Self-Assembly of a Conjugated Triblock Copolymer at the Air-Water Interface

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Self-assembly of a conjugated triblock copolymer at the air–water interface†

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Controlling the self-assembly of highly luminescent conjugated polymers is essential for preparing various optoelectronic devices. In this study, a polyisoprene-b-polystyrene-b-poly(3-hexylthiophene) (PI-PS-P3HT) triblock copolymer was synthesized and readily self-assembled into network-like morphologies via dewetting at the air–water interface. Interestingly, the monolayer thick film displayed high photoluminescence (PL) as a result of successfully transferring the amorphous conjugated P3HT chains in the PI-PS-P3HT triblock copolymer from the solution state to the solid state. A model was proposed to illustrate the supramolecular organization of the PI-PS-P3HT monolayer. To the best of our knowledge, this is the first study of a hydrophobic conjugated block copolymer at the air–water interface, from which the conjugated polymer-based monolayer with highly efficient PL formed by dewetting was achieved.

Introduction

Conjugated polymers (CPs) have garnered considerable attention as promising materials for use in organic photovoltaics, light-emitting diodes (LEDs), thin film transistors, and biosensors.1,2 Among various types of CPs, poly(3-alkylthiophenes) (P3ATs) emerge as the most widely studied organic semiconductors due to their excellent solution processability, environmental stability, high charge carrier mobility, and tailorable electrochemical properties.3 For the current thin-film device applications, P3AT films are mainly produced by conventional film preparation techniques, such as drop-casting and spin-coating, which often involve a fast and uncontrolled self-assembly process. As optical and electronic properties of solution-processed conjugated polymer thin films are largely dictated by the packing motifs of molecules in the film, it is of key importance to achieve a precise control over the assembly process. Moreover, the drive towards nanometer scale devices for electronic applications further underscores the need for nanoscale control.4 In this context, the Langmuir–Blodgett (LB) technique is a very useful tool to control the assembly of polymers at the molecular level due to the asymmetry of the air–water interface. In stark contrast to conventional film fabrication methods noted above, the organization of molecules at the air–water interface can be readily altered as a function of polymer architecture, surface pressure, trough temperature, water subphase pH, etc.5 The implementation of the LB technique on conjugated polymers has yielded a great variety of optical and electronic devices, such as LEDs6 thin film conductors,7 memory devices,6,9 ferroelectric thin films,9 nonlinear optical devices,11 sensors,12 field-effect transistors,13,14 etc.

Because of strong intermolecular interactions and weak water affinity, the stability of the P3AT monolayer at the air–water interface is usually low, making it difficult to be transferred onto a solid substrate. To date, two approaches have been broadly utilized to impart the transferring. (1) Spreading the solution of P3AT in conjunction with inert amphiphilic molecules on a water subphase. The amphiphilic molecules, e.g., fatty acid, work as the lubricant and matrix, enabling P3AT chains to come closer to each other in a relatively controllable manner after their gradual detachment from the water surface.15 (2) Modifying the molecular structure of polythiophenes to render them amphiphilic by replacing the alkyl side chains with polar ones. Recently, the LB film with newly designed amphiphilic polythiophenes has been prepared, allowing the coexistence of a fully conjugated and π-stacked polymer structural motif and a membrane forming motif (i.e., π-π stacking leads to the formation of a crystallized LB film composed of conjugated backbones, which is stabilized at the air–water interface via a strong affinity between hydrophilic side chains and the water subphase). It is worth noting that the P3AT chains in current LB
studies are mainly strongly packed and crystallized, which is a state important for applications as conductive polymeric films but detrimental to the utilization of conjugated polymers as electroluminescent devices, as the strong &pi;&ndash;&pi; stacking leads to enhanced interchain interaction, working as traps that severely quench the PL originated from the intrachain interaction.\textsuperscript{16–18} Moreover, limited work has been reported on self-assembly of conjugated block copolymers at the air–water interface that exhibit controlled ordering at different length scales\textsuperscript{19} for use in optoelectronic devices. Finally, we note that in the previous work on the LB of conjugated polymers, the existence of hydrophilic components, either as the amphiphilic phase (approach (1) as described above)\textsuperscript{25} or polar units (approach (2)),\textsuperscript{4} is found to be necessary to stabilize the P3AT monolayer; however this limits the application of the LB technique only to amphiphilic systems.

