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Poly(n-alkyl isocyanates) are rigid-rod polymers with helical conformation in liquid as well as in solid state. These polymers combine steric repulsions between the side chains with double bond character of the amide groups. Among the polyisocyanates, poly(n-hexyl isocyanate) (PHIC) is one of the most intensively studied. The well-defined PHIC can be synthesized via organotitanium mediated living coordination and living anionic polymerization techniques. PHIC is a helical semiflexible polymer with liquid crystalline (LC) properties. Moreover, PHIC forms a nematic liquid crystal at high concentrations in non-polar solvents. Even though PHIC is a lyotropic liquid crystalline polymer, its solid state properties are also promising. 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. Recently, Tanaka’s group proposed the application of PHIC in electrical devices. 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. 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. McCullough’s group reported the livingness of P3HT using the GRIM method which allows the synthesis of end functionalized P3HT. End-functionalized P3HTs have been widely used to generate various block copolymers. P3HT is a rigid rod-like polymer with a persistence length of 2.4 nm. However, P3HT does not behave like a rod above a certain molecular weight. Incorporation of helical liquid crystalline polymers like polyisocyanates, 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. A systematic study of morphology and optoelectronic properties of liquid crystalline diblock copolymers containing semiconducting units is a relatively unexplored area of research. Few reports exist regarding diblock copolymers containing main chain LC polymer and a semiconducting segment. However, it has been demonstrated that a diblock copolymer containing side chain liquid crystalline (SCLP) units and rr-P3HT undergoes self-assembly and microphase separation.
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 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 Supporting Information.

2 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. Azetotropic distillation was performed under a nitrogen atmosphere. Distillation was stopped after collecting 15 mL of toluene into the receiving flask. Cyclopentadienyltitanium trichloride (TiCpCl3) (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 hydroxyl group to titanium alkoxide using 1H NMR. Toluene was removed from the reaction mixture under vacuum.

2 Synthesis of 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 evaporated slowly in a Petri dish saturated with chloroform.

**UV-Vis analysis**

UV–Vis spectra in solution and solid state were measured using an Agilent 8453 UV–Vis spectroscopy system. For solvatochromism study, stock solutions of the precursor P3HT and the diblock copolymer (5 mg/mL 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**

1H NMR spectra of the synthesized monomers and polymers were recorded on a Bruker 500 MHz spectrometer at 25 °C. 1H NMR data are reported in parts per million as chemical shift relative to tetramethylsilane (TMS) as the internal standard. Spectra were recorded in CDCl3. 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). 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; 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 Visotec VE 3580 system equipped with ViscoGEL™ columns (GMHHR-M), connected to a refractive index (RI) detector. 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, injector volume = 100 µL, detector temperature = 30 °C, column temperature = 35 °C. All the polymers 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 (SiO2) 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 SiO2 on the back side 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 SiO2 dielectric was 17 nF/cm2. After the SiO2 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
drop casting 4-5 drops of 8 mg/mL 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 octyltrichlorosilane, the devices were
rinsed sequentially with water, acetone, hexanes and chloroform
and placed in a glass container in a solution of silane of 8x10^3 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 thin film surface morphology was
carried out using a Nanoscope IV-Multimode Veeco, equipped with an E-type vertical engage scanner. 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 mica substrate. Thin films were obtained by drop-casting chloroform solution of polymers on mica substrate. The AFM images were recorded at room temperature in air using silicon cantilevers with normal spring constant of 42 N/m and normal resonance frequency of 320 kHz.

A typical value of 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) and deposited on to mica substrate by drop casting.

For solar cell devices, the TMAFM was carried out on the active area in between the channels of the metal. Images were obtained using silicon cantilevers with spring constant of 42 N/m and resonance frequency of 300 kHz. Images were acquired at 1 Hz scan frequency. Sample scan area was 3 µm x 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 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

