of cross-linking, and the ductility of film was characterized by the crack onset strain of films. Then the kinetics of the cross-linking reaction and the quantitative correlation between the ductility of film and the degree of cross-linking were explored. It proved that cross-linking during thermal annealing at 200 °C can both improve the ductility of film and the degree of crystallization simultaneously, and it is a promising way to develop flexible electronic devices.

## EXPERIMENTAL SECTION

**Materials.** The monomers 2-bromo-5-iodo-3-hexylthiophene (M) and 2-bromo-5-iodo-3-[6-(tetrahydropyran-2-oyl)hexyl]thiophene (M) were synthesized according to the literature. M was synthesized from the coupling of 3-bromothiophene and tetrahydropyran (THP)-protected 6-bromo-1-hexanol, and then the procedure was similar to M. Tetrahydrofuran (THF) was dried over sodium/benzophenone under an inert atmosphere and distilled freshly before use. Isopropylmagnesium chloride (i-PrMgCl) (2.0 M solution in THF; from Aldrich), [1,3-bis(diphenylphosphino)-propane] dichlororinickel(II) (Ni(dppp)Cl) (99%, from Aldrich), and pyridine (99%, from Aldrich) were all used as received. All other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received.

**Characterization.** 1H NMR spectra in CDCl3 and pyridine-d5 were collected on a DCM 500 MHz system. Molecular weights of the polymers were estimated by an Agilent 1100 gel permeation chromatography (GPC) system using THF as the eluent against polystyrene standards with a UV detector. UV–vis absorption spectra were recorded on PerkinElmer Lambda 750 UV–vis spectrophotometer. FTIR measurements were carried out on a Nicolet 6700 spectrometer. Differential scanning calorimeter (DSC) was performed using TA DSC Q2000 at a heating rate of 10 °C/min under nitrogen flow. Thermogravimetric analysis (TGA) was performed on TA Q5000 under nitrogen flow. X-ray diffraction data were collected on PANalyticalX’Pert PRO X-ray diffractometer using Cu Kα radiation (λ = 1.541 Å) operating at 40 kV and 40 mA. Grazing-incidence X-ray diffraction (GIXRD) experiments were carried out at the BL14B1 beamline of Shanghai Synchrotron Radiation Facility (SSRF) in Shanghai, China, with a fixed wavelength of 1.24 Å and a sample-to-detector distance of 5 m.

**Synthesis of Poly(3-hexylthiophene) (P3HT).** 2-Bromo-5-iodo-3-hexylthiophene (M) (7.46 g, 20 mmol) was added into a predried round-bottom flask with side tubes and then evacuated under reduced pressure to remove water and oxygen inside. After the addition of dry THF (150 mL), the solution was stirred at 0 °C, and then 2 M solution of i-PrMgCl in THF (10 mL, 20 mmol) was added via a
SYNTHESIS OF POLY[3-(6-HYDROXY)HEXYLTHIOPHENE] (P3HHT)

The feed molar ratios of M1 to M2 in the polymerization of P3HT-b-P3HHT were 3:1, 1:1, and 1:3. The typical synthesis procedure of P3HT-b-P3THPHT BCP with the feed molar ratio of 1:1 was as follows: two round-bottom flasks with side tubes (flask A and B) were dried by heating under reduced pressure and cooled to room temperature. M1 (1.50 g, 4 mmol) was added into flask A and then evacuated under reduced pressure to remove water and oxygen inside. After the addition of dry THF (40 mL), the solution was stirred at 0 °C, and then 2 M solution of i-PrMgCl in THF (2 mL, 4 mmol) was added via a syringe followed by stirring at 0 °C for 30 min. Subsequently, Ni(dppp)Cl2 catalyst (0.0434 g, 0.08 mmol) was added in one portion, and the mixture was reacted at 35 °C for 7 h. The reaction was quenched with HCl (aq) (50 wt %, 200 mL), and the product was precipitated in methanol. The residue was filtered and washed by water, methanol, and hexane. The resulting polymer (1.2122 g, 69% yield, Mw = 18 500 g/mol, PDI = 1.36) as a purple solid. P3HT-b-P3THPHT BCPs with the molar ratios of 1:3 and 3:1 were synthesized in the same way to give the purple solid (1.1212 g, 69% yield, Mw = 18 500 g/mol, PDI = 1.36) as a purple solid. P3HT-b-P3HHT BCP with the feed molar ratios of 3:1 was as follows: two round-bottom flasks with side tubes (flask A and B) were dried by heating under reduced pressure and cooled to room temperature. M1 (1.50 g, 4 mmol) was added into flask A and then evacuated under reduced pressure to remove water and oxygen inside. After the addition of dry THF (40 mL), the solution was stirred at 0 °C, and then 2 M solution of i-PrMgCl in THF (2 mL, 4 mmol) was added via a syringe followed by stirring at 0 °C for 30 min. Subsequently, Ni(dppp)Cl2 catalyst (0.0434 g, 0.08 mmol) was added in one portion, and the mixture was reacted at 35 °C for 7 h. The reaction was quenched with methanol (20 mL), and the product was precipitated in methanol. The residue was filtered and washed by sequential Soxhlet extraction using methanol, hexane, and chloroform. Then the chloroform fraction was collected and dried to yield the final polymer (1.9714 g, 59% yield) as a purple solid. Mw = 16 300 g/mol, polydispersity index (PDI) = 1.12, as compared to polystyrene standards. 1H NMR (500 MHz, CDCl3, δ ppm): 6.98 (s, 1H), 4.57 (s, 1H), 3.85 (m, 1H), 3.75 (m, 1H), 3.48 (m, 1H), 3.40 (m, 1H), 2.81 (t, 2H), 1.25–1.70 (m, 8H), 0.87 (t, 3H).

