# Macromolecules

# Morphology Control of Selenophene–Thiophene Block Copolymers through Side Chain Engineering

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**Supporting Information** 

**ABSTRACT:** We report the synthesis of three fully  $\pi$ -conjugated diblock copolymers containing selenophene- and thiophene-based repeating units. All of these diblock copolymers undergo phase separation, and by systematically changing the compatibility of the two blocks through side chain modification, we are able to access different thin film morphologies. Introducing a bulky 2-ethylhexyl side chain increases solubility while retaining crystallinity of the selenophene block. While poly(3-hexylselenophene)-*b*-poly(3-hexylthiophene) and poly(3-(2-ethylhexyl)selenophene-*b*-poly(3-(2-ethylhexyl)thiophene) form more disordered fibrillar structures, poly(3-hexylthiophene)-*b*-poly(3-(2-ethylhexyl)selenophene) forms long  $(1-2 \ \mu m)$  solid state fibrillar structures that are reminiscent



of the lamellae that are formed by nonconjugated block copolymers. We further use electron energy loss spectroscopy to visualize thiophene- and selenophene-rich domains at the nanometer scale in each of these examples. By studying new polymer compositions and relating them to solid state structure, we further our understanding of heterocycle induced phase separation and phase separation in general.

# ■ INTRODUCTION

The synthesis of block copolymers is an effective strategy for the preparation of nanopatterned materials. Experimental and theoretical investigations on "classic" block copolymers (such as polystyrene, polymethyl acrylate, polyisoprene, etc.) have shown that a small number of variables determine the types of ordered structures that will result from a given copolymer.<sup>1</sup> These parameters include the average degree of polymerization of the block  $(N_{a})$ , the volume fraction of the block in the copolymer  $(f_{\lambda})$ , and the Flory interaction parameter  $(\chi)$  of the two blocks. By modifying these parameters, it is possible to access phase-separated domains on the nanometer scale that vary in size (determined by N) and symmetry (determined by the phase diagram and is dependent on  $\chi N$  and  $f_2$ ).<sup>2</sup> Common domain symmetries include lamellae, hexagonally packed cylinders, body-centered cubic, and gyroids.<sup>3,4</sup> Block copolymers are useful in many applications including nanolithography,<sup>5</sup> ultrafiltration,<sup>6</sup> and secondary alignment of small molecules or nanoparticles.<sup>7,8</sup>

Considering the success and utility of block copolymers, there has been a recent emphasis to extend this strategy to  $\pi$ -conjugated polymers. The prospect of controlling 10–20 nm domains is very appealing, as these length scales are of great importance to electronic events in organic electronic devices.<sup>9</sup> There are a number of potential block architectures that are particularly attractive. Because of the control afforded by the Kumada catalyst transfer polymerization (KCTP) of poly(3-hexylthiophene) (P3HT), almost all examples include P3HT.

Block copolymers of P3HT and fullerenes<sup>10,11</sup> are successful as compatibilizing agents, for reducing interfacial tension, and increasing phase stability.<sup>12,13</sup> P3HT has also been copolymerized with a perylene diimide-containing block by an elegant one-pot sequential polymerization that allows for controlled molecular weights and narrow polymer dispersity.<sup>14</sup> This polymer undergoes phase separation, and varying the volume fraction of the two blocks results in different phase-separated morphologies including lamellae and hexagonally packed cylinders.<sup>15</sup>

Another approach focuses on using one conjugated and one nonconjugated block (a rod-coil design). A number of P3HTbased rod-coil copolymers have been investigated.<sup>16–18</sup> The rod-coil design often improves the processability and mechanical properties of the conjugated material.<sup>19</sup> While these materials form phase-separated domains, strong rod-rod interactions in P3HT-containing block copolymers often result in a phase diagram that consists predominantly of fibrillar or lamellar structures. This is because P3HT has a short, linear, regioregular alkyl side chain, resulting in a lamellar crystalline packing structure, which is a strong driving force for nanofibril formation. The strength of this interaction is quantified by the Maier–Saupé parameter ( $\mu$ ) for rod–rod interactions. Many groups have modified  $\mu$  by altering the side chain to either a

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branched or longer linear alkyl group.<sup>20</sup> Atactic poly(3-(2ethylhexyl)thiophene) (P3EHT) incorporates a racemic branching point in the side chain which decreases rod-rod interactions, allowing for a larger phase space in P3EHT copolymers containing a nonconjugated block.<sup>21,22</sup> Several examples of poly(3-dodecylthiophene)-*block*-poly(methyl methacrylate) copolymers exhibit classical phase behavior.<sup>23-26</sup>

