The Synthesis and Purification of Amphiphilic Block Copolymers for Photovoltaic Applications

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Block copolymer/Organic Photovoltaics/Fully-conjugated/Amphiphilic

ABSTRACT: The industrial adoption of organic photovoltaic devices relies on the development of high performance materials which are solution-processable and which yield stable, reproducible morphologies in thin-film. The current state-of-the-art materials employ partially phase-separated blends of a donor and acceptor materials to provide the necessary domain structure, a strategy which is difficult to control and optimize. In this work, donor and acceptor are covalently linked into a single block-copolymer which has the potential to self-assemble into nanostructured domains. In order to enhance phase separation and solubility, hydrophilic side-chains were incorporated into the acceptor materials to generate an amphiphilic system. The chemical disparity between the blocks allowed the design of a purification technique able to isolate the block copolymer from the homopolymer contaminants, a significant improvement over previously reported syntheses which employ nonspecific purification techniques incapable of distinguishing between polymer species.

INTRODUCTION

Organic photovoltaic devices (OPVs) could provide a source of renewable energy that is inexpensive and printable on flexible substrates via roll-to-roll processes. This technology would supplement the bulky, rigid modules of traditional silicon PV with a cheap, highly-portable alternative. The field of OPV research has developed significantly over the past 15 years, with power conversion efficiencies increasing from 2.5% in 2001\textsuperscript{1} to 11.5% in 2016.\textsuperscript{2} However, the transfer from lab to industry has yet to be fully realized. For this reason, new approaches to material design and optimization must be investigated with a focus on key industrial factors like increased solvent processability, stability, and reproducibility in addition to efficiency.\textsuperscript{3-4}

In OPV, absorption of light does not generate free charges directly. The excited state generated by the light is a coulombically bound charge pair, termed an exciton. Additional driving force is required to separate this exciton...
into free charges. This is accomplished through combining materials with differing electron affinities together in a thin film, which leads to preferential migration of the electron into the acceptor material while the hole is retained in the donor material. Because charge separation occurs at the interface between donor and acceptor and because the distance that an exciton can diffuse during its lifetime is around 10 nm, control of donor/acceptor domain sizes is crucial for solar cell efficiency. Ideal domain sizes are between 10 and 20 nm, small enough that all excitons can reach a boundary but large enough to minimize recombination between the free charges.

The most common method of obtaining these domains is through blending the donor and acceptor materials and co-depositing them onto a chosen electrode. Subsequent processing steps are often used to achieve desirable phase separation. The resultant morphologies are difficult to control and maintain, and small variations in technique and material can lead to suboptimal domain sizes. For example, it’s been shown that simply operating solar cells composed of blended materials generates enough heat to induce further phase separation and detrimentally increase domain sizes in semi-crystalline materials. This hinders application of these materials in industry where reproducibility and stability are crucial. Additionally, a key advantage of OPV is the solution processability of these materials. However, in these blended materials the choice of solvent is restricted to those that can accommodate both components to some threshold level. To-date this most often dictates the use of chlorinated and toxic solvents which are disadvantageous for industrial applications.

One alternative to this blending approach is the covalent linkage of the donor and acceptor material into a single entity. This imposes some restrictions on the types of donor and acceptor employed, but also allows the researcher a number of liberties in the designing and processing of the materials. Optimally, the donor-acceptor units will self-assemble into domains on the order of the size of the individual components. Therefore, to achieve 10 nm domains the materials must necessarily be polymeric and in order to maximize chromophore density the polymers should be fully conjugated.

![Figure 1. Block copolymer self-assembly into lamellar active layer](image)

Within these constraints, the researcher is freed from balancing the solubilities of the two-component system. Rather, the solubility of the donor-acceptor pair can be tuned through modification of a single component, i.e. in-
Corporating hydrophilic side-chains into the donor or acceptor polymer will increase the solubility of the pair. Additionally, the covalent linkage of donor and acceptor physically prohibits the separation of the two materials into overly large domains. Rather than try to attain a metastable, partial phase separation as in blends, in BCP systems the optimal morphology is obtained when the materials attain complete phase separation into well-defined domains. Although BCPs with flexible backbones can adopt a variety of morphologies depending on composition, fully-conjugated BCPs are more rigid and so tend to adopt lamellar morphologies as shown in Figure 1. If properly oriented these lamella could provide excellent charge percolation pathways to the respective electrodes, ideal for OPV function.

