COMMUNICATION
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Synthesis and crystallinity of all-conjugated poly(3-hexylthiophene) block copolymers
A simplified approach towards the synthesis of high molecular weight (M_w > 50 kg mol⁻¹) poly(3-hexylthiophene) (P3HT)-based all-conjugated block copolymers is demonstrated and applied to prepare a series of all-conjugated block copolymers. Grazing-incidence X-ray scattering measurements show that P3HT crystallization is suppressed in all-conjugated block copolymers with low (<25 wt%) P3HT content.

Block copolymers comprised of two-conjugated polymer blocks, known as all-conjugated block copolymers,⁶ can potentially improve the performance of organic electronic devices, including bulk heterojunction organic photovoltaics (OPVs) and white-light emitting diodes.⁷ All-conjugated block copolymers may provide broad absorbance, efficient charge separation, white-light emission, and both hole and electron transport. Additionally, these materials are expected to self-assemble into regular nanostructures due to a reduced entropy of mixing and a balance between nanoscale phase separation, chain stretching, and interfacial energies, and if properly designed may lead to optimal nanostructures for OPV devices.

However, studies on all-conjugated block copolymers are limited, due in large part to synthetic challenges.⁴-⁵ Recent work has demonstrated the preparation of block copolypthiophenes using Grignard metathesis polymerization (GRIM)⁸,⁹,¹⁰ resulting in block copolymers with two p-type blocks and similar optoelectronic properties. Most approaches for making donor-acceptor all-conjugated block copolymers, which incorporate both n- and p-type polymer blocks, take advantage of distinct polymerization reactions for each polymer block, including GRIM, Suzuki–Miyaura, and Stille polymerization reactions.⁶,¹⁰,¹²,¹⁷ A drawback of these methods is that they typically result in relatively low molecular weight block copolymers with significant amounts of homopolymer impurities that can only be removed using tedious column purification techniques.⁴,¹⁵,¹⁶,¹⁹

In this work, we report an improved route to the synthesis of all-conjugated block copolymers via GRIM and Suzuki–Miyaura polycondensation. We show that the use of a LiCl additive during GRIM allows for the preparation of high molecular weight block copolymers with little or no homopolymer impurities. This improved synthetic method is applied to the preparation of three different P3HT block copolymers. The molecular weights, polydispersities, and block ratios are measured using a combination of size-exclusion chromatography with refractive index (SEC-RI) and UV-VIS absorbance (SEC-UVVIS) detection and nuclear magnetic resonance spectroscopy (NMR) (provided in ESI†). The morphology and thermal properties of the materials are characterized using X-ray diffraction (XRD), grazing-incidence wide-angle X-ray scattering (GIWAXS), and differential scanning calorimetry (DSC). In contrast to previous work with P3HT-based block copolymers, we observe suppression of P3HT crystallinity in high molecular weight all-conjugated block copolymers, but at more balanced block ratios crystallization of both blocks is achieved. This work provides an improved synthetic method for preparing high-molecular weight all-conjugated block copolymers and the first examples of all-conjugated block copolymers with crystallinity determined by polymer block ratios.

Our synthetic strategy involves a combination of GRIM and Suzuki–Miyaura polymerizations. GRIM is first carried out to synthesize a Br end-functionalized P3HT (P3HT-Br) macroreagent, and P3HT-Br is subsequently utilized in a Suzuki–Miyaura polymerization reaction to make all-conjugated P3HT block copolymers (Scheme 1). A high degree of end functionalization of the P3HT-Br macroreagent is required to avoid residual P3HT homopolymer impurities, and this was accomplished using LiCl as an additive for the preparation of bromo-chloromagnesio-hexylthiophene monomer. LiCl has been shown to be an effective additive for accelerating Grignard formation and producing P3HT with a high degree of end-group functionality.¹⁸-²⁰ P3HT-Br was prepared using standard methods by the addition of Ni(dppp)Cl₂ catalyst to the monomer solution to initiate GRIM.³¹ Three different sizes of P3HT were synthesized using different lithium chloride additive concentrations to provide a range of molecular weights.
synthesized with relatively low PDI and regioregularity higher than 93%. Next, P3HT-Br was reacted in a Suzuki–Miyaura polyc
condensation reaction to prepare three different types block
copolymers, each with a P3HT block and a second conjugated
polymer block: poly(9,9'-dioctyl fluorene) (PF), poly(9,9'-
dioctyl fluorene-alt-benzothiadiazole) (PFBT), and poly(2,7-(9,9'-
dioctyl-fluorene-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)
(PFTBT). PF, PFBT, and PFTBT have been previously studied for
use in bulk-heterojunction OPVs and OLEDs,\textsuperscript{32-34} and PFTBT may
be particularly promising for use in block copolymer OPVs because it exhibits a broad absorbance and a low-lying HOMO
level.\textsuperscript{35,36} A high and low molecular weight P3HT-Br macror
agent was used for each type of block copolymer, resulting in a
total of six different block copolymers, as shown in Table 1. The
formation of triblock copolymers is unlikely due to a low