By fine-tuning the block copolymer structure and composition, classical phase diagrams have been attained using P3HT blocks as well.<sup>27</sup>

Despite the increase in processability and interesting phase behavior, rod-coil copolymers possess an insulating block that hinders performance in organic electronic devices.<sup>16</sup> Allconjugated rod-rod copolymers have been prepared to address this issue. Rod-rod copolymers are largely limited to allthiophene backbones due to synthetic limitations as few monomer types are compatible with KCTP. Some research groups have circumvented this limitation by alternate syntheses, typically involving end-group control and postpolymerization techniques.<sup>28,29</sup> Some other monomer units have been shown to be amenable to block copolymerization directly through pseudoliving conditions,<sup>30</sup> and catalyst optimization will lead to the controlled polymerization of an even wider selection of conjugated monomers of varying structure and electronics.<sup>31,32</sup> Largely, however, polymer chemists are limited to polythiophene motifs in all-conjugated block copolymers, and thus alteration of side chain functional groups is a convenient route to two distinct blocks. Such alterations include variation of length<sup>33</sup> or bulkiness<sup>34</sup> of alkyl side chains or differences in the chemical nature of the side chains such as polarity,<sup>35</sup> functionality,<sup>36</sup> or optical purity.<sup>37</sup> This results in distinct structural characteristics in each block and often leads to phase separation in the solid state.

While the numbers of available thiophene side chains and combinations thereof are nearly limitless, side chain alteration

occurs adjacent to, as opposed to within, the  $\pi$ -conjugated main chain. Our group has investigated the alteration of the main chain through heteroatom substitution and the synthesis of poly(3-alkylselenophene)-block-poly(3-alkylthiophene) (P3ASb-P3AT) copolymers. P3AS is the selenium containing analogue of P3AT and differs from it in important ways. P3AS has a narrower optical band gap than P3AT due to a stabilization of the lowest unoccupied molecular orbital (LUMO), which is advantageous for electronic applications. The selenium atom is also larger and more polarizable, which results in different crystallization behavior.<sup>38</sup> Interactions between selenium atoms in the solid state could also facilitate charge transfer.<sup>39</sup> Importantly, poly(3-hexylselenophene)-blockpoly(3-hexylthiophene) (P3HS-b-P3HT) undergoes phase separation in the solid state.<sup>40</sup> Gradient and statistical copolymers have been investigated as well.<sup>41,42</sup> This is a new strategy for creating phase separating block copolymers, namely, a copolymer consisting of two blocks of 5-member heterocycles with identical side chains will undergo phase separation if the heteroatoms are not identical. Here, we present a study that considers the effect of both heteroatom and side chain on the morphology of all-conjugated diblock copolymers. We hypothesize that selecting appropriate side chain combinations will allow us to access thin film structures different from those achieved with identical side chains. For the first time we will specifically address the effect of introducing a branched side chain in P3AS-b-P3AT copolymers.

## RESULTS AND DISCUSSION

**Synthesis.** Polymers were synthesized by the chain extension of a separately formed macroinitiator using KCTP (Scheme 1). We focus on a series of three block copolymers: P3HS-*b*-P3HT, poly(3-hexylthiophene)-*block*-poly(3-(2-ethylhexyl)selenophene) (P3HT-*b*-P3EHS), and poly(3-(2-ethylhexyl)selenophene)-*block*-(3-(2-ethylhexyl)thiophene)

polymer	$Se^a \pmod{\%}$	$S^a \pmod{\%}$	$\text{GPC}^{b}$ (NMR <sup>c</sup> ) $M_{\text{n}}$ (kDa)	Đ	annealed (pristine) film $EG^d$ (eV)
P3HS(53)-b-P3HT(47)	53	47	20.2	1.34	1.67 (1.68)
P3HT(50)-b-P3EHS(50)	50	50	15.7	1.18	1.77 (1.78)
P3HT(40)-b-P3EHS(60)	60	40	25.9	1.14	1.77 (1.78)
P3EHS(53)-b-P3EHT(47)	53	47	32.2 (18.4)	1.18	1.75 (1.80)

<sup>*a*</sup>Determined by <sup>1</sup>H NMR spectroscopy. <sup>*b*</sup>1,2,4-Trichlorobenzene at 140 °C, measured against polystyrene standards. <sup>*c*</sup>Determined by comparison of *o*-tolyl-CH<sub>3</sub> peak to combined  $\alpha$ -CH<sub>2</sub> peaks. <sup>*d*</sup>Determined by onset of absorption in thin films.



Figure 1. Thin film absorption profiles of pristine (a) and annealed (b) films.

