A Semiconducting Liquid Crystalline Block Copolymer Containing Regioregular Poly-(3-hexylthiophene) and Nematic Poly(n-hexyl Isocyanate) and its Application in Bulk Heterojunction Solar Cells

UTD AUTHOR(S): Mahesh P. Bhatt, Jia Du, Elizabeth A. Rainbolt, Taniya M. S. K. Pathiranage, Peishen Huang, James F. Reuther, Bruce M. Novak, Michael C. Biewer and Mihaela C. Stefan

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A semiconducting liquid crystalline block copolymer containing regioregular poly-(3-hexylthiophene) and nematic poly(n-hexyl isocyanate) and its application in bulk heterojunction solar cells†

Mahesh P. Bhatt, Jia Du, Elizabeth A. Rainbolt, Taniya M. S. K. Pathiranage, Peishen Huang, James F. Reuther, Bruce M. Novak, Michael C. Biewer and Mihaela C. Stefan*

A liquid crystalline diblock copolymer containing regioregular poly(3-hexylthiophene) (P3HT) and poly-(n-hexyl isocyanate) (PHIC) was synthesized by the combination of Grignard metathesis polymerization (GRIM) and titanium mediated coordination polymerization methods. The poly(3-hexylthiophene)-b-poly(n-hexyl isocyanate) (P3HT-b-PHIC) diblock copolymer used in this study contained ~10 mol% of P3HT and ~90 mol% of PHIC. The diblock copolymer displayed solvatochromism in THF–water and THF–methanol mixtures. The field-effect mobilities of the synthesized block copolymer were measured in bottom gate-bottom contact organic field-effect transistors (OFETs). The surface morphology of the polymer thin film was investigated in the channel region of the OFET devices by tapping mode atomic force microscopy (TMAFM). The diblock copolymer displayed nanostructured morphology in thin film and had good mobility despite the low content of the semiconducting P3HT block. The diblock copolymer was also used as an additive to improve the performance of P3HT/PCBM bulk heterojunction (BHJ) solar cells. Liquid crystalline characteristics of the diblock copolymer were examined by cross-polarizing microscopy and X-ray diffraction.

Introduction

Poly(n-alkyl isocyanates) are rigid-rod polymers with helical conformation in the liquid as well as solid states.1–4 Poly(n-alkyl isocyanates) have been studied in a variety of fields such as liquid crystals, optical switches and chiral sensing.5–12 These polymers combine steric repulsions between the side chains with double bond character of the amide groups.13 The steric repulsion by neighbouring side chain causes the adjacent side chain to rotate out of plane giving the polymer its helical structure. A wide variety of helical conformations have been proposed for poly(n-alkyl isocyanates) including 2₁, 5₁ and 8₁ in solution, and 8₂, 8₃ and 12₃ in thin films.14–16 Among polyisocyanates, poly(n-hexyl isocyanate) (PHIC) is one of the most intensively studied.5,17–20 The well-defined PHIC can be synthesized via organotitanium mediated living coordination and living anionic polymerization techniques.21–23 PHIC is a helical semiflexible polymer with liquid crystalline (LC) properties.24–26 Moreover, PHIC forms a nematic liquid crystal at high concentrations in non-polar solvents.27,28 Even though PHIC is a lyotropic liquid crystalline polymer, its solid state properties are also promising.18 Kawaguchi reported the Langmuir–Blodgett films of PHIC with different molecular weights, indicating that PHIC can form condensed-type thin films at the air–water interface.29,30,31 Recently, Tasaka’s group proposed the application of PHIC in electrical devices.18 Due to the semiflexible and helical nature of the PHIC chain, PHIC can be integrated in a block copolymer system to attain a unique structural morphology.

Regioregular poly(3-hexylthiophene) (P3HT) is a comprehensively studied semiconducting polymer for its application in flexible electronic devices.32–33 Grignard metathesis polymerization (GRIM), reported by McCullough’s group in 1999, is a commonly employed method for the synthesis of regioregular P3HT with well-defined molecular weights.34 McCullough’s group reported the livingness of P3HT using the GRIM method which allows the synthesis of end functionalized P3HT.35–37 End-functionalized P3HTs have been widely used to generate various block copolymers.38–40 P3HT is a rigid rod-like polymer with a persistence length of 2.4 nm. However, P3HT does not behave

University of Texas at Dallas, Department of Chemistry, 800 West Campbell Road, Richardson, TX 75080, USA. E-mail: mihaela@utdallas.edu; Fax: +1-972-883-2925; Tel: +1-972-883-6581