![](image)

**Scheme 1** Preparation of all-conjugated P3HT block copolymers via Grignard metathesis polymerization with LiCl additive followed by Suzuki–Miyaura polyc
condensation. Conditions for Suzuki–Miyaura: Pd(PPh\textsubscript{3})\textsubscript{4}, toluene, water, 90 °C.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>P3HT\textsuperscript{a} M\textsubscript{n} (PDI)</th>
<th>BCP\textsuperscript{b} M\textsubscript{n} (PDI)</th>
<th>DP ratios\textsuperscript{c} (P3HT wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT36-b-PF100</td>
<td>6.1 (1.16)</td>
<td>48.4 (1.86)</td>
<td>36 : 100 (13%)</td>
</tr>
<tr>
<td>P3HT81-b-PF105</td>
<td>13.5 (1.32)</td>
<td>60.6 (1.87)</td>
<td>81 : 105 (25%)</td>
</tr>
<tr>
<td>P3HT51-b-PFBT66</td>
<td>8.5 (1.19)</td>
<td>168 (3.61)</td>
<td>51 : 66 (20%)</td>
</tr>
<tr>
<td>P3HT81-b-PFBT90</td>
<td>13.5 (1.32)</td>
<td>81.5 (2.24)</td>
<td>81 : 90 (22%)</td>
</tr>
<tr>
<td>P3HT51-b-PFTBT17</td>
<td>8.5 (1.19)</td>
<td>19.7 (1.49)</td>
<td>51 : 17 (42%)</td>
</tr>
<tr>
<td>P3HT81-b-PFTBT12</td>
<td>13.5 (1.32)</td>
<td>N/A\textsuperscript{d}</td>
<td>81 : 12 (62%)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} M\textsubscript{n} (kg mol\textsuperscript{-1}) and PDI for P3HT and block copolymers determined by comparison to a set of monodisperse polystyrene standards. Head-to
tail regioregularity of P3HT is greater than 93% for all samples as determined from \textsuperscript{1}H NMR. \textsuperscript{b} DP ratios and P3HT content were determined by \textsuperscript{1}H NMR via comparison of the integrated intensity of
P3HT aromatic peak (6.9 ppm) and fluorene alkyl peaks (2.2 ppm). \textsuperscript{c} P3HT81-b-PFTBT12 contains primarily homopolymer impurities, and therefore an estimate for block copolymer molecular weight is not provided.

content of P3HT-Br macr

**Fig. 1** SEC-RI analysis of block copolymers and corresponding P3HT-Br macror
agents. Intensities are normalized for clarity.
copolymer. However, the use of a lower molecular weight P3HT macroreagent in the polycondensation reaction of PFTBT resulted in product with majority block copolymer in P3HT51-b-PFTBT17.

Analysis of the final product using SEC with UV-VIS absorbance detection (SEC-UVVIS) provides additional information on homopolymer impurities (see ESI, Fig. S4 and S5). By using two different wavelengths for analysis, the molecular weight distributions for each polymer block can be obtained (see ESI† for details of this analysis). For all BCP samples except for P3HT81-b-PFTBT12, SEC-UVVIS analysis indicates clean block copolymer product – a clear shift in the SEC-UVVIS traces corresponding to P3HT is observed as well a good match between SEC-UVVIS traces at both wavelengths. The purity of the final product is better for block copolymers with shorter P3HT blocks; both P3HT36-b-PF100 and P3HT51-b-PFTBT66 exhibit excellent overlap between SEC-UVVIS traces corresponding to both polymer blocks, while some high molecular weight P3HT homopolymer may be present in P3HT81-b-PF105 and P3HT81-b-PFTBT90. In the case of P3HT51-b-PFTBT17, some high molecular weight PFTBT homopolymer is present, but the product is primarily block copolymer. Deconvolution of the SEC-RI trace gives an estimate of approximately 15% for PFTBT homopolymer impurities in the final P3HT51-b-PFTBT17 product.