(P3EHS-b-P3EHT). All of these polymers were prepared with a feed ratio that was expected to yield a 50:50 monomer ratio. Minor discrepancies in the feed vs incorporation ratio are unavoidable; we therefore use the notation where the values in brackets indicate the relative molar incorporation ratios of each monomer confirmed by integration of the characteristic resonances of the aromatic protons on the heterocyclic backbone units (see Supporting Information). Synthesis of P3HS(53)-b-P3HT(47) was accomplished using Ni(dppp)Cl<sub>2</sub> catalyst; however, when similar conditions were used for P3EHS-b-P3EHT, additional resonances were present in the NMR spectra in the aromatic region (see Supporting Information). These resonances are identical to the ones observed for statistical copolymers of 3-alkylthiophenes and 3alkylselenophenes. It is likely that the branch in the side chain increases the monomer bulkiness and slows the kinetics of the chain propagating transmetalation step.43 Thus, the solution contained a mixture of macroinitiator and unconsumed monomer upon the addition of the second monomer. Thus, the second block contained a statistical distribution of the first and second monomers. We therefore turned to a more active catalyst, Ni(dppe)Cl<sub>2</sub>, and found that we could prepare block copolymers without any evidence of a statistical region while maintaining molecular weight control and narrow dispersity. The Ni(dppe)Cl<sub>2</sub> catalyst was used for any polymerizations using a monomer with the 2-ethylhexyl side chain. Because the branched side chains of P3EHS-b-P3EHT were expected to affect the hydrodynamic radius of the resulting polymers (and thus the calculated gel permeation chromatography (GPC) molecular weight), we synthesized these copolymers using a published external initiation procedure that installs an o-tolyl group at one terminus, allowing for the determination of  $M_{\rm n}$ through NMR end-group analysis.<sup>44</sup> We chose to use the less soluble block as the macroinitiator in each case to avoid any

potential solubility complications upon chain extension that could broaden the dispersity of the resultant polymers. The initial three polymers used in this study are P3HS(53)-*b*-P3HT(47), P3HT(50)-*b*-P3EHS(50), and P3EHS(53)-*b*-P3EHT(47) (Table 1).

Polymer molecular weights were determined with GPC that was calibrated using narrow dispersity polystyrene standards. Dispersities are relatively low for all polymers (1.1–1.3), and polystyrene equivalent molecular weights are very close to expected values based on a theoretical degree of polymerization of 100 and typical GPC overestimation of 1.2-2.3.<sup>45</sup> End-group analysis on P3EHS(53)-*b*-P3EHT(47) allowed for quantification of the overestimation of GPC  $M_n$  by NMR. GPC overestimation was 1.75 times the NMR molecular weight, which is slightly larger than what is typically reported for P3HT homopolymers with degree of polymerization of less than 100.<sup>46</sup> This is consistent with the larger hydrodynamic radius of the monomers with larger side chains.

Optoelectronic Properties. All of the block copolymers are soluble in chlorobenzene, and polymer thin films were cast from solution (8 mg/mL) onto glass substrates that had been previously coated with poly(sodium 4-styrenesulfonate) (to facilitate delamination, vide infra) by spin-coating (1000 rpm). We note a considerable increase in solubility of any copolymer which incorporates the 2-ethylhexyl side chain. This greatly facilitates the characterization of the copolymers and aids especially in the study of selenophene-containing copolymers which are less soluble than their thiophene analogues. The onset of film optical absorption was used to estimate the optical band gap in the thin films and taken as the point at 10% absorption of the peak maximum. The effect of thermal annealing was examined by measuring optical absorption before and after a 16 h annealing step in a nitrogen-filled glovebox (Figure 1). Annealing temperatures were varied with the copolymer to the highest temperature that did not result in loss of film integrity (observed as a significant blue-shift in absorption or film disintegration upon delamination) and noted in the text as these conditions depend on the structure of the copolymers. P3HS(53)-b-P3HT(47) has the most narrow optical band gap (1.68 eV), and while the annealing step (200 °C) increases the vibronic structure in the absorption profile, the optical band gap remains relatively unchanged (1.67 eV). The optical band gap of P3HT(50)-b-P3EHS(50) (1.78 eV) is slightly larger than P3HS(53)-b-P3HT(47), likely due to the backbone twisting induced by the bulkier 2-ethylhexyl side chain. It is also relatively unchanged after annealing (200 °C). P3EHS(53)-b-P3EHT(47) has the widest pristine optical band gap (1.80 eV); however, upon annealing (100 °C) the optical band gap narrows the most significantly (1.75 eV). This is attributed to relatively large disorder of the bulky side chains that exists immediately after spin-casting and relatively large increase in order brought on by annealing. All three polymers display increased vibronic fine structure after the annealing step, suggesting that there is an increase in backbone rigidity and interchain order. The increased vibronic fine structure observed in the absorption profiles indicates that the block copolymers undergo phase separation into regions rich in either selenophene or thiophene.47