**Figure 2. Structure of previously reported block copolymers (a) and their amphiphilic analogs (b)**

While block copolymers provide a well-controlled route to a theoretically ideal morphology, obtaining clean phase separation in fully-conjugated materials has proven to be a challenge. The highest-performing example of this strategy to-date was produced by the Verduzco group and achieved a power conversion efficiency (PCE) of 3.1% employing poly(3-hexylthiophene) (P3HT) as the donor material and poly(2,7-(9’,9’-dioctyl-fluorene)-alt-5,5-(4’,7’-di-2-thienyl-2’,1’,3’-benzothiadiazole) (PFTBT) as the acceptor material in the BCP P3HT-b-PFTBT (Figure 2a, R=H). The authors observed phase separation into 9 nm domains in this system, which may have contributed to the high performance. However in a subsequent investigation of 30 closely related P3HT-b-PFTBT block copolymers, little or no phase separation was obtained regardless of processing conditions. This supports previous work done on P3HT-b-PFT6BT (Figure 2a) in which no phase separation was obtained. The researchers in both projects attributed the lack of phase separation to the incorporation of solubilizing side-chains on the
PFTBT acceptor materials, and hypothesized that additional alkyl chains led to an increased miscibility of the donor and acceptor. The poor morphologies led to a drastic decrease in OPV performance.

In this work we report the synthesis of two new polymers based on the P3HT-b-PFTBT scaffold. The materials differ from previous work in that hydrophilic tetraethylene glycol side-chains were incorporated into the PFTBT material to generate two novel block copolymers. Tetraethylene glycol is highly hydrophilic changing the solubility profile of the material, driving phase separation as well as increasing the dielectric constant of the material to enhance exciton dissociation. This rational design then is expected to produce materials with enhanced solubility, microphase separation, morphological control, and photovoltaic performance over existing organic photovoltaic active layers.

**EXPERIMENTAL PROCEDURES**

Unless otherwise noted, all materials were reagent grade and used as received without further purification. Anhydrous tetrahydrofuran, toluene, dichloromethane, and ether were provided by a Pure Processing Technology glass contour solvent purification system. $^1$H and $^{13}$C NMR spectroscopies were performed on a Varian Inova-400 (400 MHz). GPC was performed on either a Viscotek GPC Max VE2001 solvent/sample module equipped with a Viscotek VE3580 refractive index detector or a Gilson 322 equipped with a Gilson GX-241 Liquid Handler and a Gilson 159 multiwavelength UV-Vis detector. With the Viscotek, polymers were passed through three 30 cm 5 μm PL gel mixed C columns and one 30 cm 3 μm PL gel mixed E column in toluene at a flow rate of 0.6 mL/min. In the Gilson system polymers were passed through two 30 cm 5 μm PL gel mixed C columns in chloroform at a flow rate of 1 ml/min. Molecular weights were calculated relative to narrow polystyrene reference standards. A Mettler Toledo DSC 2 was used to investigate the thermal properties of the materials in nitrogen atmosphere at heating/cooling rates of 10 or 20 K/min. Absorption measurements were carried out on a JASCO V-670 spectrophotometer, and films were prepared by spincoating from 1 mg/mL solutions in chloroform. Electrochemical cyclic voltammetry (CV) was conducted on solartron SI1287 electrochemical interface. Platinum wire was the counter electrode. Glassy carbon and Ag/AgCl electrode were used as the working electrode and the reference electrode, respectively, while 0.1 M tetrabutylammonium hexafluorophosphate in CH$_3$CN was the electrolyte. Films were prepared by drop-casting from chloroform onto the glassy carbon electrode. The scan rate was 50 mV/S and the concentration of analyte was ca. 1 mM. CV curves were calibrated using ferrocence as the standard, whose oxidation potential is set at −4.8 eV with respect to zero vacuum level. The HOMO energy levels were obtained from the equation $\text{HOMO} = -(E_{\text{ox} \text{onset}} - E_{\text{ferrocene} \text{onset}} + 4.8) $ eV. The LUMO levels were obtained from the equation $\text{LUMO} = -(E_{\text{red} \text{onset}} - E_{\text{ferrocene} \text{onset}} + 4.8) $ eV
The synthetic procedure is shown in Scheme 1. All monomers were prepared according to literature procedures, the details of which are presented in the supplementary information. The block copolymers and isolated acceptor polymers were prepared via Suzuki polycondensation in the presence and absence, respectively, of a poly(3-hexylthiophene) macroinitiator as described below.