SYNTHESIS OF DIBLOCK POLY[3-HEXYLTIOPHENE]-b-POLY[3-(6-HYDROXY)HEXYLTHIOPHENE] (P3HT-b-P3HHT)

The feed molar ratios of M1 to M2 in the polymerization of P3HT-b-P3HHT BCP were 3:1, 1:1, and 1:3. The typical synthesis procedure of P3HT-b-P3THPHT BCP with the feed molar ratio of 1:1 was as follows: two round-bottom flasks with side tubes (flask A and B) were dried by heating under reduced pressure and cooled to room temperature. M1 (1.50 g, 4 mmol) was added into flask A and then evacuated under reduced pressure to remove water and oxygen inside. After the addition of dry THF (40 mL), the solution was stirred at 0 °C, and then 2 M solution of i-PrMgCl in THF (2 mL, 4 mmol) was added via a syringe followed by stirring at 0 °C for 30 min. Subsequently, Ni(dppp)Cl2 catalyst (0.0434 g, 0.08 mmol) was added in one portion, and the mixture was reacted at 35 °C for 7 h. The reaction was quenched with methanol (20 mL), and the product was precipitated in methanol. The residue was filtered and washed by sequential Soxhlet extraction using methanol, hexane, and chloroform. Then the chloroform fraction was collected and dried to yield the final polymer (1.9714 g, 59% yield) as a purple solid. Mw = 16 300 g/mol, polydispersity index (PDI) = 1.12, as compared to polystyrene standards. 1H NMR (500 MHz, CDCl3, δ ppm): 6.98 (s, 1H), 4.57 (s, 1H), 3.85 (m, 1H), 3.75 (m, 1H), 3.48 (m, 1H), 3.40 (m, 1H), 2.81 (t, 2H), 1.25–1.70 (m, 8H), 0.87 (t, 3H).
Synthesis of Poly(3-hexylthiophene)-b-poly[(6-hydroxy)-
3-ethylphenylene] (P3HT-b-P3HHT). The typical synthesis procedure
of P3HT-b-P3HHT BCP was as follows: P3HT-b-P3THPHT with the
feed molar ratio of 1:1 (18 500 g/mol, 500 mg, 2.70 mL pyridine
solution on precleaned 24 mm²) obtained in the second stage polymerization. Compared to the peaks of P3HTs
the first stage, the peaks of P3HT-7.41 (s, 1H), 3.88 (t, 2H), 3.00 (t, 2H), 1.54
n = 10 000 g/mol, PDI = 1.35). P3HT-b-P3THPHT BCPs with the molar ratios of 1:3 and 3:1
were synthesized in the same way to give the purple solid (Mn = 9900 g/mol, PDI = 1.33 and Mw = 10 900 g/mol, PDI = 1.23, respectively)
as the final product.

Film Preparation. Thick films of the homopolymers and P3HT-b-
P3THPHT BCPs for XRD measurements were drop-coated from 10 mg/
4 mL pyridine solution on precleaned 24 × 24 mm² glass slides, while
thin films were spin-coated from 10 mg/mL pyridine solution on
precleaned 24 × 24 mm² glass slides for UV measurements and on 10
× 10 mm² Si wafer precleaned by piranha solution for GIXRD and
AFM measurements at the speed of 3000 rpm for 60 s.