Herein, we report, for the first time, that the addition of hydrophobic blocks (i.e., polyisoprene (PI) and polystyrene (PS)) to conjugated polymer P3HT can stabilize the LB monolayer of all hydrophobic triblock copolymer PI-PS-P3HT, thereby greatly extending the use of the LB technique for P3AT-based devices. An interesting network-like surface morphology via dewetting was observed. Most importantly, the undesirable interchain interaction (acting as PL quenching centers) was effectively suppressed due to successfully transferring the luminescent P3HT block of the PI-PS-P3HT triblock copolymer from the solution state to the solid state, resulting in a highly photoluminescent surface morphology. The mechanism for the morphological evolution as a function of surface pressure was systematically investigated by atomic force microscopy (AFM), transmission electron microscopy (TEM), and grazing-incidence small-angle X-ray scattering (GISAXS). A model was proposed to illustrate the supramolecular organization of the PI-PS-P3HT monolayer and the energy transfer process.\textsuperscript{26} To the best of our knowledge, this is the first study of all hydrophobic conjugated block copolymers at the air–water interface, from which the conjugated polymer-based monolayer with highly efficient PL formed by dewetting was achieved. The LB-enabled self-assembly may stand out as a promising approach to yield optoelectronic thin-film devices, and afford a unique platform to investigate the complex self-assembly process and energy transfer of conjugated polymer-based systems confined in two dimensions.

**Experimental methods**

**Materials synthesis**

All reactions were conducted using oven-dried glassware under N\textsubscript{2}. Commercial chemicals purchased from Aldrich Chemical Co., Inc. were used without further purification unless otherwise noted. All solvents were freshly distilled prior to use. Tetrahydrofuran (THF) was distilled from sodium benzo-phenone ketyl. Chloroform was distilled and collected over molecular sieves. Polyisoprene-b-polystyrene-b-poly(3-hexylthiophene) (PI-PS-P3HT) triblock copolymer was synthesized by the addition of living polypolyisoprene-b-polystyryl lithium to allyl terminated poly(3-hexylthiophene).\textsuperscript{21–25} Polyisoprene-b-polystyrene-b-poly(3-hexylthiophene) (PI-PS-P3HT) triblock copolymer was synthesized by reacting the allyl-terminated poly(3-hexylthiophene) (M\textsubscript{n} = 4500 g mol\textsuperscript{-1}; D\textsubscript{P}\textsubscript{n} ([NMR] = 20) as a solution in dry THF with the living polypolyisoprene-b-polystyryl lithium (M\textsubscript{n} (GPC) = 3320 g mol\textsuperscript{-1}) in cyclohexane (Scheme S1\textsuperscript{1}). The coupling reaction was allowed to proceed for 10 min at 40 °C. The coupling reaction was performed in a glove box under a nitrogen atmosphere. The copolymer was precipitated in methanol and washed with cold cyclohexane to remove the unreacted polypolyisoprene-b-polystyrene diblock copolymer. The PI-PS-P3HT triblock copolymer contains 31.5 mol% PI, 44.2 mol% PS, and 24.3 mol% P3HT as estimated from the integration of the methylene protons of P3HT blocks vs. the vinyl protons of PI and the aromatic protons of PS blocks (SEC: M\textsubscript{n} = 7170 g mol\textsuperscript{-1}; PDI = 1.50). Based on the \textsuperscript{1}H NMR analysis, the composition of the copolymer was estimated as PI\textsubscript{29}-PS\textsubscript{32}-P3HT\textsubscript{20} (Fig. S1\textsuperscript{1}).