† Electronic supplementary information (ESI) available: 1H NMR, XRD patterns, UV-Vis spectra and SEC traces. See DOI: 10.1039/c4ta02852j
like a rod above a certain molecular weight.\textsuperscript{44} Incorporation of helical liquid crystalline polymers like polysiloxanes, which have a persistence length of 20–60 nm into the P3HT block, is expected to generate unique morphologies in thin films via supramolecular self-assembly.\textsuperscript{2} A systematic study of the morphology and optoelectronic properties of liquid crystalline diblock copolymers containing semiconducting units is a relatively unexplored area of research.\textsuperscript{42,43} Few reports exist regarding diblock copolymers containing the main chain LC polymer and a semiconducting segment.\textsuperscript{44} However, it has been demonstrated that a diblock copolymer containing side chain liquid crystalline units and rr-P3HT undergoes self-assembly and microphase separation.\textsuperscript{45}

Herein we report the synthesis and the opto-electronic properties of a diblock copolymer containing liquid crystalline poly(n-hexyl isocyanate) (PHIC) and a semiconducting rigid rod-like P3HT. The diblock copolymer was synthesized by combining GRIM and titanium mediated coordination polymerization techniques. We emphasize that both the liquid crystalline properties and semiconducting properties were evident in the block copolymer. Due to its unique nanostructure morphology and semiconducting properties, the use of P3HT-b-PHIC in thin film transistors and bulk heterojunction (BHJ) solar cells was investigated.

Experimental

Materials

All commercial chemicals were purchased from Aldrich Chemical Co. Inc. and were used without further purification unless otherwise noted. All reactions were conducted under nitrogen. The polymerization glassware and syringes were dried at 120 °C for at least 24 hours before use and cooled under a nitrogen atmosphere. Tetrahydrofuran (THF) and toluene were dried over sodium/benzophenone ketyl and freshly distilled nitrogen atmosphere. Distillation was stopped prior to use.

Synthesis of titanium alkoxide terminated P3HT

The procedures for synthesis of allyl-terminated P3HT and hydroxypropyl-terminated P3HT are given in the ESL.\textsuperscript{1}

The hydroxypropyl terminated P3HT (40 mg, 0.003 mmol) was dissolved in 30 mL of distilled toluene. Ethanol (5 mL) was added to the polymer solution. Azeotropic distillation was performed under a nitrogen atmosphere. Distillation was stopped after collecting 15 mL of toluene into the receiving flask. Cyclopentadienyltitanium trichloride (TiCpCl$_3$) (10 mg, 0.04 mmol) was added to the reaction and stirred for 5 h at reflux under a nitrogen atmosphere. At that time, a sample was taken to monitor the conversion of the hydroxyl group to titanium alkoxide using $^1$H NMR. Toluene was removed from the reaction mixture under vacuum.

Synthesis of the P3HT-b-PHIC copolymer

The preformed titanium alkoxide terminated P3HT was transferred into the glove box and dissolved in 7 mL of freshly distilled chloroform. Hexyl isocyanate (3.23 g, 0.02 mmol) was added to the reaction mixture in the glove box. After 12 h of stirring, the reaction was stopped and the reaction mixture was quenched in methanol. The polymer was filtered in a thimble and it was extracted with methanol, hexane, and chloroform using a Soxhlet extractor. The final polymer was characterized by SEC ($M_n = 21 000$ g mol$^{-1}$) and $^1$H NMR. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$H 0.91 (br, 6H), 1.32 (br, 14H), 1.57–1.65 (m, 8H), 2.84 (t, 2H), 3.45–4.03 (br, 2H), 6.98 (s, 1H).

X-Ray Diffraction (XRD)

The X-ray diffraction study was performed on a RIGAKU Ultima III diffractometer. Thin film samples were radiated by Cu-Kz ($\lambda = 1.54$ Å) and scanned from 1° to 40° (2$\theta$) at 0.04 degree interval at a rate of 2° per min. Thin films of the copolymers were obtained by drop casting a 5.0 mg mL$^{-1}$ polymer solution in chloroform onto clean SiO$_2$ substrates. The solvent was evaporated slowly in a Petri dish saturated with chloroform.

UV-Vis analysis

UV-Vis spectra in solution and solid states were recorded using an Agilent 8453 UV-Vis spectroscopy system. For the solvatochromism study, stock solutions of the precursor P3HT and the diblock copolymer (5 mg mL$^{-1}$ in THF) were prepared. Samples were obtained by mixing 0.1 mL of stock solution and 5 mL of solvent/non-solvent. For each sample the concentration of the polymer under study was kept constant.