### Results and Discussion

Synthesis and Characterization. We synthesized P3HT,
P3HHT, and a series of P3HT-b-P3HHT BCPs by using the modified
GRIM method followed by THP-ether deprotection as indicated in
Scheme 1.40–42 First, the P3HT monomer (Mf) was polymerized with Ni catalyst to obtain the end living P3HT polymers. Subsequently, the activated Mf was added to the reacting solution to obtain the THP-protected P3HT-b-
P3THPHT BCPs. Then P3HT-b-P3THPHT BCPs were prepared by
deprotection of the THP-protected P3HT-b-P3THPHT BCPs.

Figure 1 shows the GPC profiles of P3HTs synthesized in the first step and the final P3HT-b-P3THPHT BCPs after
the second-stage polymerization. Compared to the peaks of P3HTs
obtained in the first stage, the peaks of P3HT-b-P3THPHT BCPs all shift to a higher molecular weight each with a single
peak, indicating the preparation of the BCPs with little P3HT contaminant.

Table 1 provides molecular weight data of the synthesized
homopolymers and BCPs of P3HT-b-P3THPHT in the range of
12 000—18 000 with PDI values of 1.12—1.38 and the relative block ratios (molar monomer equivalent) calculated according to
1H NMR spectra (Figure S1). The peak observed at δ = 4.57 ppm could be assigned to the sp³ CH of the
tetrahydropyran ring, the peaks at δ = 3.48 and 3.40 ppm to the
sp³ CH of the hexyl side chain attached to the oxygen, and the peaks at δ = 3.85 and 3.75 ppm to the sp³ CH of the
tetrahydropyran ring attached to the oxygen in the P3THPHT block, while the triplet peak at δ = 0.91 ppm was assigned to the
sp³ CH of hexyl side chain in the P3HT block. From the
integration of the peaks in these regions, the molar ratios of the
P3HT and P3HHT segments were 23:77, 47:53, and 71:29, respectively, which were close to the feed molar ratios of 25:75,
50:50, and 75:25, respectively. On the basis of the 1H NMR results, they were denoted as H21THPH79, H48THPH52, and H71THPH29.

P3THPHT block was deprotected by stirring with HCl
solution in THF at 60 °C for 5 h to yield P3HTH block. 1H
NMR spectra (Figure S2) confirmed the absence of THP protons (3.40—3.48 and 3.75—3.85 ppm), meaning the formation of P3HHT block. The peak at δ = 3.88 could be assigned to the sp³ CH adjacent to the hydroxyl group in the
P3HHT block, and the triplet peak at δ = 0.89 ppm was assigned to the sp³ CH of hexyl side chain in the P3HT block. From the
integration of the peaks in these regions, the molar ratios of the
P3HT and P3HHT segments were 21:79, 48:52, and 71:29, respectively, which were close to the feed molar ratios of 25:75,
50:50, and 75:25, respectively. On the basis of the 1H NMR results, they were denoted as H21THPH79, H48THPH52, and H71THPH29.

Cross-Linking of the Polymers. Polymers bearing hydroxyl groups can be cross-linked by thermal annealing treatment.
In this work, the cross-linking was performed by
	

<table>
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<th>Polymers</th>
<th>Feed molar ratio</th>
<th>n.m.</th>
<th>Mn</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
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<td>0.100</td>
<td>16200</td>
<td>1.37</td>
</tr>
<tr>
<td>H21THPH79</td>
<td>25:75</td>
<td>21:79</td>
<td>13700</td>
<td>1.32</td>
</tr>
<tr>
<td>H48THPH52</td>
<td>50:50</td>
<td>48:52</td>
<td>18500</td>
<td>1.36</td>
</tr>
<tr>
<td>H71THPH29</td>
<td>75:25</td>
<td>71:29</td>
<td>12500</td>
<td>1.21</td>
</tr>
<tr>
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<td>100:0</td>
<td>100:0</td>
<td>16300</td>
<td>1.12</td>
</tr>
<tr>
<td>P3HHT</td>
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<td>11100</td>
<td>1.38</td>
</tr>
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<td>H23HH77</td>
<td>25:75</td>
<td>23:77</td>
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<td>H47HH53</td>
<td>50:50</td>
<td>47:53</td>
<td>14800</td>
<td>1.35</td>
</tr>
<tr>
<td>H71HH29</td>
<td>75:25</td>
<td>71:29</td>
<td>10900</td>
<td>1.23</td>
</tr>
</tbody>
</table>

* Determined by 1H NMR, n, m: the molar amount of the first and the second block in the synthesized BCPs, respectively.
thermal annealing of PHHT and P3HT-b-P3HHT BCPs at 200 °C. FTIR and UV−vis spectroscopies were then used to monitor the cross-linking of the film.

