

Self-Assembly of All-Conjugated Poly(3-alkylthiophene) Diblock Copolymer Nanostructures from Mixed Selective Solvents

Ming He,^{†,*} Lei Zhao,[‡] Jun Wang,[‡] Wei Han,[‡] Yuliang Yang,[†] Feng Qiu,^{†,*} and Zhiqun Lin^{‡,*}

[†]The Key Laboratory of Molecular Engineering of Polymers, Ministry of Education, Department of Macromolecular Science, Fudan University, Shanghai 200433, China, and [‡]Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011

Conjugated polymers have been widely recognized as promising materials for use in biosensors, thin film transistors, light-emitting diodes, and solar energy conversion.^{1–3} In the latter context, conjugated polymer-based photovoltaic devices capitalize on the advantages peculiar to conjugated polymers, such as lightweight, flexibility, processability, roll-to-roll production, low cost, and large area. The semiconductor-like optical and electronic properties of conjugated polymers depend explicitly on the physical conformation of polymer chains, which can be controlled by the polymer concentration, choice of solvent, presence of side group, etc. Among various types of conjugated polymers, poly(3-hexylthiophene) (P3HT) is one of the most heavily studied organic semiconductors. It is a typical hair-rod conjugated polymer, consisting of a rather rigid thiienyl backbone with flexible hexyl side chains that allow for solubilization. The P3HT structure involves two-dimensional sheets of π -stacked backbone separated by layers of hexyl side chains. P3HT possesses excellent solution processability, chemical stability, and high field-effect mobility ($0.01\text{--}0.1\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$).⁴ The charge carrier mobility of P3HT has been related to its regioregularity, molecular weight, and solvent properties.^{5–8}

Recent advances in synthesis techniques render the design of functional rod–coil block copolymers composed of conjugated block (rod-like) and coil block covalently linked at one end. Compared to conjugated homopolymer and polymer blends, rod–coil block copolymers spontaneously microphase separate into ordered, control-

ABSTRACT The use of mixed selective solvents provides an effective means to control self-assembly of the all-conjugated diblock copolymer poly(3-butylthiophene)-*b*-poly(3-hexylthiophene) (P3BHT) into nanostructured morphologies. The solvent and temperature effects on the self-assembly of P3BHT during cooling and subsequent crystallization were explored for the first time. Depending on the poor/good solvent ratio (*i.e.*, anisole/chloroform), P3BHT chains experience different kinetic pathways, yielding nanowires at a low anisole/chloroform ratio ($\leq 2:1$), and nanorings coexisted with some nanowires at a high anisole/chloroform ratio ($\geq 6:1$). The nanowires are formed as a direct consequence of strong interchain π – π stacking, while the formation of nanorings is governed by solvophobic interactions between conjugated blocks and the poor solvent anisole to minimize the unfavorable contacts between the P3BT block ($\sim 50^\circ\text{C}$) and later P3HT (below 35°C) block and anisole.

KEYWORDS: self-assembly · all-conjugated diblock copolymer · polythiophene · nanowires · nanorings

lable structures on the 10 nm length scale,⁹ which could provide optimized morphologies for charge transport. As such, it offers the opportunity to tailor and optimize the optoelectronic properties for use in photovoltaic cells as the typical exciton (bound electron–hole pairs) diffusion length of most conjugated polymers after photoexcitation is limited to 10 nm. The exciton should effectively dissociate and transport to respective electrodes prior to recombination. A variety of P3HT-based rod–coil block copolymers have been designed and synthesized^{10–12} based on atom transfer radical polymerization (ATRP), ring-opening metathesis polymerization (ROMP), or reversible addition–fragmentation chain transfer polymerization (RAFT), to realize functional assembly. In stark contrast to the rod–coil block copolymers that have been studied extensively, the research on all conjugated block copolymers (*i.e.*, rod–rod) is limited; only a few examples have been reported. The synthesis and self-assembly of rod–rod block copolymers that combine

*Address correspondence to fengqiu@fudan.edu.cn, zqlin@iastate.edu.