Structural analysis

$^1$H NMR spectra of the synthesized monomers and polymers were recorded on a Bruker 500 MHz spectrometer at 25 °C. $^1$H NMR data are reported in parts per million as a chemical shift relative to tetramethylsilane (TMS) as the internal standard. Spectra were recorded in CDCl$_3$, GC/MS was performed on an Agilent 6890–5973 GC/MS workstation. The GC column was a Hewlett-Packard fused silica capillary column cross-linked with 5% phenylmethyl siloxane. Helium was the carrier gas (1 mL min$^{-1}$). The following conditions were used for all GC/MS analyses: injector and detector temperature, 250 °C; initial temperature, 70 °C; temperature ramp, 10 °C min$^{-1}$; final temperature, 280 °C. The UV-Vis spectra of polymer solutions in chloroform solvent were carried out in 1 cm cuvettes using an Agilent 8453 UV-Vis spectrometer. Thin-films of polymer were obtained by evaporation of chloroform solvent on glass microscope slides. Molecular weights of the synthesized polymers were measured by Size Exclusion Chromatography (SEC) analysis on a Viscotec VE 3580 system equipped with ViscoGEL(TM) columns (GMHHR-M), connected to a refractive index (RI) detector. A GPC solvent/sample module (GPCmax) was used with HPLC grade THF as the eluent and calibration was based on polystyrene standards. Running conditions for SEC analysis were: flow rate = 1.0 mL min$^{-1}$, injector volume = 100 μL, detector temperature = 30 °C, column temperature = 35 °C. All the polymer samples were dissolved in THF and the solutions were filtered through PTFE filters (0.45 μm) prior to injection.
Field-effect transistor fabrication and measurement of the field-effect mobilities

Field-effect mobility measurements of the synthesized polymers were performed on thin-film transistors with a common bottom-gate, bottom-contact configuration. Highly doped, n-type silicon wafers with a resistivity of 0.001–0.003 Ω cm were used as substrates. Thermal oxide ($\text{SiO}_2$) was grown 200 nm thick at 1000 °C. Chromium metal (5 nm) followed by 100 nm of gold was deposited by E-beam evaporation as source–drain metals. The source–drain pads were formed by photo-lithographically patterning the metal layer. The $\text{SiO}_2$ on the backside was removed, the devices were cleaned of the wafer was etched with buffered oxide etchant (7 : 1 BOE from JT Baker) to generate the common bottom-gate. The resulting transistors had a channel width of 475 μm and channel length ranging from 2 μm to 80 μm. The measured capacitance density of the $\text{SiO}_2$ dielectric was 17 nF cm$^{-2}$. After the $\text{SiO}_2$ on the backside was removed, the devices were cleaned with UV-Ozone for 7 min using a Technics Series 85 RIE etcher and stored under vacuum. This process removed any residual organics on the substrate. Prior to the polymer deposition, the substrates were cleaned with water, acetone, hexanes, and chloroform with drying using nitrogen flow between different solvents. The devices were baked at 80 °C for 30 min in a vacuum oven. The devices were allowed to cool under vacuum. The polymer films were deposited in air by drop casting 4–5 drops of 8 mg mL$^{-1}$ of polymer solution, previously filtered through a 0.2 μm PTFE syringe filter, using a 25 μL syringe. The films were allowed to dry in a Petri dish saturated with chloroform. The devices were annealed under vacuum for 30 min at 120 °C prior to measurements. The devices were again allowed to cool down to room temperature under vacuum. A Keithley 4200-SCS semiconductor characterization system was used to probe the devices. The probe station used for electrical characterization was a Cascade Microtech Model Summit Microchamber. When measuring current–voltage curves and transfer curves, VG was scanned from +20 V to −100 V. All the measurements were performed at room temperature in air. For the surface treatment with octyltrichloroisilane, the devices were rinsed sequentially with water, acetone, hexanes, and chloroform and placed in a glass container in a solution of silane of 8 × 10$^{-3}$ M in dried toluene. The sealed container was placed in a glove box at ambient temperature for 48 h. After 48 h, the device was removed from the glovebox and rinsed with toluene before baking at 80 °C for 30 min in a vacuum oven. The procedure for the polymer film deposition was the same as described above.