The thermal cross-linking of hydroxyl groups was confirmed by FTIR analysis. Figure 2 shows the FTIR spectra of P3HHT before and after the thermal annealing at 200 °C for 1 h.

Figure 2. FTIR spectra of P3HHT before (black) and after (red) thermal annealing at 200 °C for 1 h.

before and after the thermal annealing at 200 °C for 1 h. The aromatic C−H stretching vibrations at 3055 cm⁻¹, the symmetric and asymmetric aliphatic C−H stretching vibrations of CH₂ at 2903 and 2855 cm⁻¹, and the thiophene ring stretching vibrations at 1508 and 1460 cm⁻¹ are similar to P3HT. The broad peak at 3320 cm⁻¹ is the typical O−H stretching vibration, and the peaks at 1290, 1170, and 1130 cm⁻¹ are O−H out-of-plane vibrations, C−O stretching vibrations, and out-of-plane vibrations, respectively. After thermal treatment at 200 °C for 1 h, the peaks at 1290 and 1170 cm⁻¹ were reduced, proving the consumption of hydroxyl groups. The peak at 3320 cm⁻¹ has not changed, probably due to the partly cross-linking of P3HHT, which will be discussed in the following part. The same experiment was performed for H23HH77, H47HH53, and H71HH29, leading to the same conclusion.

The UV−vis absorption spectra of the thin films of P3HHT homopolymer and H23HH77, H47HH53, and H71HH29 BCPs before and after thermal annealing are shown in Figure 3. The films were prepared by spin-coating from pyridine solutions onto glass substrates. The films have similar absorption peaks with P3HT at ~510, 555, and 600 nm, indicating extensive π-conjugation and π−π stacking of the polythiophene backbone. After the thermal annealing, the absorption spectra of H23HH77 (Figure 3b) and H71HH29 (Figure 3d) were slightly blue-shifted, and the peak intensity at 600 nm decreased, but the absorption spectra of P3HHT (Figure 3a) and H47HH53 (Figure 3c) remained almost the same after thermal treatment. This result indicates that cross-linking does not significantly disturb the molecular packing in P3HHT and H47HH53 but has some influences on H23HH77 and H71HH29. Such difference influences are still unclear and under further investigation.

In order to evaluate the efficiency of the cross-linking of the polymers, the solubility of the films was checked using the good solvent N-methyl-2-pyrrolidone (NMP). Thin films of P3HHT and BCPs deposited onto glass substrates were thermally annealed at 200 °C for 1 h. After their UV−vis spectra were measured, these films were immersed into NMP for 5 min. Then the samples were dried, and their UV−vis spectra were measured again to check the remaining polymers on the substrates. Figure 3 also shows the UV−vis spectra of P3HHT and the BCPs H23HH77, H47HH53, and H71HH29 before and after the solvent immersion. For the original films without thermal annealing, almost no absorption was observed...
For P3HHT, H23HH77, H47HH53, and H71HH29, the mole percent of P3HT block and P3HHT block, respectively, samples can be calculated as completely cross-linked, the total weight loss (heated to 200 °C) of di

\[
\Delta m = \frac{M_{H_2O} \Delta m_H}{2M_{HH} + nM_{HT} + mM_{HHT}} \times 100\%
\]

where \(M_{H_2O}\), \(M_{HT}\), and \(M_{HHT}\) are the molecular weight of water, P3HT block, and P3HHT block, respectively; \(n\) and \(m\) are the mole percent of P3HT block and P3HHT block, respectively. For P3HHT, H23HH77, H47HH53, and H71HH29, the \(\Delta m\) is 4.89%, 3.84%, 2.70%, and 1.51%, respectively. To determine the degree of cross-linking, the conversion of the cross-linking reaction (conv) can be calculated as

\[
\text{conv} = \frac{\Delta m}{\Delta m_t} \times 100\%
\]

where \(\Delta m\) is the actual weight loss. For the P3HT-b-P3HHT BCPs, conversion is related to the degree of cross-linking of the P3HHT block in the BCPs. In order to characterize the degree of cross-linking of the P3HT-b-P3HHT BCPs, the relative conversion can be defined as

\[
\text{rel conv} = \text{conv} \times m
\]

The \(\Delta m\) and relative conversion at typical time are summarized in Table 2 to explore the correlation between the ductility of film and the degree of cross-linking. Figure 4a,b shows the weight loss and the conversion of the cross-linking reaction of P3HHT and the BCPs with different isothermal times. In all the samples, the rate of cross-linking sharply slows down after 0.5 h and then gradually decreases to a minimum approaching to zero after about 15 h. Similar to the most solid-phase cross-linking reactions, it is difficult to approach a complete cross-linking.

