Regioregularity-Driven Morphological Transition of Poly(3-hexylthiophene)-Based Block Copolymers

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ABSTRACT: Conjugated polymer-based block copolymers (BCPs) offer great potential to provide beneficial nanostructures for efficient organic optoelectronics. However, their complicated self-assembly behavior, which is attributed to the strong crystallization of conjugated blocks, is still not well understood due to the lack of a model BCP system. Herein, we develop a series of novel conjugated polymer-based BCPs, poly(3-hexylthiophene)-block-poly(2-vinylpyridine) (P3HT-b-P2VP), in which the regioregularity (RR) of the P3HT block was varied from 95 to 73%. The tunable RR content allows for precise regulation of P3HT crystallization with minimal influence on the microphase-separation force between the P3HT and P2VP blocks. When RR is high (i.e., 95 or 85%), structure formation is controlled by crystallization of P3HT, and the ultimate structure is characterized by nanoscale P3HT fibrils in an amorphous matrix. In contrast, as RR decreases to 78 and 73%, P3HT crystallization is suppressed. The self-assembly is controlled by the enthalpic interaction between P3HT and P2VP blocks, much like typical BCPs having two flexible blocks, and thermal annealing drives the formation of well-ordered lamellar or cylindrical phases. This morphological behavior is consistent with a Monte Carlo simulation based on a newly developed coarse-grained model. Significantly, this novel class of RR-controlled P3HT-based BCPs provides a simple method to tune bulk and thin film morphology for a variety of applications in nanostructured organic electronics.

INTRODUCTION

Conjugated polymers (CPs) can be engineered to deliver excellent opto-electrical properties4−6 and unique biological functionalities,7−10 so these systems are widely investigated for applications in plastic electronics and sensors. One area that has attracted a great deal of attention is the use of conductive block copolymers (BCPs), which are based on semiflexible π-conjugated polymers11,12 linked to flexible amorphous polymers, for nanostructured optoelectronics.13−15 The strong intermolecular interactions between conjugated polymer chains (i.e., π−π interaction or supramolecular interaction) produce the unique optoelectronic properties and can also drive a strong crystallization.16−19 Self-assembly in these conjugated polymer-based BCP (CP-BCP) systems is controlled by competition between the microphase-separation process driven by the Flory–Huggins enthalpic interaction and chain entropy (χN, segregation strength between two different segments) and the strong crystallization driven by the intermolecular interactions of conjugated chains.20,21

A well-documented challenge with this class of CP-BCPs is that strong crystallization in the conjugated polymer domains often dominates over the microphase-separation process, which slows down the kinetics for assembly and produces kinetically trapped, disordered morphologies.13,22−24 For example, most poly(3-hexylthiophene) (P3HT)-based BCPs form P3HT fibrils in an amorphous matrix because of the strong tendency for crystallization and high melting temperature (∼220 °C).23,25−28 The inability to control nanoscale morphology...
and orientation of these semiconducting fibrils has led to limited utility. On the other hand, poly(alkoxyphenylene−vinylene) (PPV)-based BCPs often produced better-ordered nanostructures due to their weaker tendency to crystallize, but their charge mobility is much lower. To address this issue, many attempts have been dedicated to control the self-assembly behavior of the CP-BCPs. Modifying the conjugated polymer to include side chains with longer lengths and/or branched structures can significantly reduce the crystallization temperature of the semiflexible, conjugated blocks and enable self-assembly into lamellar and cylindrical phases. Different copolymer architectures, such as graft and star copolymers, can produce high interfacial curvature and suppress crystallization, offering greater control over morphological behavior. While these approaches provide an effective route to control the self-assembly, the introduction of different alkyl chains or new polymer architecture often degrades the optical and electrical properties of the conjugated copolymers. A model CP-BCP system with systematically tuned crystallization is urgent and crucial to expanding the current understanding of self-assembly in these complex systems.

