Synthesis, Morphology, and Field-Effect Transistor Characteristics of New Crystalline–Crystalline Diblock Copolymers of Poly(3-hexylthiopheneblock-steryl acrylate)

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ABSTRACT: We report the synthesis, morphology, and chargetransporting characteristics of new crystalline–crystalline diblock copolymers, poly(3-hexylthiophene-*block*-stearyl acrylate) (P3HT*b*-PSA). Three different diblock copolymers, **P1**, **P2**, and **P3**, with P3HT/PSA polymerization degree block ratios of 60/26, 60/50, and 60/360, respectively, were prepared for investigating the morphology-property relationship and the dependence of optoelectronic properties on the block copolymer structure. Small- and wide-angle X-ray scattering indicated the presence of both P3HT and PSA crystalline domains and the presence of microphase separation among blocks. The transmission electron microscopy and atomic force microscopy results revealed that the diblock copolymers cast from chlorobenzene, tended to form needle-like morphologies. The field-effect mobilities of the diblock copoly-

INTRODUCTION Rod-coil block copolymers have attracted great scientific interest because they can self-organize to form ordered nanostructures. A variety of morphological transformations can be manipulated by controlling various driving forces, including block length, hydrophilicity, chain flexibility, segregation among blocks, and other driving forces.¹⁻¹¹ Conjugated rod-coil block copolymers, in particular, have been extensively investigated for sensory and electronic applications because of their tunable optoelectronic properties and nanoscale morphologies, including polyfluorene,^{7,9,12,13} polythiophene,^{14–31} phenylenevinylene,^{2–4} and polyquinoline.^{6,32} Among these conjugated diblock copolymers, we are particularly interested in the diblock copolymer with regioregular poly(3-hexylthiophene) (P3HT) block, because P3HT possesses solution processability, supramolecular two-dimensional ordering, and excellent semiconducting properties, inducing high charge mobility.^{33–37}

Several amorphous nonconjugated polymer blocks have been incorporated with the P3HT block for tuning the morphology

mers deposited on untreated SiO₂ substrates, decreased with increasing PSA block length. In a sharp contrast, the mobilities enhanced with increasing PSA content when the P3HT-*b*-PSA was deposited on phenyltrichlorosilane (PTS)-treated substrates. The copolymers with a 60/360 P3HT/PSA ratio showed a good mobility of 4×10^{-3} cm² V⁻¹ s⁻¹ and a high on/off ratio of 7×10^6 on PTS-treated substrates. This study highlighted the importance of the block ratio, the substrate and self-assembly structures on the charge transport characteristics of the crystalline–crystalline conjugated diblock copolymers. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 686–695, 2012

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and properties, such as poly(4-vynilpyridine),³³ poly(2-(dimethylamino)ethyl-methacrylate),²⁰ poly(methyl acrylate) (PMA),¹⁷ poly(methyl methacrylate),¹⁸ poly(styrene) (PS),³⁸ and other coil segments.³⁹⁻⁴¹ However, the diblock copolymer of P3HT and amorphous nonconjugated polymer commonly required a significant amount of semiconducting polymers to maintain the charge transporting ability. For instance, the charge mobilities of P3HT-b-PMA showed an obvious degradation when incorporating with 57% amorphous PMA segments.¹⁷ Liu et al. reported that the electrical conductivities of P3HT-b-PS with 48% PS exhibited one to two orders of magnitude lower than the pristine P3HT. In contrast with rod-coil block copolymers with an amorphous nonconjugated coil block, the diblock copolymers consisting of a P3HT rod and a crystalline nonconjugated block have not been explored in details. Müller et al. demonstrated that adding a semicrystalline polyethylene block to P3HT is an efficient approach to enhance the mechanical property of the resulting block copolymer and obtain excellent charge

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SCHEME 1 Synthetic scheme of P3HT-b-PSA with different block length ratios.

transporting characteristics even at a P3HT content as low as 10 wt %.¹⁶ However, semicrystalline polyethylene requires a relatively high processing temperature in the range from 110 to 145 °C, depending on its molecular weight and branching,^{42,43} restricting the window of processing parameters and substrates. To reduce the processing temperature, comb-like crystalline poly(stearyl acrylate) (PSA) may be an appealing candidate to develop a P3HTbased block copolymer for device applications. PSA, with a low melting temperature of 45 °C, has been extensively studied for industrial applications, ex. shape memory,⁴⁴ and pour-point depressant,⁴⁵ which is commonly used to depress the pour point and improve low-temperature flow behaviors of crude oil.⁴⁵

In this study, we report the synthesis, morphology, and charge transporting characteristics of a new crystalline–crystalline P3HT-*b*-PSA diblock copolymer. P3HT macroinitiator was prepared by Grignard metathesis reaction (GRIM), first and then, the PSA segments with different molecular weights were prepared by atom transfer radical polymerization (ATRP), as shown in Scheme 1. Three different diblock copolymers of **P1**, **P2**, and **P3**, with the P3HT/PSA polymerization degree block ratios of 60/26, 60/50, and 60/360, respectively, were prepared. The morphology of the P3HT-*b*-PSA block copolymers was investigated by small- and wide-angle X-ray scattering (SAXS/WAXS), atomic force microscopy (AFM), and transmission electron microscopy (TEM). The charge carrier mobilities were measured on both untreated and treated SiO₂/Si substrates by field-effect transistors (FETs). The surface treatment of SiO_2 was carried out by phenyltrichlorosilane (PTS), because the presence of phenyl groups was shown to provide good interactions with aromatic semiconductors.⁴⁶ The experimental results show the importance of the P3HT/PSA block ratio, the substrate surface properties and morphology on the charge transport, and FET characteristics of diblock copolymers.