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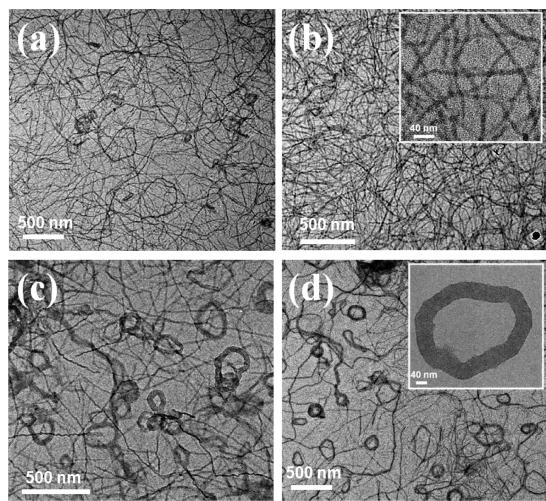


Figure 1. TEM images of P3BHT nanostructures self-assembled from the P3BHT anisole/chloroform solutions after cooling from 80 to 10 °C. Nanowires formed from the anisole/chloroform ratio of (a) 1:1 and (b) 2:1 solutions. The average diameter of nanowires is 8–10 nm (inset in b). In addition to nanowires, nanorings appeared in the anisole/chloroform (c) 6:1 and (d) 10:1 solutions. The ring width of a typical nanoring is 50 nm (inset in d).

intriguing nanostructures and electronic activity offer expanded flexibility for realizing high-performance semiconducting architectures with improved environmental stability and mechanical properties.¹³

Herein, we report a simple, facile route to controlling self-assembly of the all-conjugated diblock copolymer poly(3-butylthiophene)-*b*-poly(3-hexylthiophene) (P3BHT; P3BT:P3HT = 1:1, mol/mol) into nanostructured morphologies by manipulating the poor/good solvent ratio in mixed selective solvents of anisole/chloroform. Anisole is a poor solvent for both P3HT and P3BT blocks, while chloroform is a good solvent for both blocks. The solvent and temperature effects on the self-assembly of P3BHT during cooling and subsequent crystallization were systematically explored by means of UV-vis spectroscopy and TEM. Depending on the anisole/chloroform ratio, P3BHT chains experience different kinetic pathways, yielding nanowires at a low anisole/chloroform ratio ($\leq 2:1$), and nanorings coexisted with some nanowires at a high anisole/chloroform ratio ($\geq 6:1$). The nanowires are formed as a direct consequence of strong interchain $\pi-\pi$ stacking, while the formation of nanorings is dictated by solvophobic interactions¹⁴ between conjugated blocks and the poor solvent anisole to minimize the unfavorable contacts between the P3BT block (~ 50 °C) and later P3HT (below 35 °C) block and anisole.

RESULTS AND DISCUSSION

Formation of Nanostructured Morphologies of P3BHT. Comparison of the TEM images of P3BHT obtained from the solutions at different mixed solvent ratios revealed that the solvent ratio has a marked effect on the structure formation. Figure 1a,b show the TEM images of uni-

formly distributed nanowires formed from the anisole/chloroform ratios of 1:1 and 2:1 solutions, respectively, after slowly cooling from 80 to 10 °C (see Experimental Section). The average length of nanowires is 10 μm . The diameter of the nanowires is about 8–10 nm (inset in Figure 1b), which is very close to that of P3BT homopolymer nanowires produced in *o*-dichlorobenzene (ODCB)¹⁵ but much smaller than those of P3BT and P3HT homopolymer nanowires produced in anisole.¹⁶ It is noteworthy that conjugated nanowires with the diameter below 10 nm are of particular interest as the diameter coincides well with the exciton diffusion length in organic semiconductors, thereby rendering the efficient charge dissociation.¹³ When the anisole/chloroform ratio is increased to 6:1, in addition to nanowires, nanorings emerged in the solution (Figure 1c). With the further increase of the ratio to 10:1, more nanorings were observed with a reduction in the number of nanowires, as shown in Figure 1d. The diameter of the nanorings is in the range of 200–600 nm with the average ring width of 40–60 nm. A typical P3BHT block copolymer nanoring with a uniform ring width of 50 nm is shown in the inset in Figure 1d. Both nanowires and nanorings can be stably dispersed in the mixed solvents for a long time. Notably, the mixed solvent at the anisole/chloroform 2:1 ratio yielded the highest density of long P3BHT nanowires with uniform diameter (Figure 1).