Regioregularity (RR), which is defined as the content of head-to-tail (H−T) bonds in conjugated polymers, can be an important factor that determines the degree of crystallization. Numerous studies have demonstrated that high RR values in the P3HT polymers are important in producing long, highly crystalline fibrils, leading to high charge carrier mobility. Importantly, the crystalline properties of the P3HTs can be controlled by modulating the RR values. For example, Frechet et al. showed that the P3HT polymers with controlled RR value can produce both high photovoltaic performance and much enhanced thermal stability due to modulated crystalline and aggregated behavior of the P3HTs. Recently, we successfully developed a series of monodispersed P3HTs that have a wide range of RR from 64 to 98% and investigated the RR effect on the polymer crystallinity and mechanical properties. It was seen that the excessive crystallization of high RR P3HTs can cause problems for organic electronic applications in terms of processability and mechanical resilienties. Therefore, the RR represents the most effective factor to control the crystallization behavior of the polymers while maintaining their chemical structure, which can serve as an excellent model system for CP-BCP studies. To our knowledge, the self-assembly of BCPs based on conjugated polymers with tunable RR values have been never studied.

Herein, we designed a novel series of CP-BCPs based on poly(3-hexylthiophene)-block-poly(2-vinylpyridine) (P3HT-b-P2VP), in which the RR value of the P3HT block was systematically varied in a wide range from 95 to 73%. The methodology generates different RR values without affecting the molecular weight and polydispersity of the P3HT blocks, which allows for regulation of P3HT crystallization behavior. We observed that reducing RR suppressed the crystallization of P3HT and induced a remarkable transition of the P3HT-b-P2VP structure from fibril-like to well-ordered lamellar and cylindrical (hexagonally packed) nanostructures. This RR-controlled morphological transition was confirmed with different P2VP volume fractions ($f_{P2VP}$) using transmission electron microscopy (TEM) and grazing-incidence small-angle X-ray scattering (GI-SAXS). Experimental observations were validated with Monte Carlo simulations based on a coarse-grained model that captures the effects of RR. Our simulation results confirm that crystallization behavior of P3HT block is greatly suppressed as the RR value is decreased, enabling the self-assembly of P3HT-b-P2VP into highly ordered nanostructures that are typical of equilibrium BCP phase behavior.

## RESULTS AND DISCUSSION

The RR-controlled P3HT-b-P2VP copolymers were synthesized by “click reaction” between alkyne-terminated P3HT (P3HT-alkyne) and azide-terminated P2VP (P2VP-N₃), which are polymerized via two different controlled polymerization methods (Figure 1a). First, a series of the RR-controlled P3HT-alkyne and azide-terminated P2VP polymers are labeled as RR 95-, 85-, 78-, and 73-alkyne, respectively. P3HT-alkyne polymers were synthesized with di-alkynes that were synthesized by the method based on modified Grignard metathesis (GRIM) polymerization and “click” reaction. (b) Normalized $^1$H NMR spectra for a series of RR-controlled P3HT-alkynes. (c) SEC traces of RR 73-alkyne and derived block copolymers.

alkynes were synthesized by the method based on modified Grignard metathesis (GRIM) polymerization, in which H−H coupled bithiophene and thiophene monomer are copolymerized with different feed ratios. We previously reported that this method yielded well-defined P3HT with tunable RRs and controlled molecular weights. To decouple the RR effect on phase behavior from other effects of the molecular weight and its polydispersity, we fixed the amount of Ni-catalyst but controlled the feed ratio of H−H coupled bithiophene and thiophene monomer from 0.00 to 0.18. As a result, four P3HT-alkynes were synthesized with different RR values, determined from $^1$H NMR spectra by comparing the integrated area of the peaks at δ 2.78 (H−T bonds) and δ 2.54 (H−H bonds). These polymers are labeled as RR 95-, 85-, 78-, and 73-alkyne, respectively (Figure 1b). All of the P3HT polymers have similar number-average molecular weight ($M_n = 11−12$ kg mol$^{-1}$) and narrow dispersity ($D = 1.1−1.3$). Then, a series of P2VP-N₃ polymers with narrow $D$ of ~1.1 were polymerized through reversible addition−fragmentation transfer (RAFT) polymerization using azide-terminated chain transfer agent (CTA-N₃). These P2VPs were designed to have different chain lengths to investigate the phase behavior of the P3HT-b-P2VP copolymers as a function of the volume fractions of P2VP ($f_{P2VP}$) and P3HT-alkyne polymers and the P2VP-N₃ polymers were coupled by a copper(I)-catalyzed azide−alkyne cycloaddition (CuAAC) “click reaction” between azide and alkyne groups of each polymer, yielding P3HT-b-P2VP copolymers with different RR and $f_{P2VP}$ values.