Altogether, SEC-RI and SEC-UVVIS indicate the formation of clean all-conjugated block copolymer products. The synthetic method enables the preparation of all-conjugated block copolymers with high molecular weights ($M_w$ up to 168 kg mol$^{-1}$) and with varying molecular weight of the P3HT block. Importantly, the synthetic method is straightforward to implement, scalable, and provides the final product in good overall yield.

Prior studies on P3HT block copolymers have found that P3HT crystallization can dominate the morphology, suppressing microphase segregation and crystallization of the second block. Here, we are able to test whether this holds true in large ($M_w > 50$ kg mol$^{-1}$) all-conjugated block copolymers with a semi-crystalline polymer block attached to a minority P3HT block. For all block copolymers, DSC indicates that the crystallization of P3HT is suppressed or shifted to lower temperatures, and as expected the effect is more pronounced in block copolymers with lower P3HT block ratios (Fig. S6†). For block copolymers with larger P3HT blocks, P3HT81-b-PF105 and P3HT81-b-PFTBT90, a crystallization transition is observed at approximately 214 °C, a roughly 10 °C decrease in the crystallization temperature relative to the corresponding P3HT-Br macroreagent. P3HT crystallization is not observed for P3HT51-b-PFTBT66 while the decrease in the crystallization temperature is approximately 15 and 20 °C for P3HT36-b-PF100 and P3HT51-b-PFTBT17, respectively. P3HT81-b-PFTBT12 exhibits a transition near 224 °C matching that of the corresponding P3HT-Br homopolymer, as expected due to the presence of P3HT homopolymer impurities. In the case of P3HT36-b-PF100, as discussed below, GIWAXS analysis indicates that the observed transition at 153 °C corresponds primarily to crystallization of the PF block. Only P3HT81-b-PF105 exhibits two transitions; one at 214 °C corresponding to P3HT crystallization and a second near 150 °C, corresponding to PF crystallization.

XRD (Fig. S7†) and GIWAXS (Fig. 2 and Fig. S8†) analysis confirms the low content of P3HT crystallinity in the block copolymer samples. P3HT-b-PFBT and P3HT-b-PFTBT block copolymers show only broad scattering peaks, while P3HT-b-PF block copolymers exhibit crystalline peaks corresponding primarily to PF crystallites. Highly oriented crystallites are observed in P3HT36-b-PF100 films with features characteristic of the PF phase, confirming that the DSC transition near 150 °C reflects PF crystallization. In the case of P3HT81-b-PF105, both P3HT and PF crystallinities are observed, but P3HT crystallite peaks are less pronounced. Quantitative analysis of the GIWAXS pattern for P3HT81-b-PF105 shows scattering peaks at $q_z = 0.38, 0.75$, and $1.12\ \text{Å}^{-1}$ corresponding to the (100), (200), and (300) reflections for P3HT crystallites and a scattering peak at $q_z = 0.50\ \text{Å}^{-1}$ corresponding to PF crystallites (see ESI, Fig. S8b†). This is consistent with DSC measurements that show both a PF and a P3HT crystallization transition for P3HT81-b-PF105, the latter which is shifted to lower temperatures relative to the corresponding P3HT-Br macroreagent. Altogether, DSC, XRD, and GIWAXS results show that P3HT crystallization is reduced or suppressed in high molecular weight all-conjugated P3HT block copolymers, and at more balanced block ratios both blocks can crystallize.

In conclusion, we demonstrate a straightforward, versatile, and scalable synthetic route to prepare block copolymers comprised of a poly(alkyl thiophene) block and second polymer block made via Suzuki–Miyaura polycondensation, and block copolymers with $M_w > 50$ kg mol$^{-1}$ are achieved. Analysis of different all-conjugated block copolymers indicates that P3HT crystallinity is reduced or completely suppressed in all-conjugated P3HT block copolymers. These results indicate that proper balance of block ratios is important for the development of all-conjugated block copolymers for use in OPVs.
Acknowledgements

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Notes and references