**Monolayer preparation**

The PI-PS-P3HT triblock copolymer chloroform solutions at the concentration c = 2 mg mL\textsuperscript{-1} were prepared. Surface pressure–area (π–A) isotherms of triblock copolymer monolayers were obtained with an R&K Langmuir–Blodgett (LB) system (Riegler & Kirstein, GmbH, 160 cm\textsuperscript{2} Teflon trough). The trough was carefully cleaned with a 1 : 1 H\textsubscript{2}O\textsubscript{2} : N\textsubscript{2}H\textsubscript{4}OH solution overnight and subsequently rinsed with DI water (NanoPure, >18 MΩ cm) 5 times. A 5 μL chloroform solution was then gently placed on the water surface to ensure the initial gas state. After chloroform being evaporated for 30 min, the monolayer film was compressed at a rate of 150 μm s\textsuperscript{-1}. The Si substrate used for depositing LB films was cleaned with a mixture of sulfuric acid and Nonchromix, followed by rinsing with DI water and blown dry with N\textsubscript{2}. For LB depositions, the Si substrate was withdrawn at a rate of 35 μm s\textsuperscript{-1} while keeping the pressure constant.

**Characterization**

\textsuperscript{1}H NMR spectra of polymers were recorded on a VARIAN-INOVA-500 MHz spectrometer at 30 °C. \textsuperscript{1}H NMR data were reported in parts per million as chemical shifts relative to tetramethylsilane (TMS) as the internal standard. The spectra were recorded in CDCl\textsubscript{3}. The morphologies of LB films were examined by Atomic Force Microscopy (AFM; Dimension 3000) in tapping mode. The scanning rate was 2 Hz. Each sample was imaged at more than 5 locations to ensure the reproducibility of observed features. The fine structure was determined by TEM measurements (JEOL 1200EX scanning/transmission electron microscope (STEM); operated at 80 kV). The emission spectra of the P3HT homopolymer were taken with a Nikon Eclipse TE2000-E microscope coupled to an optical insights hyperspectral unit and a Cascade 512B camera (Roger Scientific). The PL emission of the monolayer was obtained by using a series of emission filters to measure the emission intensity (the transmission efficiency of these filters is the same). The average height, diameter and surface coverage of LB films were obtained by performing the bearing analysis and particle analysis. The GISAXS experiment was carried out at XOR 32-ID beamline of the Advanced Photon Source (APS) at Argonne National Laboratory, Illinois.
Fluorescence imaging

An upright Nikon Eclipse 80i microscope equipped with a 100× Plan Apo/1.40 oil-immersion objective and an Andor iXon EM+ 897 camera (Belfast, Northern Ireland; cooled at −50 °C, 512 × 512 imaging array, 16 μm × 16 μm pixel size) was used to collect the fluorescence images. The excitation bandpass filter has a central wavelength of 480 nm with a full width at half maximum (FWHM) of 40 nm, and the emission bandpass filter has a central wavelength of 545 nm with a FWHM of 30 nm.

Results and discussion

The chemical structure of the PI-PS-P3HT triblock copolymer used in this study is shown in Fig. 1. The Langmuir isotherm, i.e., surface pressure–area (π–A) plot, of the PI-PS-P3HT triblock copolymer is shown in Fig. 2. The continuous pressure rise was indicative of the formation of the LB monolayer. Different from the previous reports on hydrophobic block copolymers where the liquid region was commonly observed in the isotherm, the entire isotherm is extremely simple and can be divided into only two typical regions based on the slope of the isotherm (i.e., the pressure increasing rate with the molecular area). They are (i) the gas region at π = 0 mN m⁻¹ and (ii) the condensed state region at π > 0 mN m⁻¹. The absence of the liquid region, which is usually formed due to the polymer chain relaxation in response to the surface pressure, suggested that the monolayer is incompressible once formed. Notably, this is the first observation of a two-phase isotherm curve in conjugated polymer-based systems.