![Figure 1.](image_url)

**Figure 1.** (a) Synthesis route for RR-controlled P3HT-b-P2VP using modified GRIM polymerization and “click” reaction. (b) Normalized $^1$H NMR spectra for a series of RR-controlled P3HT-alkynes. (c) SEC traces of RR 73-alkyne and derived block copolymers.
After the reaction, the copolymers were purified with acetone and tetrahydrofuran/hexane cosolvent to remove unreacted P2VP and P3HT homopolymers, respectively. Successful synthesis and purification of the P3HT-b-P2VP copolymers were confirmed by the peak shift toward higher molecular weight and a monomodal distribution in size exclusion chromatography (SEC) (Figure 1c and Figure S1) and 1H NMR spectroscopy (Figures S2 and S3). For convenience, polymers are denoted by RR controlled P3HT and P2VP copolymers at two different f_{P2VP} values of ∼0.45 and ∼0.30, respectively. (a) RR 95-b-P2VP (0.45); (b) RR 85-b-P2VP (0.46); (c) RR 78-b-P2VP (0.44); (d) RR 73-b-P2VP (0.45); (e) RR 95-b-P2VP (0.30); (f) RR 85-b-P2VP (0.27); (g) RR 78-b-P2VP (0.31); and (h) RR 73-b-P2VP (0.30). The inset of each figure shows the corresponding FFT images. Exposure to iodine vapor selectively stained dark P2VP domains. The scale bars are 100 nm.

Table 1. Characteristics of Block Copolymers Used in the Study

<table>
<thead>
<tr>
<th>polymer</th>
<th>RR (°C)</th>
<th>[% H–T linkages]</th>
<th>P3HT Mₐ (kg mol⁻¹)</th>
<th>P3HT D₀</th>
<th>f_{P2VP} (°C)</th>
<th>Tₘ,P3HT (°C)</th>
<th>structure</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RR 95-b-P2VP</td>
<td>95</td>
<td>11.4</td>
<td>1.14</td>
<td>0.35</td>
<td>218.0</td>
<td>fibril-like</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>RR 95-b-P2VP</td>
<td>95</td>
<td>12.1</td>
<td>1.16</td>
<td>0.45</td>
<td>223.0</td>
<td>fibril-like</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>RR 85-b-P2VP</td>
<td>85</td>
<td>11.7</td>
<td>1.33</td>
<td>0.31</td>
<td>193.4</td>
<td>HPC</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>RR 78-b-P2VP</td>
<td>78</td>
<td>12.1</td>
<td>1.35</td>
<td>0.30</td>
<td>184.6</td>
<td>HPC</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>RR 73-b-P2VP</td>
<td>73</td>
<td>12.1</td>
<td>1.35</td>
<td>0.45</td>
<td>186.8</td>
<td>LAM</td>
<td>34</td>
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</tr>
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</table>

* Determined from 1H NMR data (Figure 1b). Obtained from SEC calibrated with polystyrene standard (Figure 1c and Figure S1). The f_{P2VP} values were calculated based on the integration of 1H NMR (Figures S2 and S3). Determined by DSC second heating cycle with a heating rate of 10 °C min⁻¹ (Figure S4). Determined from TEM and GI-SAXS measurements. Determined from GI-SAXS analysis.

Figure 2. Cross-sectional TEM images represent phase transitions of P3HT-b-P2VP copolymers depending on their RR values in the bulk state. The first and second rows of the figures show the morphologies of RR-controlled P3HT-b-P2VP copolymers at two different f_{P2VP} values of ∼0.45 and ∼0.30, respectively. (a) RR 95-b-P2VP (0.45); (b) RR 85-b-P2VP (0.46); (c) RR 78-b-P2VP (0.44); (d) RR 73-b-P2VP (0.45); (e) RR 95-b-P2VP (0.35); (f) RR 85-b-P2VP (0.27); (g) RR 78-b-P2VP (0.31); and (h) RR 73-b-P2VP (0.30). The inset of each figure shows the corresponding FFT images. Exposure to iodine vapor selectively stained dark P2VP domains. The scale bars are 100 nm.
the bulk morphologies of the P3HT-b-P2VP BCPs with different RR values of 95, 85, 78, and 73%. The BCP samples with high RR P3HT content (95%) exhibited fibril-like phases of P3HT irrespective of the \( f_{P2VP} \) values (Figures 2a,e). However, the domain spacing (\( D \)) increased from 22 (RR 95-b-P2VP (0.35)) to 28 nm (RR 95-b-P2VP (0.45)) due to the extended length of the P2VP chain. As previously discussed in the literatures, these are commonly observed morphologies in P3HT-based BCPs driven by strong crystallization of P3HT.\(^{23,25-28}\) When the RR was reduced to 85%, the BCPs showed similar but more disordered structures. The RR 85-b-P2VP (0.46) (Figure 2b) and RR 85-b-P2VP (0.27) (Figure 2f) exhibited disordered fibril-like and micelle phases with \( D \) values of 27 and 31 nm, respectively. Despite the reduction in RR value, the morphology of the BCPs was still dominated by the crystallization of P3HT, which inhibited the self-assembly into ordered nanostructures.