The reason is that with the formation of the cross-linked matrix the motion of the polymer chains becomes more and more difficult, which decreases the collision probability of the hydroxyl groups, and the rate of cross-linking reaction slows down. When the degree of cross-linking is high enough, the polymer chains are fixed and the rate of cross-linking reaction is approaching zero. Compared to P3HHT, the P3HT-b-P3HHT BCPs have less cross-linkable P3HT block and the motion ability of polymer chains is better than that of P3HHT homopolymer during cross-linking. As a result, the P3HT-b-P3HHT BCPs have faster cross-linking rate and can achieve higher conversion. Especially for H71HH29, which has the least cross-linkable P3HHT block, the conversion is almost 100% after 16 h, approaching a complete cross-linking. However, the

**Table 2. Summary of the Actual Weight Loss and Relative Conversion of Cross-Linking of P3HHT and BCPs at Typical Times**

<table>
<thead>
<tr>
<th>time (h)</th>
<th>P3HHT</th>
<th>H23HH77</th>
<th>H47HH53</th>
<th>H71HH29</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\Delta m) (%)</td>
<td>rel conv (%)</td>
<td>(\Delta m) (%)</td>
<td>rel conv (%)</td>
</tr>
<tr>
<td>0.5</td>
<td>0.63</td>
<td>12.88</td>
<td>0.55</td>
<td>11.03</td>
</tr>
<tr>
<td>1</td>
<td>0.80</td>
<td>16.36</td>
<td>0.73</td>
<td>14.64</td>
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<tr>
<td>2</td>
<td>1.04</td>
<td>21.27</td>
<td>0.94</td>
<td>18.85</td>
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<tr>
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<tr>
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<td>26.79</td>
<td>1.18</td>
<td>23.66</td>
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<td>32.92</td>
<td>1.42</td>
<td>28.47</td>
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</table>

*a* The actual weight loss. *b* The relative conversion of cross-linking reaction.
degree of cross-linking of the P3HT-b-P3HHT BCPs, which characterized by relative conversion is lower than that of P3HHT homopolymer (shown in Figure 4c), because P3HHT homopolymer has the most cross-linkable groups.

Crystallization and Microphase Morphology during Cross-Linking. In order to investigate the crystalline behavior of the P3HT-b-P3HHT BCPs, these polymers were characterized by DSC. All the samples were prepared by drop-casting from pyridine solutions, and the scan rate was 10 °C/min. Figure 5 shows the endothermic traces of the first and second heating cycle and the exothermic traces of the cooling cycle of the samples. The melting and crystallization temperatures of all these samples are summarized in Table 3. P3HHT shows a melting point at 265 °C during the first heating cycle, but no peak during the cooling cycle and the second heating cycle (shown in Figure 5 and Table 3). This result means that the polymer chains reorganizing into well-ordered crystalline structure during the cooling process, and the degree of crystallinity of P3HHT is decreased. In contrast, H47HH53 and H71HH29 show two distinct endothermic peaks with two melting points during the first heating cycle characteristic of the corresponding blocks (shown in Figure 5a and Table 3). These results indicate that the H47HH53 and H71HH29 form microphase separation structure. For H47HH53, the two melting points are 207 and 260 °C, while H71HH29 has the melting points at 207 and 227 °C. It should be noted that the melting point of P3HHT in H71HH29 is much lower than that of P3HHT homopolymer.

Table 3. Summary of DSC Measurement of the Homopolymers and the BCPs

<table>
<thead>
<tr>
<th>polymer</th>
<th>( T_m^{\text{f}} ) °C</th>
<th>( T_m^{\text{s}} ) °C</th>
<th>( T_c ) °C</th>
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<tbody>
<tr>
<td>P3HHT</td>
<td>265</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H23HH77</td>
<td>269</td>
<td></td>
<td>156</td>
</tr>
<tr>
<td>H47HH53</td>
<td>207 260</td>
<td>194 156</td>
<td></td>
</tr>
<tr>
<td>H71HH29</td>
<td>207 227</td>
<td>205 175</td>
<td></td>
</tr>
<tr>
<td>P3HT</td>
<td>220 222</td>
<td>192</td>
<td></td>
</tr>
</tbody>
</table>

*a*The melting temperature of first heating cycle (eliminating the heat history). *b*The melting temperature of second heating cycle. *c*The crystallization temperature of cooling cycle.