Fig. 3 shows the representative AFM height images of Langmuir monolayers obtained at these two regions. The intriguing worm-like domains containing dotted structures were observed at the surface pressure π = 0 mN m⁻¹ (Fig. 3a and b). As the pressure was not yet applied, the aggregation of the triblock copolymer was a direct consequence of a spontaneous self-assembly process. The driving force for self-assembly is most likely due to the interplay of the attractive interaction between the less hydrophobic thiophene units (i.e., less hydrophobic backbone of P3HT) and the water phase, and the repulsive interactions between hydrophobic chains and water as chloroform evaporated. Specifically, the P3HT block had a relatively less hydrophobic backbone, which possessed some water affinity, thus enabling the P3HT block to be fully spread on the water surface at lower lateral pressure. On the other hand, the hydrophobic components were from PS and PI blocks as well as from the side chains of the P3HT block. The close-up AFM images showed that the dots were not isolated, but rather well-connected with a spreading phase between them (Fig. 3b and S2†). To understand the microstructure of worm-like morphology, the monolayer deposited at the gas state was also characterized by TEM. As the P3HT block has a higher electron density as compared to that of PS and PI blocks (due to the existence of S atoms which have higher electron density than C and H atoms), the observed aggregated morphology from TEM solely originated from the P3HT block (Fig. 4). Clearly, the P3HT block not only existed in the dotted structures which was

Fig. 1 Chemical structure of a polyisoprene-b-polystyrene-b-poly(3-hexylthiophene) (PI-PS-P3HT) triblock copolymer.

Fig. 2 The pressure–area isotherm of a PI-PS-P3HT triblock copolymer: (I) gas region and (II) condensed region. The chemical structure of a PI-PS-P3HT triblock copolymer is shown as an inset.

Fig. 3 AFM height images of LB monolayers of the PI-PS-P3HT triblock copolymer obtained from the chloroform solution at (a and b) gas region; and (c and d) condensed region. Scan size = 20 μm × 20 μm for (a) and (c); scan size = 5 μm × 5 μm for (b) and (d). The z scale is 50 nm for all images.
consistent with AFM measurements (Fig. 3), but also in the spreading phase (i.e., between dotted structures), as evidenced in the HRTEM images (Fig. 4b and S2†) The close-up TEM image showed that the domain was totally amorphous (Fig. S3†), and no crystallized fiber-like structure was observed as broadly reported previously.25,26

With the increase of surface pressure from the gas region to the condensed state region, the dotted structures were well preserved, but the size and height increased from approximately 28.8 nm to 42.3 nm, and from roughly 4.11 nm to 5.1 nm (Table 1). Moreover, the surface coverage of domains dramatically increased from 20.4% to 41.7%, indicating the formation of a more condensed monolayer at higher surface pressure (Table 1 and Fig. 3). Interestingly, these dots no longer formed the worm-like morphology as shown in Fig. 3b, but chained into pearl-necklace-like morphology (i.e., isotropic dots self-assembled linearly into pearl-necklace-like structures with rather uniform width containing mainly one dot; Fig. 3d). Obviously, more condensed P3HT domains were observed at high surface pressure as revealed by the TEM measurement (Fig. S4†) as compared to those at low surface pressure (Fig. 4). Such a condensed monolayer was also examined by GISAXS; no diffraction patterns of crystallized P3HT (0.3 –0.4 Å−1) were observed (Fig. S5†), indicating that the P3HT block existed in its amorphous state, which was consistent with the TEM results.

**Optical property study of self-assembled structures**

The monolayer deposited at the gas region was also measured using an optical microscope (OM) coupled with an excitation lamp. In sharp contrast to the previous LB studies of conjugated polymers,27,28 where strong interchain interaction within condensed phases severely quenched the luminescence, the fluorescence emission from self-assembled PI-PS-P3HT was so strong that the monolayer-thick film can be directly observed under OM (Fig. 5a).29