Tapping mode atomic force microscopy (TMAFM)

TMAFM investigation of the thin film surface morphology was carried out using a NanoScope IV Multimode Veeeco, equipped with an E-type vertical engage scanner. The AFM measurement was performed on the OFET devices that were measured for the estimation of field-effect mobilities. AFM images were also recorded from thin films on a mica substrate. Thin films were obtained by drop-casting chloroform solution of polymers on a mica substrate. The AFM images were recorded at room temperature in air using silicon cantilevers with a normal spring constant of 42 N m$^{-1}$ and a normal resonance frequency of 320 kHz. A typical value of the AFM detector signal corresponding to a root mean square (r.m.s.) cantilever oscillation amplitude was equal to 1–2 V and the images were collected at 0.5 Hz scan frequency in 2 μm scan size. Polymer samples were prepared in chloroform solutions (1 mg mL$^{-1}$) and deposited onto a mica substrate by drop casting.

For solar cell devices, TMAFM was carried out on the active area in between the channels of the metal. Images were obtained using silicon cantilevers with a spring constant of 42 N m$^{-1}$ and a resonance frequency of 300 kHz. Images were acquired at 1 Hz scan frequency. The sample scan area was 3 μm × 3 μm.

Investigation of liquid crystalline properties

A polarizing microscope (Meiji) with an Olympus digital camera was used to study the liquid crystalline properties of polymer samples. The images were recorded using QCapture software. Experiments were performed for the polymer samples in the liquid state. The polymer sample was dissolved in xylene (40 wt%) and a drop of the polymer solution was sandwiched in between two glass slides.

Preparation of solar cell devices

Glass substrates coated with ITO were purchased from Luminescence Technology Corp. (Taiwan) and were patterned using standard photolithography. The P3HT homopolymer was synthesized with a molecular weight of 30 000 g mol$^{-1}$ by the GRIM method. The substrates were cleaned by sonication for 20 minutes in acetone, methanol, toluene, and isopropyl alcohol. The substrates were subjected to UV/ozone treatment for 20 minutes prior to use. After the ozone treatment, poly(3,4-ethylendioxythiophene): poly(styrenesulfonate) PEDOT:PSS was spin coated on the substrates (1500 rpm, 1740 rpm s$^{-1}$, 90 s). The substrates were annealed at 150 °C for 10 minutes under a nitrogen atmosphere. P3HT:PCBM (1 : 1) blends with different percentages of P3HT-b-PHIC were prepared in dichlorobenzene with a total blend concentration of 50 mg mL$^{-1}$. These blends were spin coated (2000 rpm, 1740 rpm s$^{-1}$, 60 s) onto the PEDOT:PSS treated substrate. The devices were annealed at 180 °C for 5 minutes. Films of 20 nm Ca and 100 nm Al were thermally evaporated onto the substrates at a rate of 2.75 Å s$^{-1}$ through a shadow mask to obtain the solar cell devices. IV testing was carried out under a controlled nitrogen atmosphere using a Keithley 236, model 9160 interfaced with LabView software. The solar simulator used was a THERMOORIEL equipped with a 300 W Xenon lamp; the intensity of the light was calibrated to 100 mW cm$^{-2}$ with a NREL certified Hama-matsu silicon photodiode. The active area of the devices was 0.1 cm$^2$. The active layer film thickness was measured using a Veeco Dektak VIII profilometer.

Results and discussion

Synthesis and characterization of the diblock copolymer

Synthesis of the poly(3-hexylthiophene)-b-poly(n-hexyl isooyanate) (P3HT-b-PHIC) diblock copolymer is shown in Scheme 1.
Allyl-terminated P3HT was synthesized by the in situ end capping of nickel-terminated P3HT with allyl magnesium bromide (ESI†). Hydroboration-oxidation of the allyl-terminated P3HT generated the hydroxypropyl-terminated P3HT which was subsequently reacted with cyclopentadienyltitanium trichloride. The reaction was monitored by $^1$H NMR and the appearance of a new peak at 4.5 ppm in the $^1$H NMR spectrum indicated the formation of the titanium propoxide-terminated P3HT (Fig. S3, ESI†). The complete disappearance of the methylene protons adjacent to the hydroxyl group at 3.78 ppm indicated the complete conversion of the hydroxypropyl end group to titanium propoxide. The polymerization of hexyl isocyanate with the titanium propoxide-terminated P3HT macriniitiator was performed in a glove box.