The reason is that in our experiments the crystallization of copolymers measured by DSC in the first running is influenced by the solvent evaporation process to form films. Pyridine is a good solvent for P3HHT but poor for P3HT. So P3HT block first aggregated and crystallized followed by the crystallization of P3HHT block. During the solvent-cast process, the aggregation of P3HT is favored to its crystallization, while the soluble P3HHT disturbs the P3HT crystallization. Therefore, P3HT has a lower melting point in the copolymer compared with P3HT homopolymer. Moreover, the more P3HHT in the copolymer, the lower the crystalline degree of P3HHT block is. For H23HH77, which has the best solubility among all the copolymers, the aggregation and crystallization of P3HT block are suppressed during the solvent-cast process, resulting in the observation of only P3HHT melting point. For H47HH53, its solubility in pyridine is not as good as H23HH77. The crystallization of P3HT is disturbed by P3HHT to some degree, leading to a lower melting point of P3HT block. However, when P3HHT begins to aggregate and crystallize, the previously crystallized P3HT block contributes to the crystallization of P3HT block due to their similar crystalline structures. As a result, the crystallization of P3HT block is still as good as the P3HHT homopolymer with similar melting points. For H71HH29, which has the poorest solubility among all the copolymers, there is no enough time for both P3HT and P3HHT blocks to organize into well-ordered crystalline structure during solvent evaporation process. Hence, the melting points of both blocks are lower than the corresponding homopolymers. During the cooling and the second heating processes, they show one slight exothermic peak and one slight endothermic peak corresponding to P3HT block, and there is no peak corresponding to P3HHT block (shown in Figure 5b,c and Table 3). It is also attributed to the cross-linking of P3HT block at high temperature in the P3HT-b-P3HHT BCPs, which prevents the crystallization and freezes the disorder melt state of P3HT-b-P3HHT BCPs.

To further investigate the crystalline structures of the P3HT-b-P3HHT BCPs, XRD (Figure 6) and GIXRD (Figure 7) were performed. Since the cross-linking at melt state of P3HHT block prevents crystallization of the copolymers, the films were treated by thermal annealing at 200 °C (which is close to the melting point of P3HT block but much lower than the melting point of P3HHT block) for 1 h. The results obtained from the XRD measurements are summarized in Table 4. It is notable to find that the P3HT-b-P3HHT BCPs show one single (100) diffraction peak (Figure 6). The (100) diffraction peaks of H23HH77, H47HH53, and H71HH29 are at the 2θ angle of...
5.38°, 5.46°, and 5.54°, respectively, corresponding to the d_{100} spacing of 1.64, 1.62, and 1.60 nm, which are between the corresponding values of P3HHT and P3HT. These results indicate that H23HH77, H47HH53, and H71HH29 form a uniform crystal lattice size due to their side chain length only different by a hydroxyl group, though they form microphase separation structure. Furthermore, the crystalline degree of the films is greatly improved after thermal annealing. Based on the GIXRD results (shown in Figure 7a,d), the P3HHT and H47HH53 have the “edge on” structure, comparable to P3HT homopolymers.53,50 When the films are isothermal at 300 °C for 10 min before thermal annealing at 200 °C, the “edge on” structure is destroyed and the crystalline degree of the films is decreased (shown in Figure 7b,e), which matches the results of DSC. On the contrary, the films, thermally annealed at 200 °C without isothermal at 300 °C for 10 min, remain the “edge on” structure and show the recognizable first-, second-, and third-order reflections from crystallographic (100), (200), and (300) planes with the d_{100} spacing of the cross-linked samples slightly increased (shown in Figures 6 and 7c,f). The reason that these two different processes result in two different structures is as follows. When the films are isothermal at 300 °C, the polymers are melt and at amorphous state. Meanwhile, the P3HHT block is cross-linked; thus the amorphous state is frozen. Then, during the following thermal annealing at 200 °C, the polymer chains cannot further reorganize into well-ordered crystalline structure because of the cross-linked P3HHT block. Therefore, the crystalline degree of the films is decreased. On the contrary, when the films are thermal annealed at 200 °C without isothermal at 300 °C for 10 min, the previously existing crystalline structures are not destroyed, and the P3HHT block is cross-linked at the temperature below its melting temperature. As a result, the crystalline structure still remains “edge on” structure, and the crystalline degree is improved due to the rearrangement of the un-cross-linked parts. These results demonstrate that cross-linking at 200 °C does not disrupt the crystalline structure and the overall crystallinity of the films. According to the studies of the P3ATs, there is a side-chain melting transition at about 60 °C.50−52 Similarly, the side chain of P3HHT block is at the melt state at 200 °C. As a result, the P3HHT in both the crystalline and amorphous parts have sufficient mobility to carry out the cross-linking reaction at 200 °C. However, there is no effective method to distinguish the cross-linking from crystalline part or amorphous part at present. The schematic representation of the cross-linking of the crystalline part is shown in Scheme 2 exemplified by H47HH53.