Scheme 1. Synthesis of amphiphilic block copolymers P3HT-b-PF<sub>TEG</sub>TBT and P3HT-b-PF<sub>TEG</sub>T6BT via Suzuki polycondensation from a P3HT macroinitiator

**Synthesis of PF<sub>TEG</sub>T(R)BT Acceptor Polymer**

In a general procedure, Compound 2 (0.1 mmol), Compound 3 (0.09 mmol), toluene (5 mL), tetraethylammonium hydroxide (20% solution, 1 mL), and Aliquat 336 were combined in a schlenk tube and bubbled with nitrogen for 15 minutes. The catalyst Pd(PPh<sub>3</sub>)<sub>4</sub> (11.5 mg, 0.01 mmol) was added to the mixture and bubbled with nitrogen for an additional 5 minutes. The reaction vessel was sealed and heated to 90°C with stirring overnight. The polymer was endcapped by adding phenylboronic acid in toluene (20.4 mg, 0.1 mmol) via syringe and stirring for an additional 4 hours before the reaction was allowed to come to room temperature. Chloroform and water were added, the organic phase was collected and precipitated in methanol to yield the product. The polymer was collected and purified using soxhlet extraction in methanol, petroleum spirits, and finally chloroform. Synthetic yields and molecular weights are given in Table 1 while <sup>1</sup>H NMR characterization is given in the supporting information.

**Synthesis of P3HT-b-PF<sub>TEG</sub>T(R)BT Block Copolymer**

Compound 1 (500 mg, 0.026 mmol, 19.19 kg/mol), Compound 2 (0.52 mmol), and Compound 3 (0.52 mmol), toluene (25 mL), tetraethylammonium hydroxide (20% solution, 5 mL), and Aliquat 336 were combined in a schlenk tube and bubbled with nitrogen for 15 minutes. The catalyst Pd(PPh<sub>3</sub>)<sub>4</sub> (57.75 mg, 0.05 mmol) was added to the mixture and bubbled with nitrogen for an additional 5 minutes. The reaction vessel was sealed and heated to 90°C with stirring for 24 hrs. The polymer was endcapped by adding phenylboronic acid (53 mg, 0.1 mmol) in 2 mL of degassed toluene via syringe and stirring overnight at 90°C followed by 30 μL of bromobenzene and stirring for an additional 4 hours. The reaction was allowed to come to room temperature. Chloroform and water were added and the organic phase was collected and precipitated in methanol to yield the product mixture. The polymer was collected, dissolved in chloroform, and adsorbed onto 45 mL of silica gel. The silica was then
washed with chloroform to remove unreacted P3HT, dichloromethane/methanol (9:1) to remove PF_{TEG}T(R)BT impurities, and finally chloroform/methanol (9:1) to afford the block copolymer. Yields and molecular weights are summarized in Table 1 and 'H NMR analysis is shown in the supplementary information.

RESULTS AND DISCUSSION

The synthetic strategy employed to generate the fully-conjugated amphiphilic block copolymers P3HT-\textit{b-PF_{TEG}TBT} and P3HT-\textit{b-PF_{TEG}T6BT} followed a procedure first developed by Ku et al in 2012.\textsuperscript{12} The P3HT block was prepared through Grignard metathesis polymerization (GRIM) which is known to produce polymers with well-defined molecular weight and a single bromine terminus that can be used in further condensations.\textsuperscript{13} Addition of the obtained P3HT-Br macro-reagent to a Suzuki polycondensation reaction between fluorene and dithienobenzothiadiazole monomers X and X resulted in chain extension to form the desired block copolymer (Scheme 1). This synthetic approach necessarily generates a mixture of products, including unreacted P3HT, PF_{TEG}T(R)BT homopolymer, as well as diblock and triblock copolymers. Typical purification methods for these syntheses have employed soxhlet extraction or preparative GPC for purification, however both of these techniques are fairly non-specific in the species isolated. For example, P3HT-\textit{b-PFTBT} was purified using a series of soxhlet extractions in acetone, hexanes, and finally chloroform to afford the product. However, none of the polymeric species are soluble in acetone and hexanes while all are soluble in chloroform, and so this technique is incapable of isolating the block copolymer specifically. Thus far analysis of fully-conjugated block copolymers has typically involved polymeric mixtures, with a recent report finding that out of a synthesis of 30 BCPs the percentage of diblock copolymer in the reaction mixture ranged from 33-64\%.\textsuperscript{9} In the amphiphilic block copolymer system under investigation, however, the differing solubilities of the homopolymers can be exploited to facilitate purification.