The XRD patterns of the P3BHT nanowire film prepared from the anisole/chloroform 2:1 solution and P3BHT nanowire/nanoring film prepared from the anisole/chloroform 6:1 solution are shown in Figure 2a. The emergence of the [100] and [010] peaks suggested that the P3BHT nanowires and nanorings consist of a stack of P3BHT backbones, adopting the “edge-on” orientation in which polymer backbones are aligned parallel to the substrate, as illustrated in Figure 2b.¹⁷ The [010] peak at $2\theta = 13.1^\circ$ reflects the formation of nanowires with P3BHT interchain $\pi-\pi$ stacking at the distance of 3.3 Å between adjacent coplanar planes (Figure 2b). Compared to poly(3-alkylthiophene) (P3AT) homopolymers, the $\pi-\pi$ stacking distance is slightly decreased from 3.8 Å in P3AT to 3.3 Å in the P3BHT nanowires/nanorings, indicating a much closer $\pi-\pi$ interaction of P3BHT chains along the growth direction (*i.e.*, the long axis *b*). The [100] peaks at $2\theta = 5.8$ and 8.2°, corresponding to a *d* spacing of 15.3 and 10.8 Å, are attributed to the interchain $\pi-\pi$ interaction of P3HT block (5.8°) and P3BT block (8.2°) along the *a* axis within the coplanar plane as depicted in Figure 2b. Therefore, two distinct crystalline domains (*i.e.*, P3HT and P3BT blocks) coexisted in the nanowires and nanorings. This result is in agreement with a recent study on poly(3-butylthiophene)-*b*-poly(3-octylthiophene) films annealed at 280 °C in vacuum with two crystalline domains characteristic of the two side chains (*i.e.*, butyl and octyl) observed by XRD.⁹ The decrease in the P3HT

[100] peak intensity from the anisole/chloroform 6:1 solution, compared to that from the anisole/chloroform 2:1 solution, may be attributed to the preferential crystallization of P3BT blocks to form a P3BHT bilayer and subsequently transform into nanorings, as will be discussed later, thereby restraining the ordered packing of P3HT blocks.

To explore the conformation transformations of P3BHT chains in the anisole/chloroform mixed solvents, UV-vis absorption measurements were performed. It has been demonstrated that the conformation of P3AT chains can be resolved by UV-vis spectroscopy^{9,14,16,18} based on the absorption shift and intensity variation induced by the electronic energy migration along the backbone between adjacent segments (*i.e.*, intrachain) or energy hopping among segments in close proximity (*i.e.*, interchain).¹⁹ As shown in Figure 3a, when completely dissolved in the anisole/chloroform 2:1 ratio at 80 °C, P3BHT displayed a single absorption peak at $\lambda_{\max} = 451$ nm due to the intrachain $\pi-\pi$ transition of P3BHT (*i.e.*, c axis in Figure 2b).²⁰ Not surprisingly, all solutions at the different anisole/chloroform ratio when dissolved at 80 °C exhibited the same absorption maximum (data not shown). It has been shown that, in a nonpolar poor solvent, poly(3-alkylthiophenes) (P3ATs) undergo a disorder-order transformation upon cooling,¹⁸ during which P3ATs tend to aggregate in a face-to-face manner, transitioning from flexible coils to rigid rods/wires to reduce unfavorable contacts between the thienyl backbone and the poor solvent.^{14,18} Similarly, P3BHT chains self-assemble into nanowires upon cooling to 10 °C, represented in the red shift of the absorption spectrum with the appearance of vibronic structures at longer wavelengths (490–610 nm). The two absorption maxima at $\lambda_{\max} = 490$ and 510 nm can be ascribed to the intra-chain $\pi-\pi$ transition of P3BT block and P3HT block, respectively. This coincided well with the XRD measurements, that is, the coexistence of two distinct crystalline domains of P3BT and P3HT.⁹ The shoulder peak at $\lambda_{\max} = 552$ nm is associated with the absorption of increased conjugation length due to the ordered stacking of P3BHT backbones that restricts the rotational motion of the backbones.^{16,20} Additionally, the shoulder peak at $\lambda_{\max} = 610$ nm resulted from the interchain $\pi-\pi$ interaction *via* electronic hopping along the a axis (Figure 3b), and its intensity is correlated with the degree of interchain order.^{20,21}

Figure 3b shows the absorption spectra of P3BHT solutions at different anisole/chloroform ratios after being left at 10 °C for 72 h to allow P3BHT to further crystallize. In the anisole/chloroform 1:1 solution, the intrachain $\pi-\pi$ absorption peak at $\lambda_{\max} = 464$ nm has a relatively small red shift from $\lambda_{\max} = 451$ nm at 80 °C, indicating that most of P3BHT chains are disordered in the solution due to the high ratio of good solvent, chloroform, in the mixed solvents.²² Two shoulder peaks at