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

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**Results and discussion**

**Synthesis and characterization of diblock copolymer**

Synthesis of poly(3-hexylthiophene)-b-poly(n-hexyl isocyanate) (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 (Supporting Information). Hydroboration-oxidation of the allyl-terminated P3HT generated the hydroxpropyl-terminated P3HT which was subsequently reacted with cyclopentadienyltitanium trichloride. The reaction was monitored by 1H NMR and the appearance of a new peak at 4.5 ppm in 1H NMR spectrum indicated the formation of the titanium propoxide-terminated P3HT (Figure S3, Supporting Information). The complete disappearance of the methylene protons adjacent to the hydroxyl group at 3.78 ppm indicated the complete conversion the hydroxpropyl end group to the titanium propoxide. The polymerization of hexyl isocyanate with the titanium propoxide-terminated P3HT macroinitiator was performed in a glove box.
precursor polymer and diblock copolymer was observed upon the precursor P3HT and the diblock copolymer displayed similar features except that the diblock copolymer showed a peak at 250 nm corresponding to PHIC unit (Figure S8, Supporting Information). The similarities in the UV-Vis spectra of the diblock copolymer were 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 Figure S5, Supporting Information).

**UV-Vis analysis**

UV-Vis analysis of the diblock copolymer was performed in solution as well as on thin films and it was compared with P3HT-OH precursor. The UV-Vis spectrum of the diblock copolymer in THF displayed an absorption maximum at 447 nm which was attributed to the P3HT and an absorption maximum at 250 nm which was due to the organization of helical PHIC (Figure S7, Supporting Information). 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 PHIC unit (Figure S8, Supporting Information). The similarities in the UV-Vis spectra of the precursor P3HT and the diblock copolymer, both in solution and solid state, indicated that the PHIC block did not drastically affect the effective conjugation length of the P3HT.

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 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 (Figure 1 and Figure S6, Supporting Information). 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 (Figure 1). We speculated that upon addition of water or methanol to the diblock copolymers in THF, micellar aggregates are formed with a core of hydrophobic poly(3-hexylthiophene) and a shell of poly(t-hexyl

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molecular weight (g/mol)</th>
<th>PDI</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; (nm)</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT-OH precursor</td>
<td>12000</td>
<td>1.20</td>
<td>447</td>
<td>550</td>
</tr>
<tr>
<td>P3HT-b-PHIC</td>
<td>21000</td>
<td>1.45</td>
<td>250, 447</td>
<td>250, 550</td>
</tr>
</tbody>
</table>

<sup>a</sup>measured in THF solution; <sup>b</sup>measured in thin film deposited on a glass slide.

The <sup>1</sup>H NMR 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 thiopehene 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 <sup>1</sup>H NMR (Figure S4, Supporting Information). Formation of the diblock copolymer was further confirmed by SEC traces which displayed an increase in molecular weight of the diblock copolymer as compared to the P3HT precursor.

The field-effect mobility of the polymer was measured in bottom-gate bottom-contact device configuration. A plot of I<sub>DS</sub> vs. V<sub>GS</sub> was obtained in the saturation regime and the field-effect mobility was calculated using following equation:

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

where I<sub>DS</sub> is the source-drain current, W is the channel width, L is the channel length, C<sub>i</sub> is the capacitance of the dielectric, V<sub>GS</sub> is the gate voltage and V<sub>T</sub> is the threshold voltage.

The field-effect mobility data were consistently measured from the channel length of 20 µm in the bottom gate-bottom contact OFET devices. The data were obtained from an untreated device and from the device treated with 8×10<sup>14</sup> M of octyltrichlorosilane. The average field-effect mobility measured for an untreated device was 1.8×10<sup>-4</sup> cm<sup>2</sup>/Vs with highest value of 3.2×10<sup>-4</sup> cm<sup>2</sup>/Vs (Table 2 and Figure 2). However, the diblock copolymer displayed the average field-effect mobility of 1.1×10<sup>-3</sup> cm<sup>2</sup>/Vs on a device treated with octyltrichlorosilane (OTS). The highest value measured for the OTS treated device was 2.1×10<sup>-3</sup> cm<sup>2</sup>/Vs (Table 2 and Figure 3).

The field-effect mobilities reported for various P3HT block copolymers ranged from 10<sup>2</sup> to 10<sup>3</sup> cm<sup>2</sup>/Vs. 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). The diblock copolymer contained ~57 mol% of semiconducting polymer segment and displayed a mobility of ~ 6×10<sup>-4</sup> cm<sup>2</sup>/Vs in thin film transistors. Again, we emphasize here that the investigated P3HT-b-PHIC diblock copolymer contained only 10 mol% of the semiconducting block.
Figure 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).

