

Synthesis and crystallinity of all-conjugated poly(3-hexylthiophene) block copolymerst

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Yen-Hao Lin, Kendall A. Smith, Chloe N. Kempf and Rafael Verduzco*

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A simplified approach towards the synthesis of high molecular weight ($M_w > 50 \text{ kg mol}^{-1}$) 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,¹ can potentially improve the performance of organic electronic devices, including bulk heterojunction organic photovoltaics (OPVs) and white-light emitting diodes.^{2,3} 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.^{1,4-15} Recent work has demonstrated the preparation of block copolythiophenes using Grignard metathesis polymerization (GRIM)^{9,16-26} 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.^{5,6,15,27} A drawback of these methods is that they typically result in relatively low molecular weight block copolymers with significant amounts of

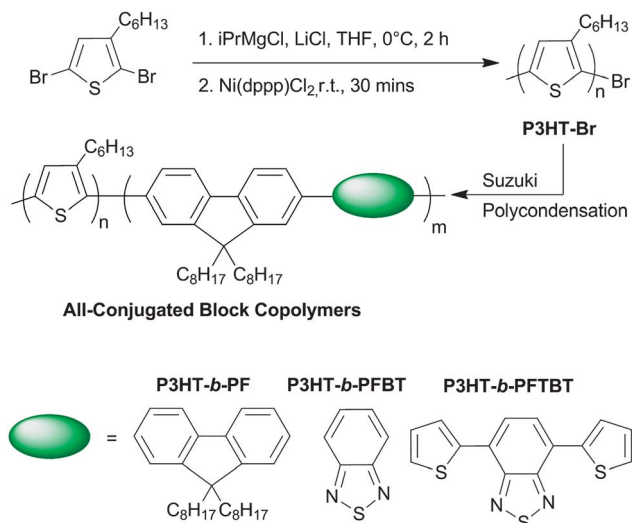
homopolymer impurities that can only be removed using tedious column purification techniques.^{6,15,26}

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-chloromagnesium-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.²⁸⁻³⁰ 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

Department of Chemical and Biomolecular Engineering, MS-362, Rice University, 6100 Main Street, Houston, Texas 77005, USA. E-mail: rafaelv@rice.edu

† Electronic supplementary information (ESI) available: Experimental methods, ¹H NMR spectra of all block polymers, UV-VIS spectra, SEC-UVVIS data, DSC, XRD, and temperature-dependent GIWAXS measurements. See DOI: 10.1039/c2py20830j



Scheme 1 Preparation of all-conjugated P3HT block copolymers *via* Grignard metathesis polymerization with LiCl additive followed by Suzuki–Miyaura polycondensation. Conditions for Suzuki–Miyaura: Pd(PPh₃)₄, toluene, water, 90 °C. An equimolar ratio of 9',9'-dioctylfluorene-2',7'-diboronic acid ester and corresponding dibromo monomer is used, as described in the ESI.†

synthesized with relatively low PDI and regioregularity higher than 93%. Next, P3HT-Br was reacted in a Suzuki–Miyaura polycondensation 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,^{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.^{35,36} A high and low molecular weight P3HT-Br macroreagent 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

Table 1 Characteristics of all-conjugated P3HT block copolymers

Polymers	P3HT ^a <i>M_w</i> (PDI)	BCP ^a <i>M_w</i> (PDI)	DP ratios ^b (P3HT wt%)
P3HT36- <i>b</i> -PF100	6.1 (1.16)	48.4 (1.86)	36 : 100 (13%)
P3HT81- <i>b</i> -PF105	13.5 (1.32)	60.6 (1.87)	81 : 105 (25%)
P3HT51- <i>b</i> -PFBT66	8.5 (1.19)	168 (3.61)	51 : 66 (20%)
P3HT81- <i>b</i> -PFBT90	13.5 (1.32)	81.5 (2.24)	81 : 90 (22%)
P3HT51- <i>b</i> -PFTBT17	8.5 (1.19)	19.7 (1.49)	51 : 17 (42%)
P3HT81- <i>b</i> -PFTBT12	13.5 (1.32)	N/A ^c	81 : 12 (62%)

^a *M_w* (kg mol⁻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 ¹H NMR. ^b DP ratios and P3HT content were determined by ¹H NMR *via* comparison of the integrated intensity of P3HT aromatic peak (6.9 ppm) and fluorene alkyl peaks (2.2 ppm). ^c P3HT81-*b*-PFTBT12 contains primarily homopolymer impurities, and therefore an estimate for block copolymer molecular weight is not provided.