The $^1$H NMR spectra of the diblock copolymer displayed a broad peak at 3.5 to 4 ppm due to the presence of the methylene protons adjacent to the nitrogen of PHIC. The peak corresponding to the methylene protons adjacent to the thiophene ring of the P3HT block was integrated with respect to the peak corresponding to the methylene protons adjacent to the nitrogen atom on the PHIC block. The final diblock copolymer contained 90 mol% of PHIC as determined by $^1$H NMR (Fig. S4, ESI†).

Formation of the diblock copolymer was further confirmed by size exclusion chromatography (SEC) measurements, which displayed an increase in molecular weight of the diblock copolymer as compared to the P3HT precursor (SEC traces are shown in Fig. S5, ESI†).

UV-Vis analysis

UV-Vis analysis of the diblock copolymer was performed in solution as well as in thin films and it was compared with the P3HT-OH precursor. The UV-Vis spectrum of the diblock copolymer in THF displayed an absorption maximum at 447 nm which was attributed to P3HT and an absorption maximum at 250 nm which was due to the organization of helical PHIC (Fig. S7, ESI†). The thin film UV-Vis spectra of the precursor P3HT and the diblock copolymer displayed similar features except that the diblock copolymer showed a peak at 250 nm corresponding to the PHIC unit (Fig. S8, ESI†). The similarities in the UV-Vis spectra of the precursor P3HT and the diblock copolymer, both in solution and solid states, indicated that the PHIC block did not drastically affect the effective conjugation length of P3HT (Table 1).

A solvatochromism study was performed for the diblock copolymer and the precursor P3HT using THF–water and THF–methanol mixtures at the same concentration of the polymer in solution. Water and methanol were chosen because they are non-solvents for P3HT. A red shift in UV-Vis spectra for both the precursor polymer and diblock copolymer was observed upon the addition of 10% of non-solvent. The solvatochromism experiments were carried out up to but not including the point when the polymer precipitated out of solution. It was noted that the P3HT precursor precipitated out of the solution for 60 : 40 v/v THF–methanol and 40 : 60 v/v THF–water mixtures (Fig. 1 and S6, ESI†). However, the P3HT–b-PHIC diblock copolymer showed solvatochromism up to 40 : 60 v/v THF–methanol and 10 : 90 v/v THF–water mixtures. For the diblock copolymer, the absorption maxima were red shifted as compared to the P3HT precursor (Fig. 1). We speculated that upon addition of water or methanol to the diblock copolymer solutions in THF, micellar aggregates are formed with a core of hydrophobic poly(3-hexylthiophene) and a shell of poly(n-hexyl isocyanate). This result is consistent with our previous reports.44,47 In the THF–water mixtures, the precursor P3HT displayed the highest absorption maximum at 545 nm with $\pi-\pi^*$ transition at 600 nm when the THF–water ratio was 50 : 50 v/v (Table S1, ESI†). At the same ratio of the solvents, the diblock copolymer showed the highest absorption maximum at 555 nm with the $\pi-\pi^*$ transition at 610 nm. However, the diblock copolymer showed the highest absorption maximum of 561 nm with the $\pi-\pi^*$ transition at 612 nm when the THF–water mixture was 10 : 90 v/v. The precursor P3HT and the diblock copolymer displayed a similar trend for THF–methanol mixtures (Fig. S6 and Table S2, ESI†).

### Field-effect mobility

The field-effect mobilities of the polymer were measured in bottom-gate bottom-contact device configuration. A plot of

### Table 1. Molecular weights and optical properties of the P3HT precursor and the P3HT–b-PHIC diblock copolymer

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molecular weight (g mol$^{-1}$)</th>
<th>PDI</th>
<th>$\lambda_{\text{max}}^a$ (nm)</th>
<th>$\lambda_{\text{max}}^b$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT-OH precursor</td>
<td>12 000</td>
<td>1.20</td>
<td>447</td>
<td>550</td>
</tr>
<tr>
<td>P3HT-b-PHIC</td>
<td>21 000</td>
<td>1.45</td>
<td>250, 447</td>
<td>250, 250, 550</td>
</tr>
</tbody>
</table>

$^a$ Measured in THF solution. $^b$ Measured in the thin film deposited on a glass slide.

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**Scheme 1** Synthesis of diblock copolymer poly(3-hexylthiophene)-b-poly(n-hexyl isocyanate) (P3HT-b-PHIC).