A stark contrast in the self-assembly behavior was observed when RR was further decreased to values of 78 and 73%. The RR 78-b-P2VP (0.44) (Figure 2c) and RR 73-b-P2VP (0.45) (Figure 2d) copolymers, which had nearly identical \( f_{P2VP} \) values, were self-assembled into a well-ordered lamellar phase (LAM) with \( D \) values of 29 and 34 nm, respectively. The corresponding fast Fourier transform (FFT) images confirm this morphological transition, exhibiting sharp peaks normal to LAM structures of RR 78-b-P2VP (0.44) and RR 73-b-P2VP (0.45), compared to the broad halo of RR 95-b-P2VP (0.45) and RR 85-b-P2VP (0.46). Overall, there was a remarkable transition from disordered to ordered morphologies when the RR value was decreased from 85 to 78%. This phenomenon was attributed to the suppressed crystallization of P3HT with decreasing RR values. Therefore, the Flory–Huggins enthalpic interaction begins to dominate phase behavior at some point between RR values of 85 and 78%, allowing assembly of P3HT-b-P2VP BCPs into well-ordered nanostructures. To the best of our knowledge, this is the first demonstration where RR is used to control morphology in a CP-BCP.

The dramatic morphological transition induced by changes in RRs (suppressed crystallinity) was also observed for different \( f_{P2VP} \) values. For example, the RR 78-b-P2VP (0.31) (Figure 2g) and RR 73-b-P2VP (0.30) (Figure 2h) exhibited hexagonally packed cylinders (HPCs) of P2VP embedded in a P3HT matrix, in sharp contrast to the disordered morphologies of RR 95-b-P2VP (0.35) (Figure 2e) and the RR 85-b-P2VP (0.27) (Figure 2f). Note that all of the polymers have similar \( f_{P2VP} \) value of \( \sim 0.30 \). The \( D \) values were determined to be 26 and 24 nm for RR 78-b-P2VP (0.31) and RR 73-b-P2VP (0.30), respectively. The FFT images confirm this transition as a function of the RR values. The FFT images of RR 95-b-P2VP (0.35) and RR 85-b-P2VP (0.27) had broad ring patterns characteristic of disordered structures. In contrast, as the RR decreased to 78 and 73%, 6-fold peaks were clearly apparent, indicative of well-ordered HPC phases. This HPC morphology, which contains a higher fraction of the electroactive P3HT phase, is of crucial importance due to its potential in controlling conducting pathways and enhancing light absorption in organic electronics.\(^{33,47}\) Consequently, the P3HT-b-P2VP with low RR values resembles the equilibrium phase behavior of classical coil–coil BCPs, which also show a transition from LAM to HPC with increasing volume asymmetry.

To clarify the effects of RR and \( f_{P2VP} \) on morphology, we performed Monte Carlo simulations of coarse-grained P3HT-b-P2VP with controlled RR values in the P3HT blocks. To simulate P3HT with different RR values, we modeled P3HT composed of two different types of beads. One bead contains a regioregular 3-hexithiophene trimer with three head-to-tail bonds (HT–HT–HT) that increases crystallinity, while the other bead contains head-to-tail, head-to-head, and tail-to-tail bonds in series (HT–HH–TT) that suppresses crystallinity of P3HT. To realize this, we put a strong potential between two HT–HT–HT beads to promote crystallization between two beads based on previous coarse-grained simulation studies.\(^{46,49}\) On the other hand, the potential between two beads containing at least one HT–HH–TT bead is designed to be relatively weak to suppress the crystallinity between the beads. This potential is based on the glass transition temperature (\(-10 ^\circ C\)) of regiorandom P3HT (see Supporting Information for simulation details). This model was developed to investigate the competition between local crystallization and microphase separation, when quenched from homogeneous melt. We modeled P3HT with 12 beads (\( N_{P3HT} = N_{HT-HT-HT} + N_{HT-HH-TT} = 12 \)) to fix an \( M_n \) value of 12.0 kg mol\(^{-1}\) for P3HT block, but with different P2VP lengths to match the volume fractions \( f_{P2VP} \) (0.50 with \( N_{P2VP} = 12 \) and 0.25 with \( N_{P2VP} = 4 \)) in experiment. The RR of P3HT is defined as the