EXPERIMENTAL

The synthetic scheme of P3HT-*b*-PSA block copolymer is shown in Scheme 1. The regioregular P3HT macroinitatior was synthesized by GRIM procedures,⁴⁷ and then, the diblock copolymer was synthesized by ATRP.^{14,20} The details of synthetic procedure, the diblock characterizations, and the electrical properties of the diblock copolymers are described below.

Materials

P3HT₆₀ was prepared according to our previous report.²⁰ Stearyl acrylate (SA), purchased from Polysciences, was recrystallized from ethanol solution. 1,1,4,7,7-Pentamethyl-diethylenetriamine (PMDETA; Acros, 99%), copper(I) bro-mide (Aldrich, 99%), and tetrahydrofuran (TEDIA, HPLC) were used as received without further purification. Common organic solvents for synthesis and ultra-anhydrous solvents for preparation of thin film transistors such as anisole, chlor-obenzene, and methanol were purchased from Aldrich.



Synthesis of P3HT-b-PSA Diblock Copolymers

The synthesis of P3HT-b-PSA diblock copolymers is shown in Scheme 1. $P3HT_{60}$ with M_n and polydispersity index of 10,080 and 1.35, respectively, was prepared via Grignard reaction. The P3HT-b-PSA copolymers with different coil lengths were synthesized from P3HT₆₀ via ATRP. As an example, the preparation of P1 is described below. A dry 10mL round-bottom flask with a magnetic stir bar was filled with the mixture of CuBr (1.42 mg, 9.92 \times 10⁻³ mmol), P3HT₆₀ macroinitiator (100 mg, 9.92 imes 10⁻³ mmol, $M_{\rm n}$ (NMR) = 10,080), SA (3.21 \times 10⁻¹ g, 9.92 \times 10⁻¹ mmol), PMDETA $(2.07 \ \mu\text{L}, 9.92 \times 10^{-3} \text{ mmol})$, and anisole (2 mL). The mixture was degassed and backfilled with nitrogen three times, stirred at ambient temperature for 1 h, and then immersed into an oil bath at 120 °C for 24 h. After cooling to ambient temperature, tetrahydrofuran (THF) was added to the mixture. The mixture was passed through an Al_2O_3 column to remove the copper catalyst and then was precipitated into methanol to obtain the P1 (yield: 26.78%) as a brown solid.

¹H NMR (CDCl₃, 400 MHz) δ (ppm): 2.52–2.79 (2H, -CH₂-CH₂-(CH₂)₃-(CH₃)), 3.99 (2H, -OCH₂(CH₂)₁₆CH₃, for SA side chain), 6.96 (1H, thiophene aromatic protons). Elemental analysis for [C₁₁₅₆H₁₉₅₆S₆₀]: C, 74.40; H, 10.49; S, 10.30. Found: C, 73.97; H, 10.32; S, 9.53.

Characterization

Size-exclusion chromatography was performed on an Asahi Techneion AT-2002 equipped with a Viscotek TDA model 302 triple detector array using THF as a carrier solvent at a flow rate of 1.0 mL/min at 40 °C. To determine the $M_{\rm n}$ and $M_{\rm w}/M_{\rm n}$ values of the resulting polymers, a calibrated curve was made with polystyrene standard. ¹H NMR spectra were recorded on a Bruker DPX (400 MHz for ¹H) in CD₂Cl₂. Chemical shifts were recorded in ppm downfield relative to CH_2Cl_2 (δ 5.33) as standards. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed under a nitrogen atmosphere at a heating rate of 20 and 10 °C/min using a TA instrument (TGA-951 and DSC-910S), respectively. UV-vis optical absorption spectra were obtained using Hitachi U-4100 spectrometer. Elementary analyses were performed by using VarioEL III (Elementar, Germany).

SAXS and WAXS measurements were performed on a Rigaku microfocused source based on Cu K α radiation ($\lambda = 0.154$ nm). For SAXS, the diffracted beam was collected on a twodimensional high-resolution gas-filled detector. For WAXS, the diffracted signal was collected on image plates. The resulting accessible window of the scattering vector q ($q = 4\pi \sin(\theta)/\lambda$, where 2 θ is the scattering angle) is 0.05–2 nm⁻¹ and 1.9–20 nm⁻¹, for SAXS and WAXS, respectively. The recorded scattered intensities were azimuthally integrated yielding scattered intensity as functions of the scattering vector. After casting from 1 wt % dichlorobenzene solutions, the samples were dried at 230 °C (50 °C higher than the melting temperature of P3HT) under high vacuum (10⁻⁹ mbar) for 12 h and then cooled at 0.1 °C/min down to room temperature. Synchrotron grazing incidence X-ray diffraction (GIXD) measurement was performed at B23A1 beamline of National Synchrotron Radiation Research Center (Taiwan). For GIXD, the thin films of **P1** and **P3** were prepared from 0.8 wt % polymer solution in chlorobenzene via spin coating at a speed rate of 600 rpm for 30 s onto the PTS-treated SiO_2 substrates.