**Fig. 1** Solvatochromism studies with the THF–water mixture: (a) P3HT and (b) P3HT–b-PHIC diblock copolymer.
$I_{DS}^{1/2}$ vs. $V_{GS}$ was obtained in the saturation regime and the field-effect mobility was calculated using the following equation:

$$\mu = \frac{2L}{WC_i} \frac{I_{DS}}{(V_{GS} - V_T)^2}$$

where $I_{DS}$ is the source–drain current, $W$ is the channel width, $L$ is the channel length, $C_i$ is the capacitance of the dielectric, $V_{GS}$ is the gate voltage and $V_T$ is the threshold voltage.

The field-effect mobility data were consistently measured from the channel length of 20 $\mu$m in the bottom gate-bottom contact OFET devices. The data were obtained from an untreated device and from the device treated with $8 \times 10^{-3}$ M of octyltrichlorosilane. The average field-effect mobility measured for an untreated device was $1.8 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ with the highest value of $3.2 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ (Table 2 and Fig. 2). However, the diblock copolymer displayed an average field-effect mobility of $1.1 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ on a device treated with octyltrichlorosilane (OTS). The highest value measured for the OTS treated device was $2.1 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ (Table 2 and Fig. 3).

The field-effect mobilities reported for various P3HT block copolymers ranged from $10^{-2}$ to $10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$.38,46-49 However, those copolymers had a semiconducting block content exceeding 10 mol%. We also reported the synthesis and electronic properties of a P3HT diblock copolymer containing poly(γ-benzyl-l-glutamate).42,44 The diblock copolymer contained ~57 mol% of semiconducting polymer segment and displayed a mobility of ~6 $\times$ $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ in thin film transistors. Again, we emphasize here that the investigated P3HT-b-PHIC diblock copolymer contained only 10 mol% of the semiconducting block and still possessed remarkable electronic properties in OFET devices. We speculated that the helical PHIC block enhanced the organization of P3HT in thin films. Moreover, the equal length side chains in both of the blocks in the rod–rod block copolymer possibly enabled the favorable structural morphology in thin films especially on the surface treated device.

### Table 2 Field-effect mobilities of poly(3-hexylthiophene)-b-poly(n-hexyl isocyanate) (P3HT-b-PHIC) measured in OFETs

<table>
<thead>
<tr>
<th>Device</th>
<th>Mobility (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$I_{on}/I_{off}$</th>
<th>$V_T$ (V)</th>
<th>Average mobility (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>$3.2 \times 10^{-4}$</td>
<td>$4.0 \times 10^4$</td>
<td>19.1</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$1.5 \times 10^{-4}$</td>
<td>$1.9 \times 10^4$</td>
<td>18.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$8.2 \times 10^{-5}$</td>
<td>$7.0 \times 10^4$</td>
<td>23.5</td>
<td></td>
</tr>
<tr>
<td>OTS treated</td>
<td>$7.5 \times 10^{-4}$</td>
<td>$6.4 \times 10^4$</td>
<td>30.3</td>
<td>$1.1 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$6.1 \times 10^{-4}$</td>
<td>$4.0 \times 10^4$</td>
<td>9.1</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 2 Current–voltage characteristics of poly(3-hexylthiophene)-b-poly(n-hexyl isocyanate) on an untreated device, output curves at different gate voltages (left); transfer curve at $V_{DS} = -100$ V ($W = 475$ $\mu$m, $L = 20$ $\mu$m) (right).](image)

Surface morphology of the thin film

The surface morphology of the polymers was investigated by TMAFM. The TMAFM analysis of the films was performed in the channel region of the OFET devices as well as on a mica substrate. Thin films of polymers were drop-cast either on a mica substrate or on OFET devices and the films were formed by the slow evaporation of the chloroform solvent in a chloroform chamber. TMAFM images were recorded for the precursor P3HT, a PHIC homopolymer, and the diblock copolymer. As expected, nano fibrillar morphology was observed for the P3HT homopolymer (Fig. 4(a) and (b)). By contrast, the PHIC homopolymer displayed a granular morphology. However, the macroscopic features were uniformly distributed in the image.

The diblock copolymer P3HT-b-PHIC displayed a nanoscale morphology that was different from the precursor P3HT (Fig. 4). This is in contrast with the surface morphology of most of the P3HT diblock copolymers reported previously. The surface morphologies of the P3HT diblock copolymers reported previously were dominated by nanofibrillar features of the P3HT block regardless of the block’s size.38-53 The images obtained for the P3HT-b-PHIC block copolymer thin film on mica were similar to the images obtained from the thin film in the OFET devices. The diblock copolymer self-assembled, leading to densely packed nanostructures. The formation of nanostructures was attributed to the self-assembly driven by the helical PHIC unit. The nanostructured morphology of the diblock copolymer thin film in the channel region of OFET devices explained the relatively good field effect mobilities which were measured for the diblock copolymers despite their very low content of P3HT semiconducting block.