As noted above, the ability to form a thin film or a well-defined surface pattern of conjugated polymers with high fluorescence emission is crucial to the fabrication of nanoscale electroluminescent devices.29 To reveal the origin of such strong fluorescence from the PI-PS-P3HT monolayer, the monolayer was characterized by photoluminescence (PL) measurements as optical properties of conjugated polymers are largely governed by the packing motifs of molecules and their configurations.30,31 The PL spectra of the P3HT homopolymer in the solution and solid states were also recorded as the reference. As evidenced in Fig. 5b, the vibronic structures of the P3HT homopolymer in both solution and solid states were observed. In the solution, the conjugated P3HT chain was broken into conformational subunits consisting of several repeated units due to the relatively low energy barrier for small-angle rotations around bonds along the backbone, resulting in blue-shifted PL emission as a result of reduced conjugated length.32 After drying (Fig. 5b, blue curve), the crystallization of P3HT greatly increased the ordering of polymer chains and the degree of interchain interaction, leading to increased conjugated length (corresponding to a red-shift).33,34 As reported by Saadeh et al.,35 the PL efficiency dramatically dropped from 30–40% to 1–4% during this process due to the increased contribution of non-radiative decay via interchain interactions.36 We note that all PL spectra in Fig. 5b were rescaled in order to provide a clear view, as the PL spectra from the solid-state P3HT and the PI-PS-P3HT monolayers were too weak as compared with the solution-state P3HT.

Quite intriguingly, the PI-PS-P3HT monolayer exhibited a similar emission position as the P3HT chains in the solution state (Fig. 5b), rather than resembling that of crystallized P3HT chains (i.e., solid-state P3HT). This clearly indicated the successful transferring of highly luminescent amorphous P3HT from the solution state to the solid film (i.e., forming the LB monolayer while maintaining high PL), representing an important step toward producing highly efficient electroluminescent devices. This result was in good agreement with the TEM and GISAXS measurements showing the amorphous state of P3HT chains in PI-PS-P3HT LB films. Thus, the fluorescence of the monolayer-thick PI-PS-P3HT LB film can be directly visualized by OM.

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**Table 1** Summary of height, diameter and surface coverage of PI-PS-P3HT domains obtained from AFM images

<table>
<thead>
<tr>
<th>Domain height (nm)</th>
<th>Domain diameter (nm)</th>
<th>Surface coverage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas state</td>
<td>4.11</td>
<td>28.87</td>
</tr>
<tr>
<td>Condensed state</td>
<td>5.13</td>
<td>42.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>41.7</td>
</tr>
</tbody>
</table>
Self-assembly process of the PI-PS-P3HT triblock copolymer at the air–water interface

The interfacial behavior of amphiphilic copolymers at the air–water interface has been extensively studied.\textsuperscript{17,20,41} To date, the so-called “pancake” and “brush” models have been established and proved effective in understanding the air–water interfacial behavior of a variety of amphiphilic copolymers, such as linear block copolymers,\textsuperscript{5,44–46} star copolymers,\textsuperscript{47–51} comb-like copolymers,\textsuperscript{52} dendritic polymers,\textsuperscript{53–55} etc. The “pancake” model refers to the morphology of the LB film of the copolymer formed at low surface pressure. In this model, the hydrophilic blocks spread over the water surface, forming the pancake-like morphology; while the hydrophobic blocks aggregate and sit on the hydrophilic “pancake” to reduce the surface energy. Under higher compression pressure, the “pancake” is transformed into the “brush”, i.e., the spread hydrophilic blocks are expelled into the water sub-phase, yielding the brush-like morphology (“brush” model).

The LB technique was initially applied for amphiphilic molecules. The recent development of this technique has progressively extended its usefulness to different non-amphiphilic systems, including hydrophobic polymers that undergo complex self-assembly, which are difficult to be addressed by the classic theory of Langmuir monolayer for amphiphilic copolymers.\textsuperscript{56} There is no general model to explain the interfacial behavior of a hydrophobic polymer at the air–water interface. However, the presence of hydrophilic components (e.g., hydrophilic units on the hydrophobic polymer) is essential for the formation of the Langmuir monolayer as they facilitate the tethering of the whole copolymer chain on the water surface.