The morphologies of polymer film surface were also studied by AFM using a Nanoscope 3D Controller (AFM, Digital Instruments) operated in tapping mode at room temperature. For AFM samples, 0.8 wt % polymer solution in chlorobenzene was filtered through a 0.22- μ m syringe filters, and then spin-coated at a speed rate of 600 rpm for 30 s onto either the bare or the PTS-treated SiO₂/Si substrate. TEM was performed using a JEOL 1230 operated at an acceleration voltage of 100 kV. The samples for TEM measurement were prepared by spin-coated coating on NaCl substrates, and then put into water. The polymer films were floated on the water surface and picked up onto 200-mesh copper grids with carbon.

Fabrication of Field-Effect Transistors

The FETs were fabricated on a highly doped n-type Si substrate with a thermal grown SiO_2 (300 nm, capacitance = 10 nF/cm²). The SiO₂ surface was also modified by phenyltrichlosilane (PTS), a silane coupling agent, by the following procedure: a clean SiO₂/Si substrate was immersed into a 10 mM solution of PTS in anhydrous toluene at room temperature overnight. Polymer solution (0.8 wt %) in chlorobenzene was filtered through a $0.22 - \mu m$ syringe filters, and then spin-coated at a speed rate of 600 rpm for 30 s onto either the original or the PTS-treated SiO₂/Si substrate. The top-contact source/drain regions were defined by gold electrodes (100 nm), deposited through a regular shadow mask, and the channel length (L) and width (W) were 50 and 1000 μ m, respectively. The output and transfer characteristics of the FET devices were measured by a Keithley 4200 semiconductor parametric analyzer. The above electrical measurements were performed in a nitrogen-filled glove box. All FETs showed typical p-type I-V characteristics with the accumulation mode operation. Field-effect mobility was estimated from saturated transfer characteristics via the slope of the plot giving $(I_d)^{1/2}$ versus V_g by the following equation:⁴⁸

$$I_{\rm d} = \frac{W C_{\rm o} \mu_{\rm h}}{2L} \left(V_{\rm g} - V_{\rm t} \right)^2 \tag{1}$$

where $I_{\rm d}$ is the drain current, $V_{\rm g}$ is the gate voltage, $V_{\rm t}$ is the threshold voltage, $\mu_{\rm h}$ is the hole mobility, W is the channel width, L is the channel length, and $C_{\rm o}$ is the capacitance of the gate insulator per unit area (SiO₂, 300 nm, $C_{\rm o} = 10$ nF/cm²), respectively.

RESULTS AND DISCUSSION

Synthesis and Thermal Properties

The chemical structures and synthesis procedure of the rodcoil block copolymers considered here are shown in Scheme 1. The ¹H NMR spectrum of the macroinitiator $P3HT_{60}$ is shown in Supporting Information Figure S1. The NMR peak



at 1.82 and 4.39-4.51 ppm is assigned to the integration of end-capped group ($-CH_3$ and -CH-). The peaks at 3.10 and 4.39-4.51 ppm are attributed to the proton resonance of the two $-CH_2$ - located between P3HT and the ester group. The signal at 6.96 ppm (1H), attributed to aromatic proton in thiophene units, is \sim 20-fold of those at 4.39–4.51 ppm (3H). This indicates that there are 60 repeated thiophene units in the macroinitiator. The ¹H NMR spectra of the macroinitiator is consistent with the proposed structure. The number-average molecular weight (M_n) of the macroinitiator P3HT₆₀ estimated from gel permeation chromatography profile (Supporting Information Fig. S3) is 10 kg mol^{-1} , and thus, the degree of polymerization is 60. The ¹H NMR spectra of the diblock copolymers are shown in Figure 1. The proton signals of the SA backbone and oxymethylene on PSA are clearly observed in the region of 2.25-2.39 and 3.99-4.13 ppm, implying the successful incorporation of the PSA block. The proton signals of the alkyl chain and thiophene ring on P3HT are in the region of 2.52-2.79 and 6.96 ppm, respectively. Note that **P1** has a much longer P3HT chain length than PSA, and thus, strong signals of the thiophene proton resonances are observed. The SA repeating units of three copolymers estimated from the peak integration of the ¹H NMR are 26, 50, and 360, named as **P1**, **P2**, and **P3**, respectively. This corresponds to a number-averaged molecular weight of 18,500, 27,180, and 126,720 g/mol, respectively, in good agreement with the expected theoretical content. Note that the NMR signals of the ester group located between P3HT and PSA are relatively weak. The similar phenomena were also observed in the material, P3HT-*b*-poly(2-(diemthylamino)ethyl methacrylate).²⁰

The relevant thermal properties of the diblock copolymers are listed in Table 1, together with the corresponding data of the individual P3HT₆₀ and PSA blocks. The thermal decomposition temperatures (T_d) of the diblock copolymers were between 352 and 365 °C, indicating their good thermal stability. The crystallization behaviors were affected by the composition of the diblock copolymers. The DSC curve of P1 (Fig. 2) shows two melting and crystallization temperatures $(T_{cPSA} \text{ and } T_{cP3HT})$ of 34 and 174 °C, corresponding to those of the PSA and P3HT blocks, respectively. T_{cPSA} is increased with the larger PSA length, whereas T_{cP3HT} exhibits an opposite trend, suggesting that the P3HT tendency to crystallize is lowered by a PSA block of increasing molecular weight. Note that the T_{cP3HT} of **P3** exhibited the largest reduction (almost 20 °C). Despite the decreased T_{cP3HT} the P3HT blocks still crystallized before the PSA segments during cooling down. It was reported that the sequence of crystallization of conjugated components conspicuously influenced the electrical performances of diblock copolymers or polymer blends, because the semiconductor polymer cannot crystallize efficiently within a crystalline insulting matrix.^{16,42} Therefore, it is strongly preferable for optimal charge mobility, when the crystallization of the P3HT block occurs first, as in the present case.