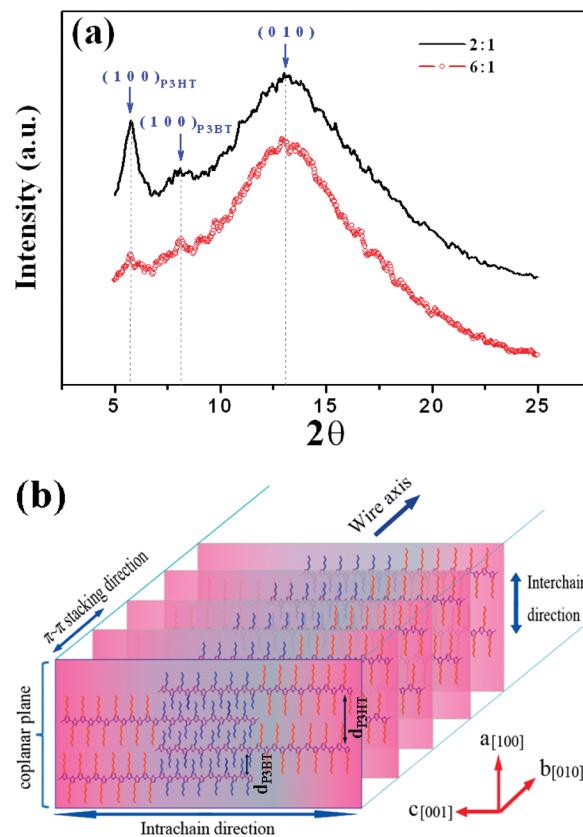


Figure 2. (a) XRD patterns of P3BHT films prepared from the P3BHT anisole/chloroform 2:1 (black curve) and 6:1 (red curve with open circles) solutions. Both solutions were drop-casted on Si substrates after leaving at 10 °C for 72 h and dried at room temperature for 24 h. (b) Schematic representation of P3BHT nanowires with the edge-on orientation, formed upon cooling from the anisole/chloroform solution.

$\lambda_{\max} = 552$ and 610 nm are indicative of existence of some ordered P3BHT nanowires. Taken together, the absorption spectrum revealed two different P3BHT conformations in the solution: one is coil-like polymer chains completely dissolved in the solution, and the other is polymer chains π -stacked against each other to form straight crystalline nanowires (Figure 1) dispersed in the solution.¹⁶ The absorption spectrum in the anisole/chloroform 2:1 solution is considerably red-shifted, signifying a higher planarized conformation in the produced nanowires. The splitting into two absorption maxima at $\lambda_{\max} = 490$ and 510 nm as noted above can be viewed as a result of better crystallization of P3BHT in the anisole/chloroform 2:1 solution. Quite intriguingly, this is consistent with the TEM measurements, where more P3BHT nanowires were observed in the anisole/chloroform 2:1 solution than those in the anisole/chloroform 1:1 solution (Figure 1a,b). On the basis of these results, we argue that the disorder-order transformation of P3BHT in anisole/chloroform is dominated by the saturating concentration of P3BHT.¹⁶ As anisole is a poor solvent and chloroform a good solvent for P3BHT, with the increase of the anisole ratio in the mixed solvents (from 1:1 to 10:1), the saturating con-