AFM analyses were performed to investigate the microphase separation morphology of the P3HT-b-P3HHT BCPs. Thin films of the BCPs were prepared by spin-coating on precleaned Si substrate and then annealing at 200 °C for 1 h. The film thickness was estimated to be 50−60 nm measured by AFM. Figure 8 shows the AFM images of H47HH53 before and after thermal annealing. Before thermal annealing, there is a recognizable lamellar-like structure with the width in the range of 10−15 nm in the phase image (Figure 8b), and clear nanofiber structures with the width in the range of 50−80 nm can be found in the height image (Figure S3c). However, after thermal annealing, the lamellae-like structures and nanofibers are damaged (Figure 8c,d). H23HH77 and H71HH29 show the same results (Figures S4 and S5). And with the increase of P3HT block, the nanofiber structures become more clearly. In contrast, P3HHT show no recognizable phase pattern before and after thermal treatment (Figure S6). Furthermore, the film roughness of all samples was calculated according to the AFM images with large image size (not shown here). All samples after thermal annealing show a higher roughness than they do before thermal annealing. P3HHT, H23HH77, H47HH53, and H71HH29 have the film roughness of 1.53, 2.30, 9.46, and 31.6 nm, respectively, before thermal annealing. While after thermal annealing, their roughness increases to 6.81, 4.16, 11.4, and 38.8 nm, respectively. The reason is that during the thermal annealing some of the crystalline and amorphous parts become cross-linked and the polymer chains are fixed.

Table 4. Summary of XRD Measurement of the Homopolymers and the BCPs

<table>
<thead>
<tr>
<th>polymer</th>
<th>2θ (deg)</th>
<th>d_{100} spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HHT</td>
<td>5.37</td>
<td>1.65</td>
</tr>
<tr>
<td>P3HH77</td>
<td>5.38</td>
<td>1.60</td>
</tr>
<tr>
<td>H23HH77</td>
<td>5.46</td>
<td>1.62</td>
</tr>
<tr>
<td>H47HH53</td>
<td>5.46</td>
<td>1.62</td>
</tr>
<tr>
<td>H71HH29</td>
<td>5.56</td>
<td>1.59</td>
</tr>
<tr>
<td>P3HT</td>
<td>5.51</td>
<td>1.60</td>
</tr>
</tbody>
</table>

“Films as cast. †Films after thermal annealing at 200 °C for 1 h.”

Figure 6. XRD spectra of P3HHT, P3HT, and the BCPs before (dotted line) and after (solid line) thermal annealing at 200 °C for 1 h.

Figure 7. GIXRD spectra of P3HHT (a, b, c) and H47HH53 (d, e, f) with different annealing process: (a, d) original films; (b, e) isothermal at 300 °C for 1 h; (c, f) thermal annealing at 200 °C for 1 h.

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un-cross-linked polymers in the amorphous part rearrange to crystalline structure. Then different chain movements lead to the increase of roughness and damage the lamellar structure and nanofibers.

Quantitative Correlation between Ductility of Thin Film and Degree of Cross-Linking. Many studies have been reported to investigate the tenacity of films of conjugated polymers by observing the crack growth when the films were stretched on a compliant substrate.\(^5\)\(^3\)\(^5\)\(^6\) The films of P3HT, P3HHT, and their BCPs were prepared by spin-coating on O\(_2\) plasma activated PDMS substrate, and the thickness of the films was estimated to be 50–60 nm measured by AFM. The crack onset strain of the films was defined as the strain at which the first crack was observed to determine the ductility of the samples. Films were stretched from 0% strain using a homemade linear actuator with a step size of 1%, and the process was observed by an optical microscope to find the first crack. Figure 9 and Table 5 summarize the crack onset strain of P3HT, P3HHT, and P3HT-b-P3HHT BCPs with different annealing times.

Figure 9. Crack onset strains of P3HT, P3HHT, and P3HT-b-P3HHT BCPs as a function of different annealing times.