Small- and Wide-Angle X-Ray Scattering

^d 5 wt % loss temperature measured by TGA under N₂.

P3HT is known to be capable of crystallizing into lamellar packing crystal structures with the P3HT backbones stacked via π - π interactions and the alkyl side chains spacing neighboring P3HT stacks.³⁷ The packing scheme is maintained also in polythiophene–polythiophene fully conjugated crystalline block copolymers.⁴⁹ To understand the crystalline

TABLE 1 Polymerization Conditions, Molecular Weights, and Thermal Properties of P3HT-b-PSA Copolymers

| Expected Composition | | M _n (g | J/mol) ^b | | | | | | |
|-------------------------|-----------------|-------------------|---------------------|------------------|--------------|-------------------------------------|-------------------------------------|--------------------------------------|--------------------------------------|
| | $[M]_0/[I]_0^a$ | P3HT | PSA | PDI ^c | T_d^d (°C) | T _{cPSA} ^e (°C) | T _{mPSA} ^e (°C) | T _{cP3HT} ^e (°C) | T _{mP3HT} ^e (°C) |
| P3HT ₆₀ | - | 10,080 | - | 1.35 | 349 | - | _ | 179.7 | 203.8 |
| P1 | 100 | 10,080 | 8,424 | 1.41 | 365 | 33.6 | 44.7 | 173.6 | 199.4 |
| P2 | 250 | 10,080 | 17,100 | 1.38 | 358 | 33.8 | 44.9 | 173.2 | 200.9 |
| P3 | 400 | 10,080 | 116,640 | 1.70 | 352 | 39.3 | 46.4 | 160.8 | 200.1 |
| PSA | - | - | 65,000 | - | 331 | 36.1 | 45.1 | _ | - |

^e Determined by DSC.

^a Feed molar ratio of the monomer [M]₀ to initiator [I]₀.

^b Determined by ¹H NMR.

^c Polydispersity index determined by GPC.





FIGURE 2 DSC curves of **P1**, P3HT, and PSA at a heating/cooling rate of 10 $^{\circ}$ C min⁻¹.

structure of the P3HT-b-PSA diblock copolymers, their WAXS and SAXS profiles were investigated, as shown in Figure 3. For P1, the typical crystal diffraction peaks (100), (200), (300), and (020) of the P3HT block can be easily distinguished at room temperature and at 70 °C in Figure 3(a); the peaks at 70 °C shift at lower q compared with room temperature due to thermal expansion. These multiple, strong, and sharp peaks of P3HT indicate its high crystalline nature. The peaks at 1.51 and 1.86 ${\rm \AA}^{-1}$, which disappeared at 70 $^\circ\text{C}$ above the melting temperature of PSA, arise from the crystallization of the PSA block. By increasing the length of the PSA block from P1 to P3, the crystallization peaks of P3HT (100), (200), and (020) are still visible at the same positions, but become broader and the (300) peak cannot be observed any longer. This suggests that the long PSA block depressed the crystallization of P3HT. Meanwhile, because the PSA block is the majority component in P3, its crystallization peaks becomes more pronounced at room temperature compared with P1, the same peaks disappearing above its melting temperature. Figure 3(b) shows the SAXS profiles of the two block copolymers. The peaks at 0.029 and 0.021 \AA^{-1} suggest that microphase separation occurred in both block copolymers, with periodicities of 21.6 nm and 30 nm for P1 and P3, respectively. Figure 3(c) illustrates the synchrotron grazing incidence X-ray diffraction (GIXD) profiles of P1 and P3 on the PTS-treated surfaces with a thickness of ${\sim}50$ nm. On the PTS-treated surface, P3 exhibits the scattering peaks at 1.51 and 1.62 $Å^{-1}$, corresponding to the crystallization of the PSA block and the (020) reflection of the crystalline P3HT segments, respectively, whereas only the peak at 1.51 ${\rm \AA}^{-1}$ is observed in the thin films of P1. This indicates that, in contrast to what observed in bulk, the long PSA block facilitates the π - π stacking of P3HT on the PTS-treated surface.

Figure 4 shows the TEM images of the thin films of P3HT-*b*-PSA cast from chlorobenzene solvent. All the diblock copolymers tend to form dark needle-like structures with an average feature size of 30 nm, as a result of the crystallization of the block copolymer.⁵⁰ Because the stained phase is P3HT, these needles identify the crystalline P3HT microphase

separated in a PSA background. As shown in Figure 4(c), the TEM image of **P3** shows the lowest number of needles which also appear shorter, as expected by the decreasing P3HT volume fraction for the block copolymer with the longest PSA block. As SAXS/WAXS analysis indicated an effect of the substrate on the crystallization behavior of the P3HT-*b*-PSA block copolymers, to gain further insight on this trend, we also performed AFM on SiO₂ and PTS-modified SiO₂ substrates. Figure 5 shows the AFM topography images of **P1** on both types of surfaces. Remarkably, a much stronger tendency to form crystalline needle-like structures can be observed on the PTS-treated surface. These AFM images,



FIGURE 3 (a) WAXS and (b) SAXS profiles of block copolymers P1 (filled dot) and P3 (open dot) in bulk, and (c) GIXRD profiles of P1 and P3 thin films on the PTS-treated SiO_2 substrates.