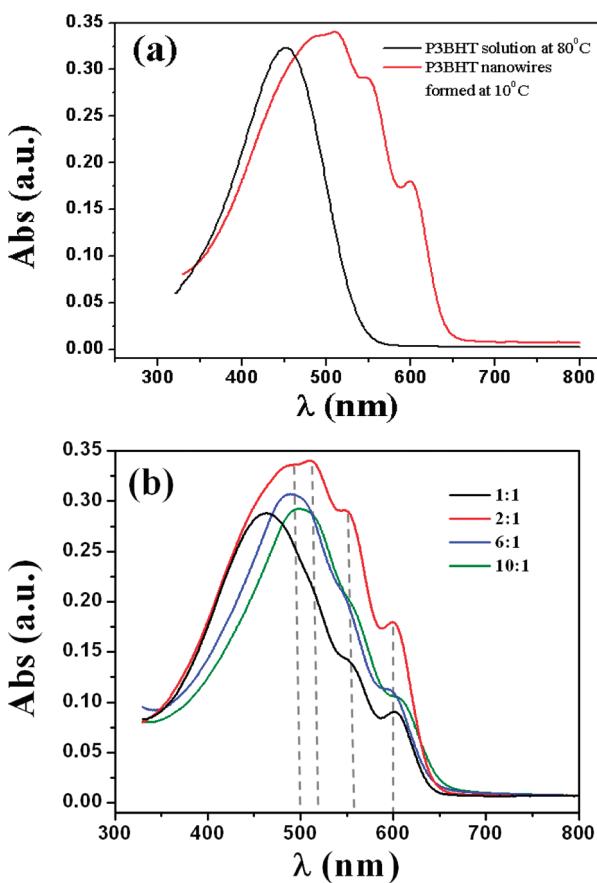


Figure 3. (a) UV–vis absorption spectra of P3BHT dissolved in the anisole/chloroform 2:1 solution at 80 °C (black curve) and after self-assembly at 10 °C for 72 h (red curve). (b) UV–vis absorption spectra of P3BHT self-assembled at 10 °C from solutions at different anisole/chloroform ratios.

centration of P3BHT is lowered. Accordingly, P3BHT chains become less soluble and result in the formation of nanowires (Figure 1b) and of nanowires together with nanorings (Figure 1c,d). A salient difference in absorption between the nanowire (*i.e.*, anisole/chloroform 2:1) and nanoring (*i.e.*, anisole/chloroform 6:1) solutions is that the latter exhibited a markedly decreased intensity at $\lambda_{\text{max}} = 552 \text{ nm}$, which can be attributed to the reduction of conjugation length due to the formation of some P3BHT nanorings.

Kinetic Pathway to the Formation of Nanowires and Nanorings. Although uniformly dispersed P3BHT nanowires can be produced, they were accompanied by the formation of some nanorings at the high anisole ratios (Figure 1c,d). It is clear that the anisole/chloroform ratio plays a crucial role in the self-assembly of P3BHT chains into nanowires and nanorings. To this end, the solvent effect and temperature effect on the formation of P3BHT nanostructures were investigated. The self-assembly process of P3BHT in anisole/chloroform solutions was monitored by comparing the absorption intensity change at $\lambda_{\text{max}} = 610 \text{ nm}$ in the solutions when cooling from 80 to 10 °C and further crystallized at 10 °C. The increase in absorption at $\lambda_{\text{max}} = 610 \text{ nm}$ is directly

correlated to the improved interchain order.^{20,21} The occurrence of this peak implies the presence of ordered structures in the solution associated with interchain π – π stacking, thereby providing insight into the kinetic process of the disorder–order transformation in the P3BHT solution.²⁰

Figure 4a shows the time-dependent absorption change during cooling followed by crystallization at 10 °C. All solutions exhibited a sigmoid in the absorption intensity, corresponding to a two-stage self-assembly process: (1) coil-to-rod conformational transition of polymer chains, and (2) crystallization of rod-like polymer chains into aggregates (*i.e.*, nanowires and nanorings).¹⁶ The latter process (*i.e.*, crystallization) is likely to be the rate-determining step; this is because, even for the anisole/chloroform 10:1 solution, it took more than 100 min to reach constant absorption (*i.e.*, $I_{\text{abs}} = 0.38$; fully crystallized) as opposed to the coil-to-rod transformation that was completed within 50 min (Figure 4a). The more anisole in the mixed solvents, the faster the crystallization rate is, implying that the crystallization is dictated by the solubility of polymer chains in the mixed solvents.¹⁸ Clearly, the presence of less of the poor solvent, anisole (anisole/chloroform $\leq 2:1$), led to a slow self-assembly of P3BHT chains into nanowires, while more anisole (anisole/chloroform $\geq 6:1$) resulted in a relatively rapid self-assembly of P3BHT chains into nanorings together with nanowires.