As for the PI-PS-P3HT monolayer in the present study, the hydrophilic component was attributed solely to P3HT, as both PS and PI are hydrophobic polymers. In order to yield a stable LB monolayer, the P3HT block has to spread on the water surface, tethering the whole molecule on the water surface (Fig. 6a, depicted in red), as it possesses the hydrophilic backbone which has affinity to the water surface.\textsuperscript{57} On the other hand, the PS and PI blocks formed aggregation to reduce the overall free energy due to unfavorable interaction between them and water (Fig. 6b, depicted in grey).\textsuperscript{52} According to this model, the P3HT block formed a continuous layer, generating the contrast in the TEM images. Due to the aggregation of highly hydrophobic PS and PI blocks, the P3HT block, regardless of its hydrophobicity, was forced to spread on the water surface to stabilize the monolayer. Under this scenario, the P3HT block was thus prohibited from π-stacking to form the crystallized state; this contrasted the previous work where P3HT chains were crystallized in LB films and the hydrophilic components (i.e., hydrophilic side chains) were strongly needed to stabilize the monolayer.\textsuperscript{4} Clearly, the addition of hydrophilic blocks (e.g., PS and PI) was proven to be an effective and robust route to a stable P3HT monolayer while retaining P3HT in its amorphous state.

The worm-like morphology formed at zero surface pressure (Fig. 3a and b and 4) is reminiscent of that formed by the dewetting process, which has been widely observed in the LB film preparation.\textsuperscript{57} When the PI-PS-P3HT triblock copolymer solution was placed on the water surface, it formed a thin continuous liquid film (300 nm thick; calculated by dividing the solution volume (5 μL) by the surface area of LB trough (160 cm²)), stabilized by the positive spreading coefficient of chloroform on the water.\textsuperscript{57} As chloroform evaporated, the liquid film became thinner (<100 nm), and the increased contribution from the unfavorable interfacial interactions between the PS chain (as well as the PI chain) and water eventually resulted in the dewetting of the thin film. The thin film dewetting may proceed via three stages.\textsuperscript{58} First, the film ruptures, thereby generating randomly distributed holes. Second, the holes then grow and the rims ahead of the holes eventually merge to form a cellular structure. Third, the resulting ribbons in the cellular pattern are unstable and decay into dot-like structures. It is clear that the observed surface morphology (i.e., self-assembly) of the PI-PS-P3HT triblock copolymer resembled that formed at the third stage of the dewetting process.\textsuperscript{57} As the holes grew during the evaporation of chloroform, the concentration of the PI-PS-P3HT triblock copolymer was greatly increased, leading to the aggregation of the triblock copolymer and thus the formation of dot-like structures. Moreover, a certain amount of the PI-PS-P3HT triblock copolymer was still left non-aggregated due to the fast dewetting process,\textsuperscript{52} forming the spreading phase between the dot-like domains (Fig. 4b and S2†). The stage two described above was not observed in the present study due to the fast evaporation of chloroform. Moreover, the concentration of the triblock copolymer may not be high enough to trigger its self-assembly at this stage.\textsuperscript{52}