FIGURE 4 TEM images of (a) P1, (b) P2, and (c) P3.

taken together with GIXD analysis, strongly support that the PTS-treated surfaces are able to greatly improve the crystallization of P3HT blocks. These results demonstrate the crucial role of the substrate surface properties on the selfassembly of diblock rod-coil crystalline block copolymers.

Optical Properties

The UV-vis absorption spectra of the diblock copolymers on the bare quartz and PTS-treated quartz surfaces are shown in Figure 6. The absorption coefficients of the diblock copolymers decreased with increasing the block lengths of the PSA segments, because PSA diluted the P3HT content. Intriguingly, the absorption peak of the diblock copolymer at 604 nm,⁵¹ which can be attributed to the interchain π - π stacking of the P3HT segments, exhibits a fairly stronger absorption intensity on the PTS-treated substrates, compared with those on the bare quartz substrates. This is a further evidence that PTS can promote the crystallization of P3HT, and thus, enhance the interchain π - π stacking of the P3HT segments.⁴⁸

Characteristics of Field-Effect Transistors

The electrical characteristics of the FET devices based on the P3HT-*b*-PSA are listed in Table 2. The experimental result suggests that the interface between the diblock copolymers and the dielectrics revealed a remarkable influence on the charge transport, as shown in Figure 7. For comparison, the mobility of the macroinitiator P3HT₆₀ was also measured. P3HT₆₀ only shows moderate mobilities of 10^{-4} to 10^{-3} cm² V⁻¹ s⁻¹, comparable with that of P3HT with the similar molecular weight.^{52,53} On the untreated SiO₂ substrate, the FET hole mobilites of P3HT₆₀, **P1**, **P2**, and **P3** are 6.38 × 10^{-4} , 3.41×10^{-4} , 2.88×10^{-5} , and 2.26×10^{-6} cm² V⁻¹ s⁻¹, respectively. The hole mobility of the block copolymer decreases with enhancing the PSA block length. This may be



FIGURE 5 AFM topography images of **P1** on the (a) untreated and (b) PTS-treated surface surfaces.





FIGURE 6 UV-vis absorption spectra of $P3HT_{60}$ (square), **P1** (sphere), **P2** (up triangle), and **P3** (down triangle) on the untreated (hollow) and PTS-treated (solid) quartz substrates.

related to the morphology in which fewer crystalline needles form in the thin films with increasing PSA lengths, reducing the volume fraction of effective domains for charge transport. In contrast, on the PTS-treated SiO₂/Si surface, the FET hole mobilites of P3HT₆₀, **P1**, **P2**, and **P3** on the PTS-treated surface are 1.19×10^{-3} , 4.51×10^{-4} , 6.30×10^{-4} , and 4.16×10^{-3} cm² V⁻¹ s⁻¹, respectively. The polymers have then an enhanced electrical performance with increasing the PSA block length. Furthermore, the mobilities measured on the PTS-treated surface are systematically higher than that on the bare surface, implying that the modification of substrate surface is crucial for the charge transport of the P3HT segments.⁵⁴ This conclusion joins the recent report on the critical effects of interfacial engineering for efficient organic photovoltaic design.³³ The mobility of the block copolymers on PTS-treated substrates initially decreases for the short PSA segment, but then becomes enhanced at a high PSA content. The best FET mobility of 4.16 \times 10⁻³ cm² V⁻¹ s⁻¹ is obtained from the P3 on the PTS-treated substrates, which is three orders of magnitude higher than that on the untreated SiO₂/Si substrate. Similar trend of the hole mobilites of P3HT-b-PMA on the octyltrichlorosilanetreated surface was reported by Sauvé and McCullough.¹⁷ They proposed that the factor affecting the tendency of the mobilities could arise from a repulsive interaction of the hydrophilic PMA segments with hydrophobic octyltrichlorosilane-treated interfaces,¹⁷ leading to a different

structural order of P3HT at the interface. However, in our case, both P3HT and PSA segments are hydrophobic. Therefore, we assume that the factor affecting the mobilities is attributed to the π - π interaction between P3HT and the phenyl groups on the PTS-treated surfaces. The phenyl groups may trigger P3HT stacking via the π - π interactions between thiophene units and phenyl groups. Therefore, the PTS-treated surface improves the interchain π - π stacking within the P3HT segments and initiates and improves P3HT crystallization during the film deposition. This is evidenced by the results of the GIXD, UV-vis spectra, AFM, and hole mobility.