The change in the absorption intensity as a function of temperature upon cooling during the first 120 min (Figure 4a) is shown in Figure 4b. The P3BHT solution with more anisole (anisole/chloroform $\geq 6:1$) displayed a relatively rapid coil-to-rod conformational transition occurring at a higher temperature ($T \geq 50$ °C), followed by a steep increase in the absorbance, indicating increased degree of interchain order.²⁰ Conversely, the P3BHT solution with less anisole (anisole/chloroform $\leq 2:1$) took a longer time to complete coil-to-rod transformation at a lower temperature ($T = 35$ °C), followed by a slow increase in the absorbance. Notably, these kinetic processes do not bear resemblance to that of P3AT homopolymers. It has been shown that P3ATs with long alkyl side chains (*e.g.*, P3HT) show a slow coil-to-rod transformation (at 35 °C for P3HT) but a fast subsequent crystallization.¹⁶ For P3ATs with short alkyl side chains (*e.g.*, P3BT), they exhibit a fast coil-to-rod transformation (at 50 °C for P3BT) but a slow crystallization due to high free energy change for critical nucleus formation.¹⁶ In this context, we argue that, for the P3BHT block copolymer, the completion of the coil-to-rod transformation at the high anisole ratio occurred at 50 °C (resembling P3BT homopolymer¹⁶), followed by a rapid crystallization (resembling P3HT homopolymer¹⁶). At the low anisole ratio, the coil-to-rod transformation occurred at 35 °C (resembling P3HT homopolymer¹⁶), followed by a slow crystallization (resembling P3BT homopolymer¹⁶). This new kinetic behavior is believed to

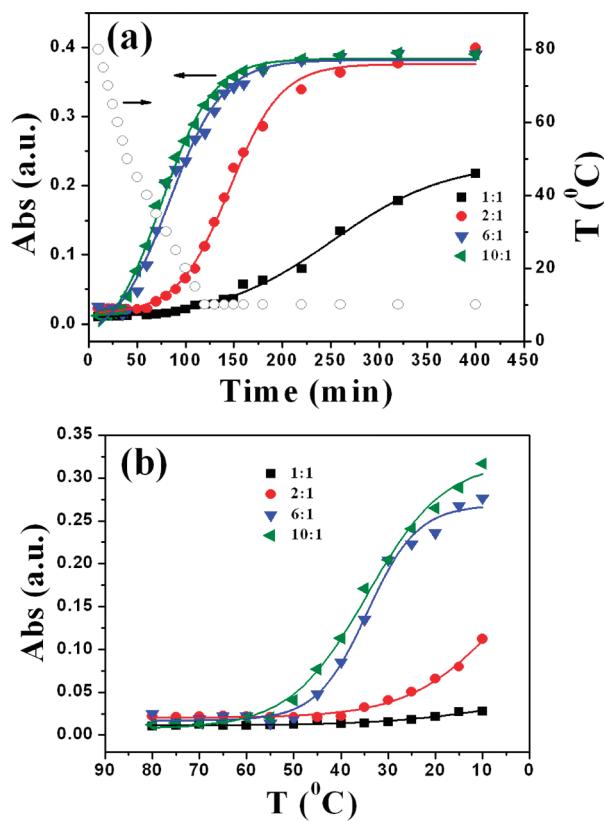


Figure 4. Kinetic processes of P3BHT self-assembled in different anisole/chloroform solutions. (a) Time-dependent absorption change monitored at $\lambda_{\text{max}} = 610 \text{ nm}$. The open circle is the temperature change as a function of time. (b) Temperature-dependent absorption change monitored at $\lambda_{\text{max}} = 610 \text{ nm}$. In both panels, the solutions were cooled from 80 to 10 °C at a cooling rate of 2 °C/min and then maintained at 10 °C to allow for further crystallization.

be responsible for the selective formation of nanowires and nanorings in different P3BHT solutions as further discussed below.

Mechanism of Nanostructure Formation. It is crucial to understand the mechanism for the generation of functional nanostructures in conjugated polymers at the molecular level. Thus, we turn our attention to elucidate qualitatively the possible reason that leads to the formation of nanowires and nanorings. Upon the cooling of P3BHT diblock copolymer in the anisole/chloroform mixed solvents, the conjugated chains first transformed from coil-like to rod-like conformation and then self-assembled into order structures (Figure 4). For the P3BHT solution with high good solvent ratio (anisole/chloroform $\leq 2:1$), the polymer chains do not start to crystallize into ordered nanostructures until the coil-to-rod transformation was achieved at 35 °C (Figure 4b), at which time both P3BT and P3HT blocks transformed into rigid rod-like chains. The resulting rod–rod P3BHT chains readily self-organize into ordered nanowires *via* strong interchain π – π stacking, as illustrated in Figure 5a. The presence of crystalline P3BT and P3HT blocks was clearly evidenced by the XRD and UV–vis absorption measurements (Figures 2 and 3).