**Wide-Angle X-ray Diffraction.** To probe the crystalline nature of the samples, we turned to X-ray diffraction experiments. Films were drop-cast from chlorobenzene solution onto silicon substrates, annealed as described above, and 2-dimensional diffraction patterns were collected. All polymers have a strong diffraction peak which is strongly aligned in the out-of-plane direction at  $5^{\circ}-7^{\circ}$  (Figure 2). This is assigned as



**Figure 2.** Annealed thin film XRD pattern for P3HS(53)-*b*-P3HT(47) and P3HT(50)-*b*-P3EHS(50) and P3EHS(53)-*b*-P3EHT(47). Inset is representative 2D area detector image of P3HS(53)-*b*-P3HT(47).

the lamellar spacing dictated by the length of the alkyl side chains in an edge-on orientation. P3HS(53)-b-P3HT(47) has a single sharp diffraction peak which corresponds to an interlayer spacing (*d*-spacing) of 15.8 Å. This is in agreement with previous reports.<sup>40</sup> Only one diffraction peak is present in this case because the *d*-spacings of both the P3HT and P3HS are not sufficiently different to produce two resolved peaks. P3EHS(53)-b-P3EHT(47) also has a single diffraction peak which corresponds to an interlayer distance of 14.1 Å, notably smaller than the copolymers with linear hexyl side chains. A smaller *d*-spacing for the 2-ethylhexyl side chain compared to the hexyl side chain has been reported previously, along with a concurrent increase in  $\pi$ - $\pi$  stacking distance.<sup>20,48</sup> When considering both the optical absorption and XRD data, it appears that the EH side chain increases backbone twisting, and this allows the polymer chains to pack more tightly in the edgeon plane. The diffraction pattern for P3HT(50)-*b*-P3EHS(50) contains two diffraction peaks that correspond to interlayer distances of 15.8 and 14.1 Å. These diffraction peaks are consistent with crystalline P3HT and P3EHS, respectively. Interestingly, when a P3HT-*b*-P3EHT block copolymer was examined in a previous study, only one diffraction peak is observed.<sup>48</sup> It should be noted that the relative amount of P3EHT in the previous study was relatively low (17%) and is the likely explanation for the lack of the expected higher angle peak.

**Differential Scanning Calorimetry.** DSC was carried out to determine thermal properties. Each polymer was subjected to a heat-cool-heat cycle to examine both the as-cast and post-melt behavior. While literature data exist for P3HT ( $T_m =$ 240 °C), P3HS ( $T_m = 110$  and 250 °C),<sup>49</sup> and P3EHT ( $T_m =$ 71 and 83 °C),<sup>20</sup> P3EHS homopolymer was previously unknown and was examined first. P3EHS has a melting transition of 107 °C (see Supporting Information). P3HS(53)*b*-P3HT(47) exhibits two melting transitions in its first heating cycle (120 and 230 °C), as we have previously reported (Figure 3).<sup>40</sup> The transition at 120 °C corresponds to the type 2



**Figure 3.** DSC profiles of copolymers. First heating and cooling cycle (top) displaced from second heating cycle (bottom).

polymorph of P3HS and is not present in the second heating cycle, as this polymorph is readily converted to the type 1 polymorph upon heating. The transition at 230 °C corresponds to the melting transition of both P3HT and P3HS (both the type 1 polymorphs). While these two blocks have nominally different melting transitions, these copolymers often exhibit only a single melting peak due the proximity of the two transitions. The thermal profile of P3HT(50)-*b*-P3EHS(50) exhibits transitions at approximately 220 and 230 °C in both heating cycles that likely both correspond to the P3HT block. Multiple melting transitions have been reported previously for P3HT and are attributed to a "melting–recrystallization–melting" process.<sup>50</sup> The absence of the P3EHS transition is likely due to the low crystallinity of this block, in agreement with XRD data and melting enthalpy. The melting enthalpy of P3EHS (6.3 J/g) is notably less than that of P3HT (23.7 J/g<sup>51</sup>).