To further investigate the quantitative correlation between the ductility of the films and the degree of cross-linking, the crack onset strain as a function of the relative conversion in cross-linking reaction (controlled by different annealing times) is presented in Figure 10. As we can see, the ductility of the cross-linkable P3HHT and P3HT-b-P3HHT BCPs films rises with the increased degree of cross-linking. P3HHT and
The cross-linking reaction of P3HHT and H47HH53 is of particular interest due to their higher relative conversion of cross-linking, which can simultaneously improve the thin film ductility and the degree of crystallization. This study also demonstrates the potential of cross-linkable block copolymers in flexible electronic devices.

### Table 5. Summary of the Crack Onset Strains of the Homopolymers and the BCPs

<table>
<thead>
<tr>
<th>time (h)</th>
<th>P3HHT</th>
<th>H23HH77</th>
<th>H47HH53</th>
<th>H71HH29</th>
<th>P3HT</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.3 ± 1.5</td>
<td>4.4 ± 1.2</td>
<td>4.1 ± 1.4</td>
<td>5.2 ± 1.2</td>
<td>9.4 ± 1.1</td>
</tr>
<tr>
<td>0.5</td>
<td>9.7 ± 0.8</td>
<td>10.7 ± 0.9</td>
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<td>12.7 ± 1.5</td>
<td>9.2 ± 1.2</td>
</tr>
<tr>
<td>1</td>
<td>12.7 ± 1.3</td>
<td>12.9 ± 1.1</td>
<td>13.0 ± 1.6</td>
<td>13.7 ± 1.6</td>
<td>10.0 ± 1.4</td>
</tr>
<tr>
<td>2</td>
<td>16.6 ± 2.1</td>
<td>15.9 ± 1.6</td>
<td>17.0 ± 1.3</td>
<td>14.3 ± 1.9</td>
<td>9.9 ± 1.1</td>
</tr>
<tr>
<td>3</td>
<td>20.3 ± 1.8</td>
<td>16.9 ± 0.9</td>
<td>18.0 ± 1.1</td>
<td>15.9 ± 1.6</td>
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<tr>
<td>4</td>
<td>23.4 ± 2.1</td>
<td>18.1 ± 1.3</td>
<td>19.8 ± 0.9</td>
<td>18.2 ± 1.6</td>
<td>9.9 ± 1.1</td>
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<tr>
<td>5</td>
<td>27.7 ± 1.4</td>
<td>18.9 ± 1.2</td>
<td>22.2 ± 1.5</td>
<td>19.1 ± 2.5</td>
<td>10.0 ± 1.5</td>
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<tr>
<td>6</td>
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<td>21.0 ± 1.3</td>
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<td>10.3 ± 1.4</td>
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<tr>
<td>7</td>
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<td>21.5 ± 1.4</td>
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<tr>
<td>8</td>
<td>28.9 ± 1.4</td>
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<td>25.8 ± 1.6</td>
<td>19.0 ± 1.5</td>
<td>10.4 ± 1.3</td>
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</table>

*Errors in the crack onset strains were the standard deviations of the samples tested.*

### Figure 10
Crack onset strains of P3HHT and P3HT-b-P3HHT BCPs as a function of different degrees of cross-linking.

### Figure 11
Degree of cross-linking, crack onset strains, and the degree of crystallinity of P3HHT and H47HH53 as a function of different annealing times.

### CONCLUSIONS
In this study, we have synthesized a series of P3HT-b-P3HHT BCPs with different block ratios which can be cross-linked during thermal annealing. The crystallization and microphase morphology were investigated by DSC, GIXRD, XRD, and AFM. The BCPs formed microphase separation structure due to the difference of polarity of the two blocks. Although after thermal annealing at 200 °C, the cross-linking of P3HHT block damaged the microphase separation structure and the roughness of the films increased, the crystalline structure still remains “edge on” and the degree of crystallization greatly improved. Based on the weight loss in the cross-linking reaction, the degree of cross-linking was calculated and the film ductility was characterized by the crack onset strain. Then we established a quantitative correlation between the film ductility and the degree of cross-linking and found that the ductility of the cross-linkable P3HHT and P3HT-b-P3HHT BCPs films rises with the growth of the degree of cross-linking. Our results prove that cross-linking during thermal annealing at 200 °C can simultaneously improve the thin film ductility and the degree of crystallization, help to provide guide to develop flexible electronic devices, and enrich the understanding of microphase separation and crystallization in cross-linkable conjugated block copolymers.

### ASSOCIATED CONTENT

#### Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b02001.

Figures S1–S7 (PDF)

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**Notes**
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**REFERENCES**

(2) Müller, A. J.; Balsamo, V.; Arnal, M. L. Block Copolym. II. 2005, 190, 1–63.

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