For this work, the purification began with the P3HT macro-initiator. The PF_{TEG}TXBT acceptor materials are readily soluble in dichloromethane, and so ideally the P3HT would be insoluble in dichloromethane to allow differentiation between the species. This was accomplished through successive soxhlet extractions of the P3HT material in acetone, petroleum ether, and dichloromethane to remove all lower molecular weight material. A final chloroform rinse recovered the desired P3HT macro-initiator. Addition of this P3HT-Br to the Suzuki polycondensation reaction described in Scheme 1 generated the desired block copolymer as well as the other expected polymeric contaminants. The crude reaction mixture was then adsorbed on an excess of silica gel. The tetraethylene glycol moieties on the PF_{TEG}TBT polymers bind more tightly to the silica than P3HT, thus simply washing the silica with chloroform removes the unreacted macro-reagent. Because P3HT-\textit{b-PF_{TEG}TBT-\textit{b-P3HT} triblock copolymers are dominated by the solubility of P3HT, these too are removed in the chloroform wash. The addition of methanol to
the eluent disrupts the strong association of the tetraethylene glycol moieties, and washing the silica gel with 10% methanol in dichloromethane removes the PF$_{\text{TEG}}$TBT homopolymer. Because the P3HT macro-initiator employed in the block copolymer is not soluble in dichloromethane by design, only a small amount of block copolymer is lost in this wash. Finally, washing with 10% methanol in chloroform affords the block copolymer with a minimum amount of polymeric contaminants.

Analysis of the washes using gel permeation chromatography in conjunction with a multi-wavelength detector reveals the efficacy of the purification technique. In solution, PFTBT-based materials have characteristic absorption maxima in the 360 nm range while P3HT absorbs most strongly at 450 nm (Figure 4). By analyzing GPC results at these two wavelengths the composition of the fractions can be inferred. In Figure 3, it can clearly be seen that the chloroform washes are predominantly unreacted P3HT macroinitiator as well as triblock copolymer. The dichloromethane/methanol washes absorb more strongly at 360 nm indicating a higher concentration of PFTBT homopolymers. The chloroform/methanol wash, in contrast, has equal absorption at 450 nm and 360 nm and is clearly shifted to molecular weights roughly double that of the P3HT macroinitiator.

The molecular weights of the resultant block copolymers and the corresponding homopolymers are summarized in Table 1. Gel permeation chromatography (GPC) P3HT-b-PF$_{\text{TEG}}$TBT and P3HT-b-PF$_{\text{TEG}}$T6BT of the polymers indicates that they are 42% and 47% P3HT by weight respectively. Molecular weight was also estimated through the integration of NMR signals corresponding to the donor and acceptor and are given in parenthesis in
Table 1. These values are in reasonable agreement with GPC data, although they suggest a lower P3HT fraction. This could be an indication of persistent high molecular weight PF\textsubscript{TEG}TXBT homopolymer contamination, although the NMR peak broadening which is characteristic of polymeric materials makes this quantification less reliable.

### Table 1. Molecular weights and yield of polymer syntheses where $M_n$ and $M_w$ are molecular weight and number average molecular weight, respectively, as determined by GPC. In parentheses is given the number average molecular weight as determined by NMR. The percent of P3HT is calculated from NMR backbone signals.

<table>
<thead>
<tr>
<th></th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w$ (kg/mol)</th>
<th>PDI</th>
<th>P3HT (%)</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>18.0</td>
<td>17.8</td>
<td>1.1</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>P3HT-b-PF\textsubscript{TEG}TBT</td>
<td>74.5</td>
<td>42.1 (61.2)</td>
<td>1.9</td>
<td>43</td>
<td>17</td>
</tr>
<tr>
<td>PF\textsubscript{TEG}TBT</td>
<td>32.3</td>
<td>15.1</td>
<td>2.1</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>P3HT</td>
<td>18.0</td>
<td>17.6</td>
<td>1.1</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>P3HT-b-PF\textsubscript{TEG}T6BT</td>
<td>70.9</td>
<td>37.3 (48)</td>
<td>19</td>
<td>37</td>
<td>29</td>
</tr>
<tr>
<td>PF\textsubscript{TEG}T6BT</td>
<td>85.1</td>
<td>30.5</td>
<td>2.1</td>
<td>84</td>
<td></td>
</tr>
</tbody>
</table>

The as-spun film UV/Vis absorption spectra of the two amphiphilic polymers and their component homopolymers are shown in Figure 5. The addition of solubilizing hexyl side chains in the PF\textsubscript{TEG}T6BT material leads to a red shift in absorption, which can be understood as a result of increased steric bulk disrupting the planarity of the conjugated backbone and decreasing the effective conjugation length.\textsuperscript{14} An increase in absorption at 450 nm is seen in both block copolymers indicating a contribution from the P3HT block. The P3HT absorption is more pronounced in the P3HT-b-PF\textsubscript{TEG}T6BT materials, a function of the decreased absorption coefficient of the acceptor material resulting from the additional side-chains.\textsuperscript{15} The onsets of absorption and the maximum absorption are