To verify our hypothesis, we measured water contact angles on the P3HT-b-PSA films spin coated on both SiO₂ and PTStreated SiO₂. Because the hydrophobicity of P3HT and PSA is different, the water contact-angle measurement is a simple approach to recognize the changes of the interfacial composition of the diblock copolymers on the different substrates. The water contact angle as a function of mol % PSA on the different SiO₂ surface is shown in Figure 8. On the PTStreated surface, the contact angles of water on the various diblock copolymers films are similar to that of the pristine PSA film (114°). This already suggests a selectivity of P3HT segments for phenyl group at the substrate interface, displacing PSA blocks towards the free surface of the block copolymer. On the other hand, on the untreated SiO₂ surface, the contact angles of water against the diblock copolymers films were between that of the PSA film (114°) and the P3HT film (107°), implying that there is no groups selectivity for interaction between the silanol of the SiO2 and either the PSA or P3HT segments. With the increased length of the PSA segments, the degree of the crystallization of the PSA increases, leading to denser packing of the P3HT segments on the PTStreated surface. It is interesting to note that, the on-off ratios and threshold voltages had remarkable improvements on the PTS-treated surface, greatly exceeding even those of the P3HT₆₀. On the PTS-treated surface, P3, with the longest PSA block, exhibits the highest on-off ratios of 7.38 \times 10⁶ and a reduced threshold voltage of -12 V. This implies that the crystalline PSA segments provides an excellent barrier to prevent the invasion of oxygen and moisture, which are commonly considered as dopants, leading to the reduced OFF current and threshold voltages.

The effects of thermal annealing on morphology, optoelectronic properties, and charge transport were also studied. From the AFM images (Supporting Information Fig. S5),

TABLE 2 Electrical Properties of P3HT-b-PSA Based FET Devices on Both Untreated and PTS-Treated Dielectric Surfaces

| | Unti | eated SiO ₂ | | PTS-Treated SiO ₂ | | | |
|--------------------|--|------------------------|------------------|--|----------------------|---------------------|--|
| Polymer | μ^{Avg} (cm ² V ⁻¹ s ⁻¹) | On/Off | $V_{\rm th}$ (V) | μ^{Avg} (cm ² V ⁻¹ s ⁻¹) | On/Off | V _{th} (V) | |
| P3HT ₆₀ | (6.38 \pm 2.50) $	imes$ 10 ⁻⁴ | 2.52×10^2 | 83 ± 3 | $(1.19 \pm 0.17) 	imes 10^{-3}$ | 3.10×10^2 | 76 ± 2 | |
| P1 | (3.41 \pm 0.17) $	imes$ 10 ⁻⁴ | 1.91×10^3 | 0 ± 7 | (4.51 \pm 0.28) $	imes$ 10 ⁻⁴ | 2.50×10^3 | 20 ± 5 | |
| P2 | (2.88 \pm 0.85) \times 10^{-5} | 1.89×10^3 | 14 ± 6 | (6.30 \pm 0.61) $	imes$ 10 ⁻⁴ | 8.21×10^3 | 12 ± 1 | |
| P3 | (2.26 \pm 1.09) $	imes$ 10 ⁻⁶ | 7.30×10^3 | -22 ± 3 | (4.16 \pm 1.33) $	imes$ 10 ⁻³ | 7.38×10^{6} | -12 ± 1 | |



FIGURE 7 Transfer characteristics of the field-effect transistors prepared from **P1**, **P2**, and **P3** on the (a) untreated and (b) PTS-treated surface, where $V_{\text{DS}} = -100$ V. (c) Average FET mobility as a function of PSA content of the diblock copolymers.

there were several large aggregates appeared on the surface of the **P3** film after thermal treatments. In addition, the main peak of the absorption spectra of **P3** exhibited an obvious blue shift of 10 nm after thermal annealing at 150 °C, as shown in Supporting Information Figure S6. It indicates that the thermal annealing reduces the π -conjugation of the

P3HT segments in **P3** film. The thermal annealing also led to the significant reduction on the electrical properties of the P3HT-*b*-PSA FETs, as shown in Supporting Information Figure S7. The mobilities of the thermal annealed FETs exhibited an order of magnitude smaller than those without annealing. This poor thermal stability is probably due to the low melting point (45 °C) of the PSA segments, causing the reduced π - π stacking during thermal annealing. Despite the thermal degradation, **P3** still exhibits a lower off current than that of **P1**, implying that incorporating long PSA segments provides the good insulting ability during thermal annealing.

CONCLUSIONS

We have demonstrated the optical properties, morphology, and charge transporting characteristics of the novel diblock copolymers with different P3HT/PSA polymerization degree block ratios of 60/26, 60/50, and 60/360, respectively, and thus, on the different SiO₂ and PTS-treated SiO₂ surfaces. The block ratios of P3HT/PSA and surface treatments significantly affected the morphology, molecular packing, and electrical properties of the diblock copolymers. SAXS and WAXS indicated a microphase separation between crystalline P3HT and PSA blocks. AFM and TEM further allowed to resolve needle-like P3HT domains within a PSA continuous phase with an average diameter of 30 nm. The number of the P3HT domains decreased with increasing PSA length. The UV-vis absorption spectra showed that the interchain π - π stacking of the P3HT segments on the PTS-treated quartz substrates was stronger than on untreated substrates, indicating that PTS can increase the interchain stacking of the P3HT segments via π - π stacking. GIXD result also showed that the long PSA block facilitates the π - π stacking of P3HT on the PTS-treated surface. In line with these observations, the charge transport performance of the diblock copolymers



FIGURE 8 Average water contact angles of the diblock copolymers with different PSA content on the untreated (circle) and PTS-treated (square) SiO_2 surfaces, respectively.

was remarkably improved by the PTS-treated surface. This significant improvement was due to the enhancement of the π - π stacking interactions of the P3HT blocks with the PTS-modified interface. This study demonstrated explicitly that the block ratios of the crystalline–crystalline diblock copolymers and the substrate surface modification played important roles on their self-assembly behavior and the FET electrical performance.