By contrast, for the P3BHT solution with high poor solvent ratio (anisole/chloroform $\geq 6:1$), the coil-to-rod transformation was accomplished at a much higher temperature (*i.e.*, 50 °C for anisole/chloroform 6:1 and 55 °C for anisole/chloroform 10:1 by extrapolating the intensity rise to zero; Figure 4b) due to decreased solubility of P3BT block in the solution. However, at this temperature, the P3HT block may still be soluble and remains coil-like, as P3HT usually becomes rod-like at temperature below 35 °C in pure anisole.¹⁶ This is not surprising as

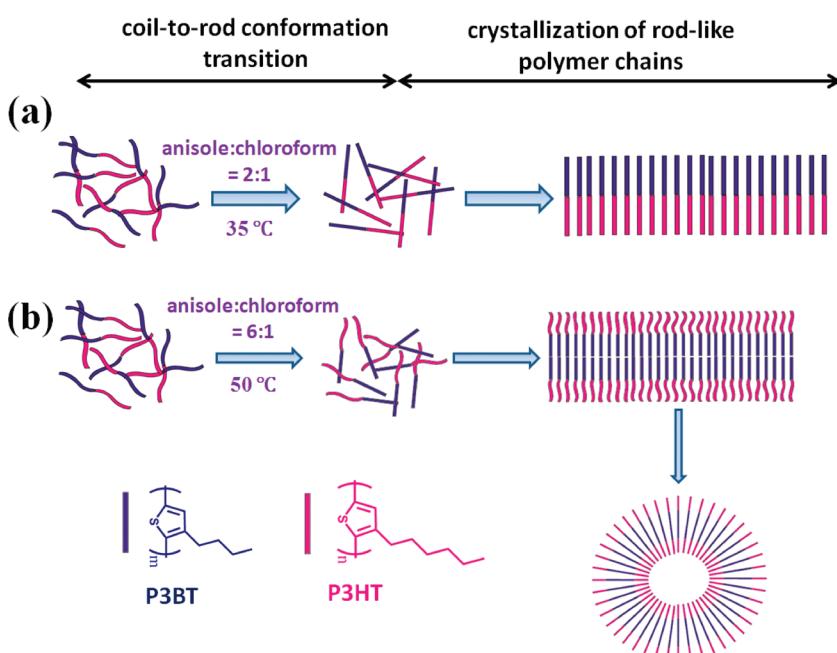


Figure 5. Stepwise representation of possible mechanisms for P3BHT to self-assemble into (a) nanowires and (b) nanorings.

P3BT has a shorter side chain than P3HT and thus lower solubility in anisole. It is likely that, at this stage, P3BHT can be viewed as an “amphiphilic” rod–coil block copolymer with a solvophilic coil-like of P3HT block and a solvophobic rod-like P3BT block, defined by the poorer solubility of P3BT block in the anisole/chloroform $\geq 6:1$ solutions. As a result, the P3BHT bilayer structure (thick nanowires in Figure 1c,d) was formed by packing the P3BT blocks inside and leaving the P3HT blocks outside to minimize the unfavorable contacts between the P3BT block and anisole, as depicted in Figure 5b. The increase in the absorption intensity of P3BHT at 50 °C indicates that the P3BT block packed into ordered structures (Figure 4b), as at this temperature the P3HT block is still coil-like (Figure 5b). A single P3BHT chain in the fully stretched state is nearly 30 nm calculated based on its molecular weight ($M_n = 11\,400$ g/mol) and a repeating period of 8.36 Å along the polymer backbone direction.²³ The width of thick P3BHT nanowires in Figure 1c,d was approximately 50 nm, which clearly supports the formation of a P3BHT bilayer structure.

For conjugated polymers, they possess low internal degrees of freedom and low conformational entropy.²⁴ The entropy loss is thus small when conjugated P3BHT block polymer chains are forced into various structures. As a result, the minimization of the interfacial area between solvophobic polymer chains and the poor solvent dominates the free energy of the system.²⁴ In the present study, with temperature cooled below 35 °C, the solubility of the P3HT block in the anisole/chloroform $\geq 6:1$ solutions decreased, as well. Consequently, the bilayer structure curled into nanorings to reduce the unfavorable interfacial interaction between solvophobic P3HT blocks and anisole (Figure 5b). In the anisole/chloroform $\geq 6:1$ solutions, during the P3HT blocks transforming into rod-like chains below 35 °C, some rod–rod P3BHT may also form and self-assemble into nanowires (*i.e.*, thin nanowire as illustrated in Figure 5a).