To further probe this observation, we examined a more P3EHS-rich version of this polymer [P3HT(40)-*b*-P3EHS-(60)], and in this case a low temperature melting transition (100 °C) that is assigned to the P3EHS block is observed. The profile of P3EHS(53)-*b*-P3EHT(47) contains a single melting transition at approximately 110 °C in both heating cycles which corresponds roughly to the expected transition of the P3EHS block. The expected transition of the P3EHS block. The expected transition of the P3EHT block is absent; however, this transition is not always observed.<sup>48</sup> Both P3HS(53)-*b*-P3HT(47) and P3HT(50)-*b*-P3EHS(50) exhibit a recrystallization transition during their cooling cycles; however, no such exotherm is observed for P3EHS(53)-*b*-P3EHT(47). For P3EHS(53)-*b*-P3EHT(47), a recrystallization exotherm appears in the second heating cycle at 75 °C.

**Electron Microscopy.** To visualize the structures formed by these polymers, we utilized transmission electron microscopy (TEM). For this purpose, we delaminated the films used for absorption measurements and collected the samples onto TEM grids. In order to facilitate delamination, we first coated the glass substrates with a thin film of poly(sodium 4styrenesulfonate). Films were imaged after annealing. The structure of P3HS(53)-*b*-P3HT(47) consists of nanofibrillar crystallites that are typical of P3HT-type polymers and mostly disorganized at larger (micrometer) scales (Figure 4). P3EHS(53)-*b*-P3EHT(47) forms more continuous films of fibrillar type structures that are broader. These fibrillar



Figure 4. Bright field TEM images of copolymers. Scale bar: 500 nm.

structures are still quite disordered on larger scales. Interestingly, P3HT(50)-*b*-P3EHS(50) forms long fibrillar structures that are highly aligned on the scale of the TEM images and reminiscent of the lamellar phase of a classical block copolymer system. Domains persist for a minimum of  $1-3 \mu m$  and are ordered on these scales to a much greater degree than P3HS(53)-*b*-P3HT(47) or P3EHS(53)-*b*-P3EHT(47).

This interesting difference in thin film morphology led us to investigate other compositions of P3EHS-*b*-P3EHT and P3HT*b*-P3EHS. P3EHS(88)-*b*-P3EHT(12) forms very similar morphologies as P3EHS(53)-*b*-P3EHT(47) (see Supporting Information). P3HT(40)-*b*-P3EHS(60), which possesses a slight excess of selenophene, results in material that forms long lamellar domains similar to P3HT(50)-*b*-P3EHS(50) (see Supporting Information).

We next turned to electron energy loss spectroscopy (EELS) to examine the elemental composition of the structures observed in TEM. Although selenium does not produce a strong signal using EELS, sulfur does, and combining a dark field TEM image with EELS images of sulfur is informative (Figure 5). In the dark field image, regions rich in heavier



**Figure 5.** Dark field TEM (top row), EELS-sulfur image (middle row), and composite image (bottom row) of P3HS(53)-*b*-P3HT(47) (left column), P3HT(40)-*b*-P3EHS(60) (center column), and P3EHS(53)-*b*-P3EHT(47) (right column). Bright regions in the EELS image are sulfur-rich and dark regions are sulfur-deficient. The red regions of the composite image are the bright regions from the dark field image, and the blue regions are bright regions in the EELS image. Scale bars: 200 nm.

elements (selenium) appear brighter and regions with lighter elements (sulfur) appear darker. In the case of P3HS(53)-*b*-P3HT(47), the disordered fibrils that appear dark in the bright field image appear bright in the dark field image. This suggests the heavier selenium atom is present in this region but could also correspond to a more crystalline P3HT region. Turning to the EELS sulfur-selective image, we observe that the bright regions in the dark field image correspond with dark features in the EELS image. This confirms that these regions are sulfurdeficient and selenium-rich. Sulfur appears to be diffusely present in the sample, but more concentrated immediately adjacent to the dark regions, as one would expect from these phase-separated block copolymer structures. A similar observation is made when examining both P3EHS(53)-*b*-P3EHT(47) and P3HT(40)-*b*-P3EHS(60). The alternating bright and dark lamellar regions present in the dark field image invert when compared to the EELS sulfur image, confirming that the lamellae consist of alternating selenium and sulfur rich domains. It is notable that although all of these copolymers form similar crystalline structures (that is, they are all similarly ordered on the 1–2 µm scale), they do not possess the same order on the 1–2 µm scale. The origin of these differences is still not clear but could lie in the decreased rod–rod interactions and change in  $\chi$  that is achieved in the specific case of P3HT-*b*-P3EHS.