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REFERENCES AND NOTES

1 (a) Lee, M.; Cho, B. K.; Zin, W. C. *Chem. Rev.* **2001**, *101*, 3869–3892; (b) Leclère, P.; Hennebicq, E.; Calderone, A.; Brocorens, P.; Grimsdale, A. C.; Müllen, K.; Brédas, J. L.; Lazzaroni, R. *Prog. Polym. Sci.* **2003**, *28*, 55–81; (c) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A.P. H. J. *Chem. Rev.* **2005**, *105*, 1491–1546; (d) Olsen, B. D.; Segalman, R. A. *Mater. Sci. Eng. R* **2008**, *62*, 37–66; (e) Liu, C. L.; Lin, C. H.; Kuo, C. C.; Lin, S. T.; Chen, W. C. *Prog. Polym. Sci.* **2011**, *36*, 603–637.

2 Sary, N.; Rubatat, L.; Brochon, C.; Hadziioannou, G.; Ruokolainen, J.; Mezzenga, R. *Macromolecules* **2007**, *40*, 6990–6997.

3 Sary, N.; Mezzenga, R.; Brochon, C.; Hadziioannou, G.; Ruokolainen, J. *Macromolecules* **2007**, *40*, 3277–3286.

4 Sary, N.; Brochon, C.; Hadziioannou, G.; Mezzenga, R. *Eur. Phys. J. E* **2007**, *24*, 379–384.

5 (a) Higashihara, T.; Ueda, M. *Macromolecules* **2009**, *42*, 8794–8800; (b) Higashihara, T.; Takahashi, A.; Tajima, S.; Jin, S.; Rho, Y.; Ree, M.; Ueda, M. *Polym. J.* **2010**, *42*, 43–50.

6 Jenekhe, S. A. Science 1998, 279, 1903-1907.

7 Lin, C.-H.; Tung, Y.-C.; Ruokolainen, J.; Mezzenga, R.; Chen, W.-C. *Macromolecules* 2008, *41*, 8759–8769.

8 Lin, S. T.; Fuchise, K.; Chen, Y. G.; Sakai, R.; Satoh, T.; Kakuchi, T.; Chen, W. C. *Soft Matter* **2009**, *5*, 3761–3770.

9 Lin, S.-T.; Tung, Y.-C.; Chen, W.-C. *J. Mater. Chem.* **2008**, *18*, 3985–3992.

10 Rajaram, S.; Armstrong, P. B.; Kim, B. J.; Frechet, J. M. J. *Chem. Mater.* **2009**, *21*, 1775–1777.

11 Zhang, Q. L.; Cirpan, A.; Emrick, T.; Russell, T. P. *Macromolecules* 2009, *42*, 1079–1082.

12 Tzeng, P.; Kuo, C.-C.; Lin, S.-T.; Chiu, Y.-C.; Chen, W.-C. *Macromol. Chem. Phys.* **2010**, *211*, 1408–1416.

13 Kuo, C.-C.; Tung, Y.-C.; Lin, C.-H.; Chen, W.-C. *Macromol. Rapid Commun.* **2008**, *29*, 1711–1715.

14 Fang, Y.-K.; Liu, C.-L.; Li, C.; Lin, C.-J.; Mezzenga, R.; Chen, W.-C. *Adv. Funct. Mater.* **2010**, *20*, 3012–3024.

15 Chueh, C.-C.; Higashihara, T.; Tsai, J.-H.; Ueda, M.; Chen, W.-C. *Org. Electron.* **2009**, *10*, 1541–1548.

16 Müller, C.; Goffri, S.; Breiby, D. W.; Andreasen, J. W.; Chanzy, H. D.; Janssen, R. A. J.; Nielsen, M. M.; Radano, C. P.; Sirringhaus, H.; Smith, P.; Stingelin-Stutzmann, N. *Adv. Funct. Mater.* **2007**, *17*, 2674–2679.

17 Sauvé, G.; McCullough, R. D. *Adv. Mater.* 2007, *19*, 1822–1825.

18 Lim, H.; Huang, K.-T.; Su, W.-F.; Chao, C.-Y. J. Polym. Sci. Part A: Polym. Chem. **2010**, 48, 3311–3322.

19 Radano, C. P.; Scherman, O. A.; Stingelin-Stutzmann, N.; Muller, C.; Breiby, D. W.; Smith, P.; Janssen, R. A. J.; Meijer, E. W. *J. Am. Chem. Soc.* **2005**, *127*, 12502–12503.

20 Huang, K. K.; Fang, Y. K.; Hsu, J. C.; Kuo, C. C.; Chang, W. H.; Chen, W. C. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 147–155.

21 Huettner, S.; Sommer, M.; Hodgkiss, J.; Kohn, P.; Thurn-Albrecht, T.; Friend, R. H.; Steiner, U.; Thelakkat, M. *ACS Nano* **2011**, *5*, 3506–3515.