Table 2. Field-effect mobilities of poly(3-hexylthiophene)-b-poly(n-hexylisocyanate) (P3HT-b-PHIC) measured in OFET

<table>
<thead>
<tr>
<th>Device</th>
<th>Mobility (cm$^2$/Vs)</th>
<th>$I_{on}/I_{off}$</th>
<th>$V_T$ (V)</th>
<th>Average mobility (cm$^2$/Vs)</th>
<th>$I_{DS}$ (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>3.2×10$^{-4}$</td>
<td>4.0×10$^{-4}$</td>
<td>19.1</td>
<td>1.8×10$^{-4}$</td>
<td>6.0×10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>1.5×10$^{-4}$</td>
<td>1.9×10$^{-4}$</td>
<td>18.3</td>
<td></td>
<td>8.0×10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>8.2×10$^{-4}$</td>
<td>7.0×10$^{-4}$</td>
<td>23.5</td>
<td></td>
<td>1.0×10$^{-3}$</td>
</tr>
<tr>
<td>OTS treated</td>
<td>2.1×10$^{-4}$</td>
<td>2.3×10$^{-4}$</td>
<td>17.4</td>
<td>1.1×10$^{-3}$</td>
<td>6.0×10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>7.5×10$^{-4}$</td>
<td>6.4×10$^{-4}$</td>
<td>30.3</td>
<td></td>
<td>8.0×10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>6.1×10$^{-4}$</td>
<td>4.0×10$^{-4}$</td>
<td>9.1</td>
<td></td>
<td>1.0×10$^{-3}$</td>
</tr>
</tbody>
</table>

Figure 3. Current-voltage characteristics of poly(3-hexylthiophene)-b-poly(n-hexyl isocyanate) (P3HT-b-PHIC) on a device treated with OTS, output curves at different gate voltages (left); (b) transfer curve at $V_{DS} = -100$ V ($W = 475 \mu m$, $L = 20 \mu m$) (right).

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 surface treated device.

Surface morphology on 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 mica substrate. Thin films of polymers were drop-casted either on 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, nanofibrillar morphology was observed for the P3HT homopolymer (Figure 4 (a) and (b)). By contrast, the PHIC homopolymer displayed a granular morphology. However, the granular features were uniformly distributed in the image.

Figure 4. TMAFM images of: (a) Height and (b) phase images of P3HT on mica (0.5 mg/mL in chloroform); (c) Height and (d) phase images of PHIC on mica (8 mg/mL in chloroform); (e) Height and (f) phase images of P3HT-b-PHIC on mica (8 mg/mL in chloroform); (g) Height and (h) phase images of P3HT-b-PHIC on the channel region of OFET (8 mg/mL) (Scan size: 2×2 µm).
The diblock copolymer P3HT-b-PHIC displayed a nanoscale morphology that was different from the precursor P3HT (Figure 4). This is in contrast with the surface morphology of most of the P3HT diblock copolymers reported previously, which were dominated by nanofibrillar features of the P3HT block regardless of the block’s size.26,27 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_{71}BM, and PCE lower than 0.1% was obtained. This was attributed to the large content of the insulating block. Due to the poor performance of diblock copolymer in BHJ, we decided to use the diblock copolymer in a P3HT:PCBM:P3HT-b-PHIC ternary blend. Adding the 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_{71}BM:P3HT-b-PHIC blend solar cells were recorded under AM 1.5 AMG illumination. Figure 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_{71}BM binary blend was 2.43 %. As shown in Figure 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 layers for the devices with 0 wt., 15 wt., and 30 wt.% P3HT-b-PHIC (Figure 6, Figure S9, Supporting Information). 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 roughness indicated that the morphology changed as a function of weight % of P3HT-b-PHIC added.

**Table 3. Photovoltaic properties of devices with different percentage of P3HT-b-PHIC**

<table>
<thead>
<tr>
<th>P3HT-b-PHIC (%)</th>
<th>J_{sc} (mA/cm²)</th>
<th>V_{oc} (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>7.99 (7.62)</td>
<td>0.55</td>
<td>55%</td>
<td>2.71 (2.65)</td>
<td>231.5</td>
</tr>
<tr>
<td>15%</td>
<td>8.46 (8.58)</td>
<td>0.57</td>
<td>55%</td>
<td>2.66 (2.65)</td>
<td>229.5</td>
</tr>
<tr>
<td>20%</td>
<td>8.29 (8.58)</td>
<td>0.57</td>
<td>55%</td>
<td>2.60 (2.65)</td>
<td>229.5</td>
</tr>
<tr>
<td>30%</td>
<td>7.57 (7.62)</td>
<td>0.58</td>
<td>55%</td>
<td>2.46 (2.48)</td>
<td>215.3</td>
</tr>
</tbody>
</table>

*PC_{71}BM was used as acceptor.