Figure 3. Monte Carlo simulation snapshots of self-assembled P3HT-b-P2VP copolymers depending on their RR values. Pink line represents P3HT while blue line represents P2VP. The first and second rows of figures show the morphologies of RR controlled P3HT-b-P2VP copolymers at two different \( f_{P2VP} \) values of 0.50, and 0.25, respectively. (a) RR 94-b-P2VP (0.50); (b) RR 83-b-P2VP (0.50); (c) RR 78-b-P2VP (0.50); (d) RR 72-b-P2VP (0.50); (e) RR 94-b-P2VP (0.25); (f) RR 83-b-P2VP (0.25); (g) RR 78-b-P2VP (0.25); and (h) RR 72-b-P2VP (0.25).
fraction of (H–T) bonds along the polymer chain (RR = 100N_{HT}/(N_{HT} + N_{HH} + N_{TT})), and it is expressed as 100(N_{P3HT} + 2N_{HT-HT})/(3N_{P3HT}) in our model. In this way, we model P3HT with four different N_{HT-HT} (7, 8, 9, and 11) to match four RR values (72, 78, 83, and 94%). Positions of (HT–HT–HT) beads are randomly distributed along the chain to mimic the random polymerization process in experiment. To match the annealing condition for the samples in TEM and X-ray analysis, we ran 107 Monte Carlo movement steps (each step corresponds to accepted movements of entire molecules simultaneously) at an effective temperature of 240 °C. Figure 3 shows snapshots of simulated self-assembled morphologies of the P3HT-b-P2VP model polymers with four different RR (94, 83, 78, and 72%) and two f_{P2VP} (0.50 and 0.25) values. Consistent with experimental results, the simulated systems having high RR (94 and 83%) show a poorly ordered phase-separated morphology, which resembles the disordered morphology observed in TEM. The polymer systems with higher RR have a higher probability of intermolecular stacking, which can increase the number of domains of crystallized P3HTs. In our simulated condition (P3HT-b-P2VP with a M_0 value of 12.0 kg mol⁻¹ for P3HT block, annealed at 240 °C), crystallized domains of P3HTs induced by the intermolecular interaction become unstable when the RR value is lower than 83%. For example, at the RR values of 78 and 72%, polymers are self-assembled into LAM phase for f_{P2VP} = 0.50 and HPC phase for f_{P2VP} = 0.25, which are well-known morphologies for coil–coil BCPs with minority block volume fraction of 0.50 and 0.25 (Figures 3c,d,g,h). The transition point in terms of the RR values is independent of the f_{P2VP} values because the transition of fibril-to-ordered morphology is mainly affected by the local crystallization of P3HT block. It is worthwhile to note that the RR value (between 83 and 78%) for the phase transition are in excellent agreement with the RR value from our experimental observations. Thus, the phase behavior of BCPs with RR lower than this transition point depends mainly on the enthalpic interaction of BCPs.

Thin films of conjugated polymers are used for polymer-based optoelectronic devices. It is well-known that confinement of the BCPs in a thin film geometry can drive a preferred domain orientation, such as layering of cylindrical or lamellar domains parallel to the interfaces, and also impact the phase behavior.⁵⁰,⁵¹ We used GI-SAXS to evaluate the morphology of the P3HT-b-P2VP polymers in 100 nm films subjected to the same annealing protocol as bulk samples. Figure 4 presents the GI-SAXS patterns from RR 95-b-P2VP (0.35), RR 85-b-P2VP (0.27), RR 78-b-P2VP (0.31), and RR 73-b-P2VP (0.30) with f_{P2VP} value of ~0.3. Following the methods detailed elsewhere,⁴ the experimental patterns are compared with predicted peak positions for different packing symmetries, such as the parallel orientation of the HPC phase. Two peaks are observed for scattering from each plane, and these are designated by “+” and “−” symbols in Figure 4.