We also find that the domain sizes of the features observed in the diblock copolymers differ depending on the nature of the side chains. The fibrils in P3EHS(53)-*b*-P3EHT(47) are qualitatively wider than the domains formed in either P3HS(53)-*b*-P3HT(47) or P3HT(40)-*b*-P3EHS(60). P3ATtype polymers are known to align along this axis (normal to the long axis of the fibril),<sup>52</sup> and so higher molecular weight polymers (as is the case with P3EHS(53)-*b*-P3EHT(47)) should account for these observations.

### CONCLUSIONS

In this study, we synthesized a series of thiopheneselenophene diblock copolymers. Modification of the side chains of each block results in notable changes in processability, optical properties, and most importantly thin film morphology. Selenophene-thiophene block copolymers with identical side chains produce thin films that are ordered on the 1-2 nm scale, as demonstrated by WAXD peaks, but relatively disordered on the 1–2  $\mu$ m scale. Compositional differences were examined; however, no changes were observed in morphology within the compositions studied. By using different side chains on each block, the 1-2 nm scale order is maintained, and a much more ordered lamellar structure is observed on the 1–2  $\mu$ m scale. The unstained images of these films are striking and elemental mapping experiments allow us to concretely determine where each domain is present in the film. Overall these polymers are important for advancing our understanding of phase separation and by further changing the composition we expect to access additional structures with these systems. Experiments are underway to thoroughly explore the complete phase diagram of these copolymers across a broader compositional range and confirm the long-range order observed in TEM imaging through more advanced X-ray scattering experiments.

#### EXPERIMENTAL SECTION

**General Considerations.** All reagents were used as received unless otherwise specified. 2,5-Dibromo-3-hexylselenophene,<sup>42</sup> 2,5-dibromo-3(2-ethylhexyl)thiophene,<sup>20</sup> and 3-chloromethyl-5-ethyl-1-nonyn-3-ol<sup>33</sup> were synthesized as previously reported. 2,5-Dibromo-3-hexylthiophene, isopropylmagnesium chloride (2.0 M solution in THF), Ni(dppp)Cl<sub>2</sub>, Ni(dppe)Cl<sub>2</sub>, 2-bromotoluene, and N-bromo-succinimide (NBS) were purchased from Sigma-Aldrich. Solvents were dried using an Innovative Technology solvent purification system.

**Instrumentation.** <sup>1</sup>H NMR was performed using a Varian Mercury 400 (400 MHz) spectrometer. GPC measurements were carried out using a Malvern 350 HT-GPC system at 140 °C with 1,2,4-trichlorobenzene stabilized with butylated hydroxytoluene and calibrated with narrow dispersity polystyrene standards. Absorption spectra were recorded using a Varian Cary 5000 spectrophotometer.

Wide-angle X-ray diffraction experiments were carried out using a Bruker D8 Discover diffractometer with a cobalt sealed tube source. Data were collected using a Vantec 500 area detector. Differential scanning calorimetry was performed on a TA Instruments Q100 DSC (block copolymers) or a TA Instruments SDT Q600 TGA/DSC (P3EHS). Bright field TEM was performed on a Hitachi H-7000 transmission electron microscope at 100 kV accelerating voltage. Dark field TEM and EELS imaging were carried out on an FEI Tecnai 20 transmission electron microscope at 200 kV accelerating voltage.

Thin Film Preparation. Glass slides  $2 \times 2$  cm were placed in piranha solution for 15 min then cleaned with distilled water and dried with a stream of nitrogen. A solution of poly(sodium 4-styrenesulfonate) (10 mg/mL in a 1:1 vol·vol mixture of water and ethanol) was spin-coated onto the slide (500 rpm 1.5 s, 4000 rpm 60 s) and then annealed at 130 °C for 15 min in air. A solution of polymer (8 mg/mL in chlorobenzene) was then coated onto the slide (500 rpm 1.5 s, 1000 rpm 60 s) and annealed in a nitrogen-filled glovebox at the described temperature for 16 h. These films were then used for absorption measurements. To prepare TEM samples, the films were scored then the slide was immersed in water to delaminate the films. The films were collected on a copper TEM grid.