![Figure 5. UV/Vis absorption spectra of block copolymers an their constituent homopolymers in film, spun from 1 wt% in chloroform.](chart)
Table 2. Energy gaps as determined by absorption onset and CV measurements

<table>
<thead>
<tr>
<th></th>
<th>λ_{onset} (nm)</th>
<th>λ_{peak} (nm)</th>
<th>E_g^{opt} (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>E_g^{GC} (eV)</th>
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</thead>
<tbody>
<tr>
<td>P3HT-b-PFT_{EG}TBT</td>
<td>670</td>
<td>402/563</td>
<td>1.85</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PFT_{EG}TBT</td>
<td>670</td>
<td>403/583</td>
<td>1.85</td>
<td>-5.3</td>
<td>-3.5</td>
<td>1.8</td>
</tr>
<tr>
<td>P3HT-b-PFT_{EG}T6BT</td>
<td>642</td>
<td>379/526</td>
<td>1.93</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PFT_{EG}T6BT</td>
<td>618</td>
<td>380/531</td>
<td>2.01</td>
<td>-5.4</td>
<td>-3.4</td>
<td>2.0</td>
</tr>
</tbody>
</table>

given in Table 2 and indicate optical energy gaps of 1.8 eV and 1.9 eV for P3HT-b-PFT_{EG}TBT and P3HT-b-PFT_{EG}T6BT respectively, values which are consistent with those determined from cyclic voltammetry of films (Supplementary Information). Films of regioregular P3HT are semicrystalline and show characteristic vibronic structure at 530, 560, and 610 nm.\cite{16} The presence of this vibronic structure in block copolymers incorporating P3HT is an indication that the P3HT is able to form crystallites, and in turn is also an indication of phase separation.\cite{10} In as-spun films of both block copolymers the vibronic structure is suppressed, implying a lack of P3HT crystallinity and a potential lack of microphase separation.

Differential scanning calorimetry was employed to determine melting and crystallization temperatures and enthalpies of the block copolymers. Neither of the isolated PFT_{EG}TXBT homopolymers showed any melting or crystallization peaks indicating their amorphous nature, which was expected from investigations on similar materials.\cite{10,17} As shown in Figure 6, small melting and crystallization peaks corresponding to P3HT were seen for both block copolymers. The enthalpy of melting for the isolated macro-initiator was also measured, and from the composition of the polymers (i.e. 43 and 37% P3HT) and the measured enthalpy of melting the degree to which the P3HT in these block copolymers is able to crystallize can be calculated. These results are summarized in Table 2, and clearly show that P3HT crystallization is inhibited in both block copolymers under examination. Interestingly, P3HT-b-PFT_{EG}TBT showed an additional melting point at around 170°C which may be attributed to a different P3HT polymorph present in the block copolymer film.
Figure 6. DSC traces of the isolated P3HT macroinitiator and the two block copolymers

Table 3. Melting ($T_m$) and crystallization ($T_c$) temperatures of the block copolymers as well as the enthalpy of melting ($\Delta H_m$) and degree of P3HT crystallinity ($D_{P3HT}$)

<table>
<thead>
<tr>
<th></th>
<th>$T_m$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$D_{P3HT}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT Macroinitiator</td>
<td>238</td>
<td>205</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>P3HT-b-PF$_{TEG}$TBT</td>
<td>220</td>
<td>181</td>
<td>1.6</td>
<td>15.5</td>
</tr>
<tr>
<td>P3HT Macroinitiator</td>
<td>234</td>
<td>202</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>P3HT-b-PF$_{TEG}$T6BT</td>
<td>209</td>
<td>163</td>
<td>2.4</td>
<td>29.5</td>
</tr>
</tbody>
</table>

Conclusion

In this work two novel block copolymers with potential application in organic photovoltaics were synthesized and purified. These amphiphilic block copolymers are to our knowledge the first of their kind to employ this strategy towards enhancing microphase separation and solubility of fully-conjugated donor-acceptor block copolymers. The unique design allowed facile purification of these materials through the exploitation of the chemical disparity between the blocks, easily producing block copolymer species with a minimum of homopolymer contaminants. Although initial evaluations show an inhibition of P3HT crystallinity implying limited phase separation, through careful selection of solvent deposition conditions it is expected that microphase separation can be greatly enhanced in film due to the amphiphilic nature of the polymers. The synthetic and purification strategy presented could inform future research into block copolymer materials, contributing to their more widespread implementation
in OPV research. The morphological and photovoltaic properties of these new materials are currently under investigation.
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