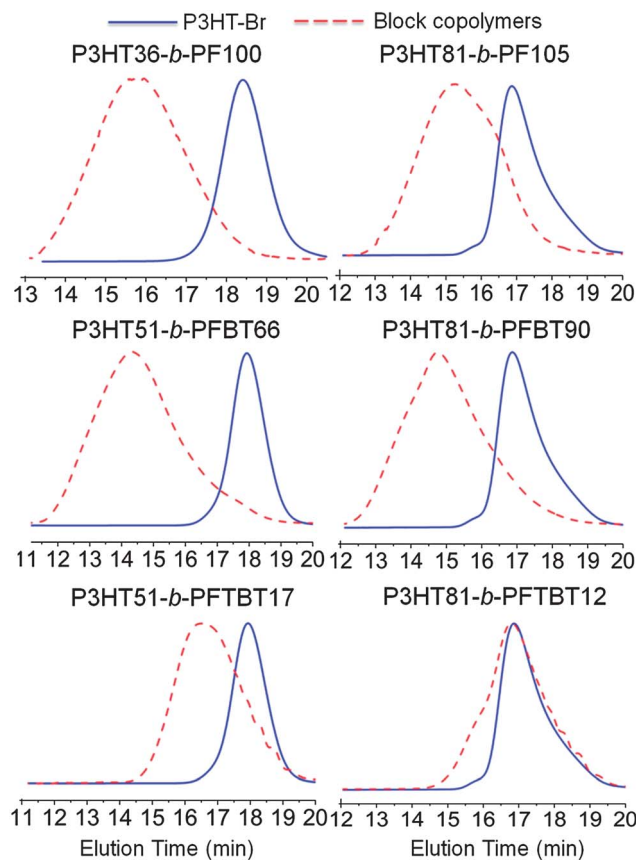


Fig. 1 SEC-RI analysis of block copolymers and corresponding P3HT-Br macroreagents. Intensities are normalized for clarity.

content of P3HT-Br macroreagent used in the Suzuki–Miyaura polycondensation step (roughly 1 mole% relative to monomers).

A comparison of the characteristics of final block copolymer products produced (Fig. 1 and Table 1) with previous reports using similar methods^{6,15} indicates that the use of an LiCl additive enables the preparation of much cleaner and higher molecular weight block copolymers. With the exception of P3HT81-*b*-PFTBT12, a clear shift in the molecular weight distribution of the final products is observed relative to the starting P3HT homopolymers. For comparison, our previous attempts at making similar all-conjugated block copolymers using similar methods (but without the LiCl additive) resulted in only modest shifts in the molecular weight distribution along with homopolymer impurities.¹⁵ Other reports using similar synthetic methods report the presence of significant homopolymer impurities or relatively low molecular weights for the second polymer block.^{6,26} The clear shift in the molecular weight distributions of the block copolymer products shown in Fig. 1 indicates that little or no residual P3HT homopolymer remains, and all-conjugated block copolymers with a mass-averaged molecular weight *M_w* as high as 168 kg mol⁻¹ (relative to polystyrene) are produced. Number-averaged molecular weights for each block estimated by SEC-RI are in relatively good agreement with ¹H NMR estimates of P3HT content of the final block copolymers (see Table 1 and ESI, Fig. S1–S3†). In the case of P3HT81-*b*-PFTBT12, the synthesis failed to produce significant amounts of block copolymer due to poor solubility of the PFTBT block and the resulting block

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-UUVIS) 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-UUVIS analysis indicates clean block copolymer product – a clear shift in the SEC-UUVIS traces corresponding to P3HT is observed as well as a good match between SEC-UUVIS 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*-PFBT66 exhibit excellent overlap between SEC-UUVIS traces corresponding to both polymer blocks, while some high molecular weight P3HT homopolymer may be present in P3HT81-*b*-PF105 and P3HT81-*b*-PFBT90. 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-UUVIS 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 micro-phase segregation and crystallization of the second block.^{18,37–39} 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*-PFBT90, 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*-PFBT66 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

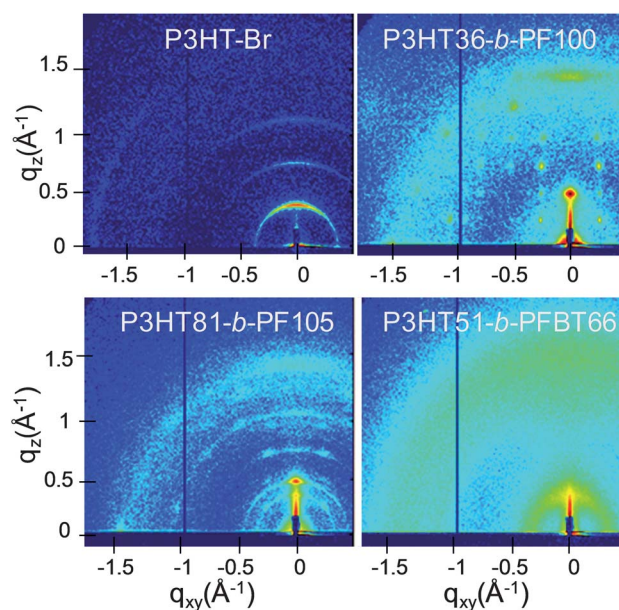


Fig. 2 GIWAXS measurement for P3HT-Br, P3HT36-*b*-PF100, P3HT81-*b*-PF105, and P3HT51-*b*-PFBT66. All samples were thermally annealed at 230 °C and measured at 80 °C. Samples were measured at an incident angle of 0.25° and 20 seconds exposure time. All images plotted using the same color scale for the scattered intensity.

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,⁴⁰ 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 \AA^{-1} corresponding to the (100), (200), and (300) reflections for P3HT crystallites and a scattering peak at $q_z = 0.50 \text{ \AA}^{-1}$ 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.

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