The GI-SAXS data for samples with f_{P2VP} ≈ 0.3 show a dramatic morphology transition as a function of RR value. Samples with 95% RR exhibit both in-plane and out-of-plane order with a domain periodicity of D = 22 nm but are poorly ordered, showing broad and extremely weak peaks (Figure 4a). These scattering patterns are consistent with mixed-oriented fibril-like domain structure. The Supporting Information includes additional details that pertain to this conclusion (Figure S5). Samples with 85% RR are highly disordered along both in-plane and out-of-plane directions (Figure 4b), and the scattering cannot be assigned to a typical BCP lattice symmetry. Instead, we propose the domains are micelle-like with a correlation length near D ≈ 27 nm. In contrast, the GI-SAXS patterns for samples with low RR (78 and 73%) content are consistent with highly ordered HPCs, confirmed by comparing the predicted and observed Bragg peak positions for D ≈ 25 nm (Figures 4c,d). The cylindrical domains are oriented with the long axis in the plane of the film and stacked with hexagonal symmetry through the film thickness. Interestingly, from inspection of the in-plane line shapes, as well as the number of out-of-plane Bragg peaks, we conclude that ordering is much higher in polymers with 73% RR compared with 78% RR. For example, the RR 73-b-P2VP (0.30) film showed highly ordered HPC phases with very sharp and distinct peaks, which is typically observed in well-ordered coil–coil BCP structure (Figure 4d and Figure S6). This enhanced ordering of RR 73% BCP is due to a weaker tendency to crystallize. Therefore, the GI-SAXS results confirm a dramatic morphological transition from disordered fibril-like to well-ordered HPC phases with decreasing RR values, which are consistent with bulk TEM and simulation results.

When f_{P2VP} ≈ 0.45, all films exhibit a lamellar structure with layering parallel to the interfaces (Figure 4e). Compared to bulk TEM images, the improvement in lamellar ordering of 95 and 85% RR BCPs is attributed to geometric confinement in thin film assembly.⁵⁰,⁵¹ The beam stop blocks most of the signal from lamellar out-of-plane Bragg peaks, so it is difficult to comment on the extent of ordering. However, the intensity profiles near the beam stop are much stronger for samples with low RR (78 and 73%), which suggests that ordering is significantly improved in these samples. Figure S8 includes out-
of-plane line cuts that offer additional evidence of the structural assignments proposed here. In summary, the GI-SAXS results provide clear evidence that RR can be manipulated to suppress crystallization and allow for BCP assembly into highly ordered nanostructures.

**CONCLUSIONS**

We successfully demonstrated that the morphology of P3HT-b-P2VP block copolymers can be tuned through control of P3HT regioregularity. A series of model P3HT-b-P2VPs were synthesized with polymerization techniques that afford independent control of Mw composition and regioregularity RR with low dispersity. Bulk samples of P3HT-b-P2VP with low RR (78 and 73%) assembled into well-ordered LAM and HPC structures, depending on fP2VP values, whereas those of high RR (95 and 85%) P3HT-b-P2VP only showed disordered fibril-like structures. These morphologies are explained in the context of crystallization versus equilibrium BCP self-assembly, using a simple coarse-grained model as a guide: When RR is high, crystallization dominates and controls the ultimate structure. However, when RR is low, the BCP can self-assemble into the highly ordered nanostructures that are typical of equilibrium BCP phase behavior. In addition, we investigated the thin film structures of P3HT-b-P2VP using GI-SAXS and confirmed that highly ordered thin film structures are achieved at low RR for all polymer compositions. The RR controlled P3HT-b-P2VP polymers provide a novel model system for fundamental studies on the self-assembly of conjugated polymers and opportunities to explore the functionality in a broader class of nanomorphologies for optoelectronic applications.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.7b00128.

Materials and methods, detailed experimental procedures, and additional characterization data (PDF)

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The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This research was supported by the National Research Foundation Grant (2012M3A6A7055540, 2015M1A2A2057509), funded by the Korean Government. This research was also supported by the Research Projects of the KAIST-KUSTAR and the CRH (Climate Change Research Hub) of KAIST. G.E.S. acknowledges the support from NSF-DMR-1151468.

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