22 Patra, S. K.; Ahmed, R.; Whittell, G. R.; Lunn, D. J.; Dunphy, E. L.; Winnik, M. A.; Manners, I. *J. Am. Chem. Soc.* **2011**, *133*, 8842–8845.

23 Gu, Z. J.; Kanto, T.; Tsuchiya, K.; Shimomura, T.; Ogino, K. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 2645–2652.

24 Han, Y. C.; Zhao, K.; Ding, Z. C.; Xue, L. J. *Macromol. Rapid Commun.* 2010, *31*, 532–538.

25 Choi, S. Y.; Lee, J. U.; Lee, J. W.; Lee, S.; Song, Y. J.; Jo, W. H.; Kim, S. H. *Macromolecules* **2011**, *44*, 1771–1774.

26 Moon, H. C.; Anthonysamy, A.; Lee, Y.; Kim, J. K. *Macromolecules* 2010, *43*, 1747–1752.

27 Dai, C. A.; Yen, W. C.; Lee, Y. H.; Ho, C. C.; Su, W. F. *J. Am. Chem. Soc.* **2007**, *129*, 11036–11038.

28 Yang, C.; Lee, J. K.; Heeger, A. J.; Wudl, F. *J. Mater. Chem.* 2009, *19*, 5416–5423.

29 Boudouris, B. W.; Frisbie, C. D.; Hillmyer, M. A. *Macromolecules* **2010**, *43*, 3566–3569.

30 Botiz, I.; Darling, S. B. Macromolecules 2009, 42, 8211-8217.

31 Botiz, I.; Martinson, A. B. F.; Darling, S. B. *Langmuir* **2010**, *26*, 8756–8761.

32 Kuo, C.-C.; Tung, Y.-C.; Chen, W.-C. *Macromol. Rapid Commun.* **2010**, *31*, 65–70.

33 Sary, N.; Richard, F.; Brochon, C.; Leclerc, N.; Leveque, P.; Audinot, J. N.; Berson, S.; Heiser, T.; Hadziioannou, G.; Mezzenga, R. *Adv. Mater.* **2010**, *22*, 763–768.

34 Bao, Z.; Lovinger, A. J.; Dodabalapur, A. *Appl. Phys. Lett.* **1996**, *69*, 3066–3068.

35 Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99–117.

36 Sirringhaus, H. Science 1998, 280, 1741-1744.

37 Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature* **1999**, *401*, 685–688.

38 Liu, J. S.; Sheina, E.; Kowalewski, T.; McCullough, R. D. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 329–332.

39 Ho, V.; Boudouris, B. W.; McCulloch, B. L.; Shuttle, C. G.; Burkhardt, M.; Chabinyc, M. L.; Segalman, R. A. *J. Am. Chem. Soc.* **2011**, *133*, 9270–9273.

40 Hundt, N.; Quan, H.; Hien, N.; Sista, P.; Hao, J.; Servello, J.; Palaniappan, K.; Alemseghed, M.; Biewer, M. C.; Stefan, M. C. *Macromol. Rapid Commun.* **2011**, *32*, 302–308.

41 Xiao, K.; Yui, X.; Chen, J. H.; Lavrik, N. V.; Hong, K. L.; Sumpter, B. G.; Geohegan, D. B. *ACS Nano* **2011**, *5*, 3559–3567.

42 Goffri, S.; Müller, C.; Stingelin-Stutzmann, N.; Breiby, D. W.; Radano, C. P.; Andreasen, J. W.; Thompson, R.; Janssen, R. A. J.; Nielsen, M. M.; Smith, P.; Sirringhaus, H. *Nat. Mater.* **2006**, *5*, 950–956.

43 Wang, X.-Y.; Salovey, R. J. Appl. Polym. Sci. **1987**, 34, 593–599.

44 Osada, Y.; Matsuda, A. Nature 1995, 376, 219-219.

45 Qin, S. H.; Saget, J.; Pyun, J. R.; Jia, S. J.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 8969–8977.

46 Li, Y. N.; Wu, Y. L.; Ong, B. S. *Macromolecules* 2006, *39*, 6521–6527.

47 Iovu, M. C.; Jeffries-El, M.; Sheina, E. E.; Cooper, J. R.; McCullough, R. D. *Polymer* **2005**, *46*, 8582–8586.

48 Zaumseil, J.; Sirringhaus, H. Chem. Rev. 2007, 107, 1296–1323.

49 Wu, P.-T.; Ren, G.; Li, C.; Mezzenga, R.; Jenekhe, S. A. *Macromolecules* **2009**, *42*, 2317–2320.

50 Liu, J.; Sun, Y.; Gao, X. A.; Xing, R. B.; Zheng, L. D.; Wu, S. P.; Geng, Y. H.; Han, Y. C. *Langmuir* **2011**, *27*, 4212–4219.

51 Brown, P.; Thomas, D.; Köhler, A.; Wilson, J.; Kim, J.-S.; Ramsdale, C.; Sirringhaus, H.; Friend, R. *Phys. Rev. B* **2003**, *67*, 064203-1–064203-16.

52 Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J. S.; Frechet, J. M. J. Adv. Mater. 2003, 15, 1519–1522.

53 Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J. S.; Frechet, J. M. J.; Toney, M. F. *Macromolecules* 2005, *38*, 3312–3319.

54 Yoon, M.-H.; Kim, C.; Facchetti, A.; Marks, T. J. J. Am. Chem. Soc. 2006, 128, 12851–12869.