### Bulk heterojunction solar cell studies

The diblock copolymer was tested in BHJ solar cells with PC$_{61}$BM and a PCE lower than 0.1% was obtained. This was...
attributed to the large content of the insulating block. Due to the poor performance of the diblock copolymer in BHJ, we decided to use the diblock copolymer in a P3HT:PCBM:P3HT-$b$-PHIC ternary blend. Addition of P3HT-$b$-PHIC was expected to modify the P3HT:PCBM microstructure and improve the performance of solar cells.

The current–voltage ($J-V$) characteristics of P3HT:PC$_{61}$BM:P3HT-$b$-PHIC blend solar cells were recorded under AM 1.5 AMG illumination. Fig. 5 shows the cell data obtained for the blends with various contents of P3HT-$b$-PHIC. A summary of the averaged $J-V$ characteristics is given in Table 3. The PCE for the P3HT:PC$_{61}$BM binary blend was 2.43%. As shown in Fig. 5 and Table 3, by adding 15 wt% diblock copolymer, the PCE increased to 2.66%. The ternary blend with 20 wt% and 30 wt% P3HT-$b$-PHIC diblock copolymer gave an overall reduction of PCE to 2.60% and 2.46%, respectively. The TMAFM analysis was performed on the active layer blends for the devices with 0 wt%,

<table>
<thead>
<tr>
<th>P3HT-$b$-PHIC (%)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>0.55</td>
<td>7.79 (7.99)</td>
<td>55%</td>
<td>2.43 (2.46)</td>
<td>246.2</td>
</tr>
<tr>
<td>15%</td>
<td>0.57</td>
<td>8.46 (8.80)</td>
<td>55%</td>
<td>2.66 (2.71)</td>
<td>231.5</td>
</tr>
<tr>
<td>20%</td>
<td>0.57</td>
<td>8.29 (8.58)</td>
<td>55%</td>
<td>2.60 (2.65)</td>
<td>229.5</td>
</tr>
<tr>
<td>30%</td>
<td>0.58</td>
<td>7.57 (7.62)</td>
<td>55%</td>
<td>2.46 (2.48)</td>
<td>215.3</td>
</tr>
</tbody>
</table>

$^a$ PC$_{61}$BM was used as an acceptor. $^b$ Data in the parentheses represent the highest value (four devices were tested and the average values were determined).

15 wt%, and 30 wt% P3HT-$b$-PHIC (Fig. 6 and S9, ESI†). The average surface roughness (r.m.s.) measured was 1.24 nm, 3.13 nm, and 6.55 nm for 0 wt%, 15 wt%, and 30 wt% P3HT-$b$-PHIC,
respectively. The different roughnesses indicated that the morphology changed as a function of weight% of P3HT-b-PHIC added.

When 15 wt% P3HT-b-PHIC was added, more phase separation in the active layer resulted, which most likely contributed to better charge transport. An increase in $J_{sc}$ (8.46 mA cm$^{-2}$) was obtained when 15 wt% P3HT-b-PHIC was added as compared with the P3HT:PC$_{61}$BM device (7.79 mA cm$^{-2}$). However, when 30 wt% P3HT-b-PHIC was added, the surface of the active layer became rougher and large isolated domains appeared as shown in Fig. 6. A decrease of $J_{sc}$ to 7.57 mA cm$^{-2}$ was attributed to the rough surface and the presence of large domains.

In order to confirm the effect of P3HT-b-PHIC, PC$_{71}$BM was also used as an acceptor for BHJ solar cells. The photovoltaic properties are summarized in Fig. 7 and Table 4. An increase in the PCE from 2.57% to 2.83% was also observed when 15 wt% P3HT-b-PHIC was added to the active layer blend. By varying the content of P3HT-b-PHIC, the PCE showed the same trend as it was observed for PC$_{61}$BM blends.