Synthesis. 3-(2-Ethylhexyl)selenophene. A three-neck flask was charged with selenium powder (3.9 g, 50.1 mmol), then evacuated, and backfilled with nitrogen (flask 1). Ethanol (160 mL) was degassed and added to the selenium. Sodium borohydride (3.03 g, 80.2 mmol) was added in portions. After the solution turned clear and colorless, the mixture was cooled in an ice bath. A solution of 3-chloromethyl-5ethyl-1-nonyn-3-ol (5.91 g, 31.3 mmol) in ethanol (15 mL) was degassed and added to flask 1. The reaction was allowed to warm to room temperature and stirred for 1.5 h. A solution of KOH (2.81 g, 50.1 mmol) was dissolved in 28 mL of ethanol with 1 mL of water. The mixture in flask 1 was heated to reflux, and the KOH solution was added and allowed to reflux for an additional 2 h. The reaction was cooled in an ice bath, and 5% HCl was added. The reaction mixture was diluted with ethyl ether, and the mixture was filtered. The liquor was washed with acid, water, and brine, and then the solvent was removed under reduced pressure. The resulting yellow oil was subjected to a short silica column eluting with hexanes to yield the final product (4.13 g, 54%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  [ppm] = 7.90 (dd, J1 = 5.4, J2 = 2.4 Hz, 1H); 7.51 (m, 1H); 7.18 (dd, J1 = 5.2, J2 = 1.2 Hz, 1H); 2.54 (d, J = 7.2, 2H); 1.55 (m, 1H); 1.32–1.23 (m, 8H); 0.90–0.85 (m, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  [ppm] = 144.0, 131.9, 129.4, 124.7, 40.3, 36.1, 32.6, 29.0, 25.7, 23.1, 14.2, 10.9. HRMS-DART: calcd 245.08085; found 245.08071;  $\Delta = 0.56$  ppm.

2,5-Dibromo-3-(2-ethylhexyl)selenophene. A degassed solution of NBS (2.30 g, 12.9 mmol) in DMF (50 mL) was added dropwise to a degassed solution of 3-(2-ethylhexyl)selenophene (1.26 g, 5.18 mmol) in DMF (50 mL) in an ice bath in the dark. This reaction was allowed to warm to room temperature and stirred for 16 h. The reaction was quenched with saturated sodium thiosulfate solution and diluted with Et<sub>2</sub>O. The phases were separated, and the organic phase was washed three times with water and twice with brine and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure to yield an orange oil. Column chromatography (hexanes) afforded the product as a pale yellow oil (1.5 g, 72%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  [ppm] = 6.95 (s, 1H), 2.41 (d, *J* = 7.2 Hz, 1H), 1.59–1.51 (m, 1H), 1.32–1.21 (m, 8H), 0.91–0.86 (m, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  [ppm] = 144.3, 134.7, 113.5, 111.7, 40.0, 35.0, 32.5, 28.8, 25.7, 23.1, 14.2, 10.9. HRMS-DART: calcd 400.90187; found 400.90146;  $\Delta$  = 1.02 ppm.

o-Tolylmagnesium Bromide. Magnesium turnings (0.63 g, 25.9 mmol) were added to a Schlenk flask with an argon atmosphere. Dry THF (20 mL) was added to the flask, and the mixture was cooled in an ice bath. 2-Bromotoluene (2.2 mL, 3.15 g, 18.4 mmol) was added slowly, and the mixture was allowed to reflux for 45 min and then cooled to room temperature. The solution was allowed to settle, and the solution was transferred to a sealed flask via a cannula fitted with a filter to remove excess magnesium. The concentration of the solution (0.8 M) was determined by titration with salicylaldehyde phenylhydrazone.<sup>54</sup>

Polymer Synthesis. P3HS(53)-b-P3HT(47). 2,5-Dibromo-3-hexylselenophene (178 mg, 0.477 mmol) was loaded into a Schlenk flask placed under vacuum for 20 min. Dry THF (3.4 mL) was added followed by *i*-PrMgCl (0.23 mL, 0.46 mmol) solution at room temperature. In a separate flask, 2,5-dibromo-3-hexylthiophene (153 mg, 0.469 mmol) was prepared in the same manner. After 1 h, the 2,5dibromo-3-hexylselenophene/i-PrMgCl solution was added to a separate flask containing Ni(dppp)Cl<sub>2</sub> (5.1 mg, 0.0094 mmol) and heated to 40 °C. The solution turned bright orange, and the reaction was allowed to continue for 15 min, at which time the thiophene solution (which had also reacted with the *i*-PrMgCl for 1 h) was added slowly to the polymerization flask and allowed to react for an additional 15 min. The reaction was quenched with 5% HCl and precipitated in methanol, filtered through a Soxhlet thimble, and extracted with methanol, hexanes, and chloroform. The chloroform fraction was collected and concentrated and then passed through a short silica column using chloroform. The solvent was removed under reduced pressure to yield the polymer as a purple solid (113 mg, 63%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  [ppm] = 7.12 (s, 0.53 H), 6.98 (s, 0.47 H), 2.80 (t, J = 8 Hz, 1H), 2.73 (t, J = 8 Hz, 1H), 1.75-1.65 (m, 2H), 1.47-1.39 (m, 2H), 1.39-1.30 (m, 4H), 0.95-0.88 (m, 3H). GPC (1,2,4-trichlorobenzene, 140 °C):  $M_n = 20.2$  kDa,  $M_w = 27.1$ kDa,  $\bar{D} = 1.34$ .