With the increase in surface pressure from the gas region to the condensed state region, the spread PI-PS-P3HT polymer was
pushed to merge with the existing dotted domains under the lateral compression. Therefore, the size of dots increased, and the monolayer was more condensed (Fig. 3 and Table 1). In addition, the dotted domains became more compressed under this lateral force, causing little increase of domain height (Table 1). As the polymer already existed in a highly aggregated state after dewetting, the monolayer was less compressible; this was responsible for the absence of the liquid region in the isotherm (Fig. 2). Remarkably, due to gradual merging of the spreading phase with dot-like domains under surface pressure, the dotted domains became connected with one another, chaining into a pearl-necklace-like morphology. The anisotropic assembly of individual constituents with isotropic interaction (i.e., the chaining process) has been commonly observed, including molecules,59,60 surface micelles,60 colloidal particles,61 etc. It is generally attributed to the competition between short-range attractive forces and long-range repulsion between them.62 For example, recently the chaining of polystyrene-block-poly(ethylene oxide) stars at the air-water interface has been reported due to the attraction of PS aggregation and the repulsion between the spread PEO blocks.63 Similarly, the chaining of the PS-PI-P3HT domain also resulted from the competition between short-range attractive and long-range repulsive forces. The attractive force stemmed from hydrophobic PI and PS aggregates when they were close enough (Fig. 6, labeled in grey), while the spread P3HT chains generated the long range repulsive force due to their stronger affinity for water.64 Specifically, upon compression, the cores (i.e., the PS–PI aggregates) were brought close together and the P3HT on the periphery of the PS–PI cores was thus forced to shift to the side, forming places of high P3HT chain density (i.e., positions B and C, Fig. 6b). Eventually, the PS–PI cores moved closely enough to chain with one another, and the P3HT chains were pushed to either side of elongated PS–PI aggregates.65 Thus, further chaining was more likely to occur in the area of low P3HT density, and the most probable location for additional aggregation was the position A as illustrated in Fig. 6b.66

Conclusions

In summary, we synthesized a hydrophobic polyisoprene-b-poly(ethylene oxide) (PI-PS-P3HT) triblock copolymer and systematically explored its self-assembly behavior at the air–water interface. The PI-PS-P3HT triblock copolymer was readily self-assembled into an interesting surface morphology via dewetting. The P3HT block formed a continuous monolayer on the water surface, with the presence of PI and PS blocks as aggregates on its top. The increase in lateral surface pressure resulted in the chaining of aggregates, originating from the competition between the short-range attractive (hydrophobic PI and PS aggregates) and the long-range repulsive forces (spread P3HT monolayer). The incorporation of hydrophobic PI and PS blocks, instead of hydrophilic components as in copious past work, allowed for the preparation of a stable monolayer at the solid state in which the P3HT block was amorphous, and retained high PI as in the solution state. Such LB-enabled self-assembly of all hydrophobic conjugated polymer-based materials may open up new ways to fabricate optoelectronic thin-film devices, and provide a platform to interrogate the complex self-assembly and energy transfer processes of conjugated polymer-based systems confined in two dimensions.

Acknowledgements

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References

Supporting Information

Self-Assembly of Conjugated Triblock Copolymer
at the Air/Water Interface

Lei Zhao, Chaowei Feng, Xinchang Pang, Jae-han Jung, Mihaela C. Stefan,* Prakash Sista,
Rui Han, Ning Fang, and Zhiqun Lin*

Scheme S1

Scheme S1. Synthesis of polyisoprene-\textit{b}-polystyrene-\textit{b}-poly(3-hexylthiophene) (PI-PS-P3HT) triblock copolymer by coupling living polyisoprene-\textit{b}-polystyril lithium with allyl-terminated regioregular poly(3-hexylthiophene)
The composition of block copolymer was estimated from \(^1\text{H}\) NMR spectrum by integrating protons \(a\) vs protons \(c\) and \(e\) (Figure S1). The triblock copolymer contains 28 mol% regioregular poly(3-hexylthiophene), 38.2 mol% polyisoprene, and 33.2 mol% polystyrene (SEC: \(M_n=7170\) g/mol; PDI = 1.50).

**Figure S1**

![NMR Spectrum](image)

**Figure S1.** \(^1\text{H}\) NMR spectrum of PI-PS-P3HT triblock copolymer.
Figure S2

Figure S2. AFM height image of LB monolayer of PI-PS-P3HT triblock copolymer obtained at the gas region. Scan size = 1.5 μm × 1.5 μm and z scale = 30 nm.
**Figure S3.** HRTEM image of the monolayer of PI-PS-P3HT triblock copolymer deposited at the gas region.
Figure S4

**Figure S4.** TEM image of the monolayer of PI-PS-P3HT triblock copolymer deposited at the condensed gas region.
Figure S5

Figure S5. GISAXS pattern of the monolayer of PI-PS-P3HT deposited at the condensed region.