For the binary blend P3HT:PC$_{71}$BM device, a $V_{oc}$ of 0.56 V, $J_{sc}$ of 8.20 mA cm$^{-2}$, and FF of 56% were measured. For the ternary blend devices with 15 wt% P3HT-b-PHIC, an increase in $J_{sc}$ to 8.82 mA cm$^{-2}$ was observed. The PCE decreased when the content of P3HT-b-PHIC was increased above 15 wt%. The TMAFM images were obtained for devices with 0 wt%, 15 wt%, and 30 wt% P3HT-b-PHIC (Fig. 8). An increase of the average roughness from 2.59 nm to 5.01 nm upon addition of 15 wt% P3HT-b-PHIC indicated that P3HT-b-PHIC affected the morphology of the active layer. Presumably a better phase separation for devices with 15 wt% P3HT-b-PHIC improved the charge transport and thus resulted in the increase of $J_{sc}$ to 8.82 mA cm$^{-2}$. By contrast, the addition of 30 wt% P3HT-b-PHIC in the blend created larger domains and presumably a less favourable morphology of the active layer blend. $J_{sc}$ of 7.53 mA cm$^{-2}$ was measured for the blend with 30 wt% P3HT-b-PHIC, which is in agreement with the data obtained with the PC$_{61}$BM acceptor.

### Liquid crystalline properties

The liquid crystalline properties of the diblock copolymer were investigated using a polarizing microscope under a cross-polarizer. The polarized optical micrograph of a concentrated solution of the diblock copolymer in xylene (40 wt%), which was viewed at 10× magnification under crossed polarizers, is shown in Fig. 9. The micrograph indicated that PHIC in the diblock...
copoloymer was predominant and thus the block copolymer solution retained the liquid crystalline properties of PHIC.

**X-ray diffraction studies**

Thin film XRD measurements were performed for the P3HT precursor, PHIC homopolymer ($M_n = 13\,000\,\text{g}\,\text{mol}^{-1}$), and the P3HT-b-PHIC diblock copolymer films deposited from chloroform.

The XRD pattern obtained for the precursor P3HT indicated the presence of a peak at $2\theta = 5.38^\circ$ ($d = 16.4\,\text{Å}$) corresponding to the (100) lamellar stacking of P3HT. The film also showed higher order reflections of the P3HT stacking (200) and (300) at $2\theta = 10.87^\circ$ and $2\theta = 16.48^\circ$ corresponding to $d$-spacings of 8.13 Å and 5.37 Å respectively (Fig. 10(a)).

These data are consistent with the data reported for the XRD of the P3HT homopolymer. The XRD pattern obtained from the PHIC homopolymer thin film showed peaks at $2\theta = 5.41^\circ$, $6.48^\circ$, $13.55^\circ$, and $16.84^\circ$ corresponding to the $d$-spacings of 16.32 Å, 13.63 Å, 6.53 Å, and 5.26 Å, respectively (Fig. S11, ESI†). The P3HT-b-PHIC block copolymer displayed six characteristic peaks, indicating that the block copolymer self-assembled and preserved the crystallinity of its constituent blocks. While the peak corresponding to the first order lamellar stacking (100) of 16.53 Å may not be concretely assigned to one block over the other, the higher order reflections reveal that the inherent ordering of the two individual blocks was maintained (Fig. 10(b)). The second ($2\theta = 10.86^\circ$) and the third ($2\theta = 16.30^\circ$) order lamellar stacking with the $d$-spacing of ~8.1 Å and ~5.4 Å were clearly evident in the diffraction profiles for both the precursor P3HT (Fig. 10(a)) and the diblock copolymer (Fig. 10(b)). The XRD pattern also revealed the higher order reflection peaks of the PHIC block ($2\theta = 13.66^\circ$), ($2\theta = 18.48^\circ$), and ($2\theta = 21.07^\circ$) corresponding to the $d$-spacing of 6.47 Å, 4.79 Å, and 4.21 Å, respectively. These results indicate that the diblock copolymer self-assembled in such a way that PHIC and P3HT domains demonstrate long range ordering comparable to that of the corresponding homopolymers.

**Conclusions**

A semiconducting diblock copolymer containing a liquid crystalline segment was synthesized by the combination of GRIM and titanium mediated coordination polymerization methods. The electronic properties and liquid crystallinity of the copolymer were investigated and revealed. The block copolymer displayed a mesophase under a cross-polarizing microscope and also showed promising results in OFETs. The TMAFM images of the block copolymer thin films displayed nanoscale morphology. The use of the diblock copolymer as an additive for P3HT/PCBM bulk heterojunction solar cells was investigated. Upon addition of 15% P3HT-b-PHIC to the photoactive layer, the PCE improved by about 9%. The X-ray diffraction pattern obtained for the block copolymer showed that the overall structural morphology is driven by the liquid crystalline block.

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**Notes and references**