1Data in the parenthesis represents the highest value (four devices were tested and the average values were determined).

When 15 wt.% P3HT-b-PHIC was added, more phase separation in the active layer resulted, which most likely contributed to better charge transport.34,35 An increase in the J_{sc} (8.46 mA/cm²) was obtained when 15 wt.% P3HT-b-PHIC was added as compared with the P3HT:PC_{71}BM device (7.79 mA/cm²). 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 Figure 6. A decrease of the J_{sc} to 7.57 mA/cm² 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 Figure 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.

Figure 7. J-V curves for devices with different percentage of P3HT-b-PHIC

Table 4. Photovoltaic properties of devices with different percentage of P3HT-b-PHIC

<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>0.56</td>
<td>8.20 (8.37)</td>
<td>56%</td>
<td>2.52</td>
<td>244.6</td>
</tr>
<tr>
<td>15%</td>
<td>0.56</td>
<td>8.82 (8.91)</td>
<td>58%</td>
<td>2.83</td>
<td>219.6</td>
</tr>
<tr>
<td>20%</td>
<td>0.57</td>
<td>8.24 (8.44)</td>
<td>58%</td>
<td>2.72</td>
<td>218.6</td>
</tr>
<tr>
<td>30%</td>
<td>0.57</td>
<td>7.53 (7.90)</td>
<td>55%</td>
<td>2.36</td>
<td>206.2</td>
</tr>
</tbody>
</table>

*PC_{61}BM was used as acceptor.

**Data in the parenthesis represents the highest value (four devices were tested and the average values were calculated).

For the binary blend P3HT:PC_{61}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 the \( J_{sc} \) 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. 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 the \( J_{sc} \) 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. A \( J_{sc} \) 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 PC_{61}BM acceptor.

**Liquid crystalline properties**

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

Figure 8. 3D TMAFM images of the solar cell devices with (a) 0% P3HT-b-PHIC (r.m.s=2.59 nm); (b) 15% P3HT-b-PHIC (r.m.s=5.01 nm); (c) 30% P3HT-b-PHIC (r.m.s=10.30 nm); scan size (3×3µm)

Figure 9. Optical micrograph of P3HT-b-PHIC; 40 wt% of polymer in xylene

**X-Ray diffraction studies**

Thin film XRD measurements were performed for the P3HT precursor, PHIC homopolymer (M\(_n\) = 13000 g 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 20 = 5.38° (d = 16.4 Å) corresponding to the (100) lamellar stacking of P3HT. The film also showed higher order reflections of the P3HT stacking (200) and (300) at 20 = 10.87° and 20 = 16.48° corresponding to d-spacings of 8.13 Å and 5.37 Å respectively (Figure 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 20 = 5.41°, 6.48°, 13.55°, and 16.84° corresponding to the d-spacing of 16.32 Å, 13.63 Å, 6.53 Å, and 5.26 Å, respectively (Figure S11, Supporting Information). 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 be 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 (Figure 10 (b)). The second (20 = 10.86°) and third (20 = 16.30°) 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 (Figure 10 (a)) and the diblock copolymer (Figure 10 (b)). The XRD pattern also revealed the higher order reflection peaks of the PHIC block (20 = 13.66°), (20 = 18.48°), and (20 = 21.07°) 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 liquid crystalline segment was synthesized by the combination of GRIM and titanium mediated coordination polymerization methods. Electronic properties and liquid crystallinity of the copolymer were investigated and revealed. The block copolymer displayed a mesophase under cross polarized microscope and also showed promising results in OFETs. The TMAFM images of the block copolymer thin films displayed nanoscale morphology. The use of diblock copolymer as 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%. X-ray diffraction pattern obtained for the block copolymer showed that the overall structural morphology is driven by the liquid crystalline block.

Financial support for this project from Welch Foundation (AT-1740) and NSF (Career DMR-0956116) is gratefully acknowledged. We gratefully acknowledge the NSF-MRI grant (CHE-1126177) used to purchase the Bruker Avance III 500 NMR instrument.

Notes and references