*P3HT(50)-b-P3EHS(50).* This polymer was prepared and isolated in an analogous manner as P3HS(53)-*b*-P3HT(47), using Ni(dppe)Cl<sub>2</sub> (1 mol %), to yield a purple solid (99 mg, 48%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ [ppm] = 7.09 (s, 0.5H), 6.98 (s, 0.5H), 2.81 (t, *J* = 8 Hz, 1H), 2.66 (d, *J* = 7.2 Hz, 1H), 1.75−1.66 (m, 1.5H), 1.48−1.25 (m, 7.5H), 0.95−0.86 (m, 4.5H). GPC (1,2,4-trichlorobenzene, 140 °C):  $M_n$  = 15.7 kDa,  $M_w$  = 18.5 kDa, D = 1.18.

*P3HT*(40)-*b*-*P3EHS*(60). This polymer was prepared and isolated in an analogous manner as P3HT(50)-*b*-P3EHS(50) to yield a purple solid (171 mg, 62%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ [ppm] = 7.09 (s, 0.6H), 6.98 (s, 0.4H), 2.81 (t, *J* = 8 Hz, 0.8H), 2.67 (d, *J* = 7.2 Hz, 1.2H), 1.75–1.66 (m, 1.4H), 1.48–1.25 (m, 7.5H), 0.95–0.86 (m, 4.5H). GPC (1,2,4-trichlorobenzene, 140 °C):  $M_n$  = 25.9 kDa,  $M_w$  = 29.5 kDa, D = 1.14.

P3EHS(53)-b-P3EHT(47). Ni(dppe)Cl<sub>2</sub> (73 mg, 0.14 mmol) was suspended in THF (10 mL) and cooled in an ice bath. o-Tolylmagnesium chloride solution (0.170 mL, 0.14 mmol) was added slowly, and the solution turned dark brown (catalyst solution). The catalyst solution was allowed to react for 1.5 h. 2,5-Dibromo-3-(2ethylhexyl)selenophene (223.5 mg, 0.557 mmol) and 2,5-dibromo-3-(2-ethylhexyl)thiophene (199.0 mg, 0.562 mmol) were dissolved in two separate flasks containing THF (4 mL) and each treated with a solution of *i*-PrMgCl (0.28 mL, 0.55 mmol) at room temperature for 1 h. The catalyst solution (0.81 mL, 0.011 mmol) was then added in one portion to the selenophene monomer flask and allowed to react for 15 min. The thiophene monomer solution was then added in one portion to the polymerization flask and allowed to react for an additional 15 min. The reaction was guenched with 5% HCl solution and precipitated into cold methanol. The resulting purple solid was filtered through a Soxhlet thimble and washed with methanol. The polymer was extracted with methanol, ethyl acetate, and hexanes where the polymer was isolated as a purple solid from the hexanes fraction (243 mg, 71%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  [ppm] = 7.08 (s, 0.54H), 6.98 (s, 0.46H), 2.76–2.64 (doublet pair, J = 7.2. 7.6 Hz, 2H), 1.75-1.66 (m, 1H), 1.44-1.24 (m, 8 H), 0.95-0.86 (m, 6H). GPC (1,2,4-trichlorobenzene, 140 °C):  $M_{\rm n}$  = 32.2 kDa,  $M_{\rm w}$  = 38.2 kDa, D = 1.18. NMR end-group analysis:  $M_{\rm n} = 18.4$  kDa.

*P3EHS(88)-b-P3EHT(12).* This polymer was prepared in an analogous manner as P3EHS(53)-*b*-P3EHT(47). The polymer was extracted with methanol and hexanes where the polymer was isolated as a purple solid from the hexane fraction (243 mg, 71%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ [ppm] = 7.08 (s, 0.88H), 6.98 (s, 0.12H), 2.76–2.64 (m, 2H), 1.75–1.66 (m, 1H), 1.44–1.24 (m, 8 H), 0.95–0.86 (m, 6H). GPC (1,2,4-trichlorobenzene, 140 °C):  $M_n$  = 17.6 kDa,  $M_w$  = 19.0 kDa, D = 1.08. NMR end-group analysis:  $M_n$  = 11.6 kDa.

# ASSOCIATED CONTENT

#### **Supporting Information**

<sup>1</sup>H NMR spectra, GPC elution profiles, additional absorption profiles, two-dimensional XRD patterns, additional DSC profiles, and TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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