This explains the coexistence of nanowires of different width in conjunction with nanorings measured by TEM (Figure 1c,d). It is worth noting that the diameter of thin nanowires was 8–10 nm instead of 30 nm, indicating that a few layers of polymer backbones (*i.e.*, folding of P3BHT chains) may be laminated perpendicular to the long axis of the nanowires (*i.e.*, *b* axis in Figure 2b); this will be the subject of future studies scrutinized by grazing-incidence small-angle X-ray scattering (GISAXS).

CONCLUSIONS

Self-assembly of the all-conjugated diblock copolymer P3BHT in the anisole/chloroform mixed selective solvents was explored for the first time. The change in the anisole/chloroform ratio exerted a profound influence on the assemblies of P3BHT chains during the cooling, leading to the formation of nanostructured morphologies. Uniformly dispersed, high-aspect-ratio P3BHT nanowires with diameters of 8–10 nm and lengths of micrometers were readily achieved in the anisole/chloroform $\leq 2:1$ solutions. Quite intriguingly, by increasing anisole (*i.e.*, anisole/chloroform $\geq 6:1$), a poor solvent for P3BHT, some P3BHT chains self-organized into two-dimensional nanorings. This was promoted by the enhanced solvophobic interaction between P3BHT blocks and anisole, thereby minimizing the unfavorable interfacial area per unit volume in the solution. The diameter of nanorings is in the range of 200–600 nm with the average ring width of 40–60 nm. The strategy by using mixed solvent can be extended to produce intriguing nanostructures in other all-conjugated block copolymers as well as electronic and optoelectronic devices based upon them, such as thin film transistors and photovoltaic cells, where efficient formation of various nanostructures is readily enabled by simply manipulating the selective solvent ratio.

EXPERIMENTAL SECTION

Materials. Anhydrous anisole (99.7%) and chloroform were purchased from Sigma-Aldrich. Poly(3-butylthiophene)-*b*-poly(3-hexylthiophene) (P3BHT) diblock copolymer was synthesized by a modified Grignard metathesis procedure.⁹ Subsequently, it was Soxhlet-extracted with methanol, hexane, and chloroform. The product was dried in a vacuum oven at 70 °C for 24 h to obtain purified P3BHT ($M_n = 11\,400$ g/mol, PDI = 1.34, determined by gel permeation chromatography (GPC)). The ¹H NMR spectra (CDCl₃) (ppm) are as follows: 6.98 (1H), 2.83–2.79 (2H), 1.70–1.67 (2H), 1.49–1.34 (3.96H), 0.98 (1.53H), and 0.91 (1.47H). The molar compositions of butylthiophene and hexylthiophene in P3BHT were determined from the ratio of integrated peaks based on terminal methyl groups of the butyl and hexyl side chains, which shows resonance at 0.98 and 0.91 ppm. The ratio of butylthiophene block to hexylthiophene block is nearly 1:1, as shown in Figure S1 (Supporting Information).

Sample Preparation. The anisole/chloroform mixed selective solvents at different volume ratios of anisole to chloroform (1:1, 2:1, 6:1, and 10:1) were prepared in 20 mL vials. The P3BHT anisole/chloroform solutions were prepared by adding 4 mg of

P3BHT to the vial and stirring at 80 °C overnight until P3BHT completely dissolved to yield a set of 0.2 mg/mL P3BHT solutions with different anisole/chloroform ratios. Four solutions were then slowly cooled to 10 °C at a cooling rate of 2 °C/min, followed by leaving at 10 °C for 72 h to allow P3BHT to further crystallize, during which an apparent color change from originally transparent orange to translucent deep violet was observed (Figure S2, Supporting Information), suggesting the formation of nanostructures.

Characterization. ¹H NMR spectra of P3BHT in CDCl₃ were collected on a DMX 500 MHz spectrometer using tetramethylsilane as the internal standard. GPC was operated using an Agilent 1100 system equipped with a UV detector (eluent, THF; calibration, polystyrene standards). Transmission electron microscope (TEM) imaging was performed on a JEOL 2100 scanning transmission electron microscope operated at 200 kV; the samples were prepared by drop-casting 10 μL of a deep violet solution onto copper grids and dried overnight. UV–vis absorption spectra were recorded with a Nikon Eclipse TE2000-E microscope coupled with an optical insights hyper-spectral unit and a Cascade 512B camera (Roger Scientific).

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Supporting Information Available: ^1H NMR spectrum of P3BHT diblock copolymer and digital images of the P3BHT anisole/chloroform solutions cooled from high temperature to low temperature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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