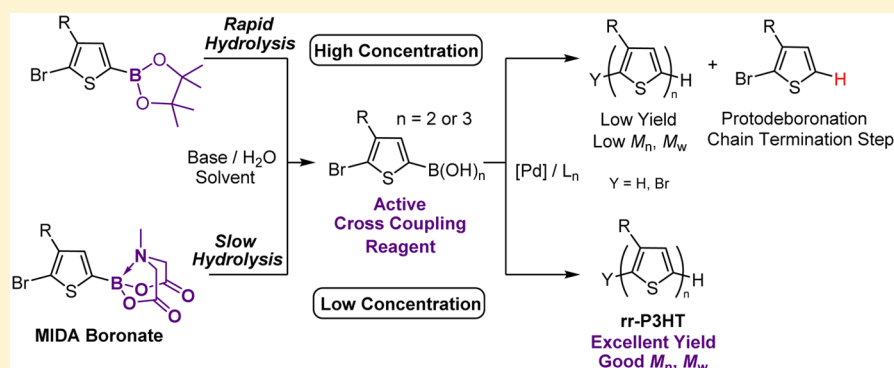


## Thienyl MIDA Boronate Esters as Highly Effective Monomers for Suzuki–Miyaura Polymerization Reactions

Josué Ayuso Carrillo, Michael J. Ingleson,\* and Michael L. Turner\*

School of Chemistry, University of Manchester, Oxford Road, M13 9PL Manchester, United Kingdom

## Supporting Information



**ABSTRACT:** The synthesis of highly regioregular poly(3-hexylthiophene-2,5-diyl), rr-P3HT, by Suzuki–Miyaura polymerization is reported. The key *N*-methyliminodiacetic acid (MIDA) boronate ester thienyl monomer was synthesized using a one-pot multigram scale procedure, in high purity, and in good isolated yield (80%) by direct electrophilic borylation. Conditions for the hydrolysis of the MIDA protecting group and the polymerization reaction were investigated. The optimal procedure gave rr-P3HT with >98% HT couplings, excellent isolated yields (up to 94%), and polymer molecular weights up to  $M_n = 18.7$  kDa and  $M_w = 42.7$  kDa. The performance of the MIDA containing monomer was compared to that of the pinacol boronate ester under identical polymerization conditions, with the latter producing lower molecular weight polymers in reduced yield.

## INTRODUCTION

Poly(3-hexylthiophene-2,5-diyl), P3HT, is one of the most studied  $\pi$ -conjugated polymers as it can be processed from solution into robust thin films that exhibit good performance in devices such as organic field-effect transistors, environmental sensors, and solar cells.<sup>1,2</sup> The asymmetric nature of the repeating unit requires control of the regiochemistry in the polymerization reaction to deliver regioregular (rr) polymer, rr-P3HT, with only head-to-tail (HT) couplings. This polymer shows an extended planar backbone conformation that self-assembles in thin films leading to improved charge mobilities, higher wavelength absorption, and other desirable properties.<sup>3,4</sup>

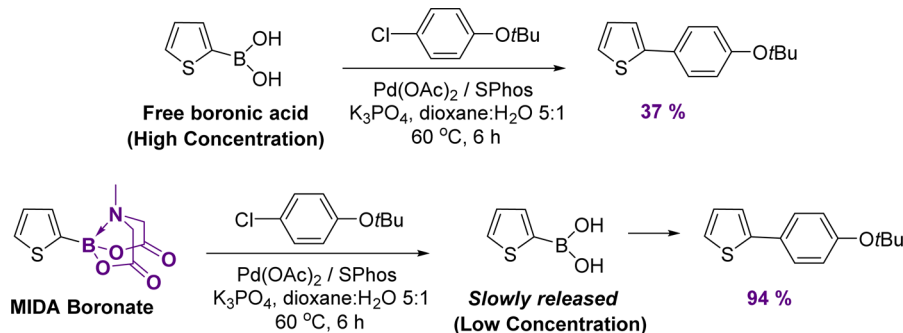
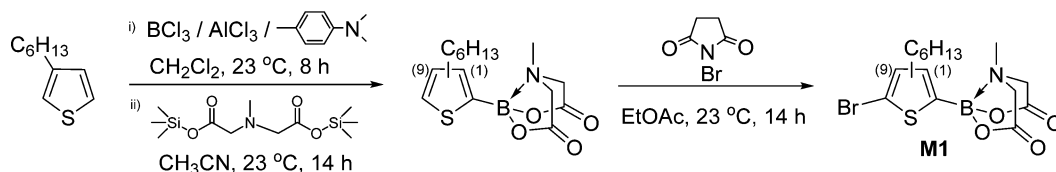
Several synthetic routes to highly regioregular P3HT have been reported, the most widely used in industry and academia are the Grignard metathesis (GRIM),<sup>5</sup> Rieke,<sup>6</sup> and Stille<sup>7</sup> methods, although other routes have been recently developed.<sup>8–11</sup> The Suzuki–Miyaura polymerization<sup>12</sup> offers advantages over these methods, such as air-stable precursors, mild and easy to use aqueous reaction conditions, wide functional group tolerance, high regioselectivity, and easy removal of low-toxicity byproducts.<sup>13,14</sup> However, the application of Suzuki–Miyaura polymerization to produce polythiophenes of desirable polymer molecular weight is challenging due to: (i) Difficulties with the synthesis of thiophene-derived boronic acids and esters in high purity in good yield as they undergo acid-, base-, and

metal-catalyzed hydrolytic protodeboronation.<sup>15–17</sup> (ii) During polymerization protodeboronation of the starting monomer and the growing chain can lead to premature chain termination giving low molecular weights and poor yields of polymer.<sup>18–21</sup> For example, polymerization of 5-bromo-4-hexylthien-2-yl-pinacol boronate ester produced P3HT with moderate molecular weights and low yields (e.g.,  $M_w = 9.9$  kDa, 25% yield, and 96% HT couplings). Both outcomes were attributed to significant protodeboronation of the monomer and the growing chain during the reaction.<sup>20</sup> Recently, considerable progress has been made in this area, with the generation of higher molecular weight polythiophenes in high yield by Suzuki–Miyaura polymerization achieved using highly active palladium catalysts.<sup>8,22,23</sup> While a significant advance, the yields for formation of the thienyl boronate esters used as monomers in these reports were still low ( $\leq 30\%$ ), presumably due to sensitivity to protodeboronation.

Highly effective boron protecting groups have been recently reported that provide enhanced stability to protic media and enable efficient Suzuki–Miyaura cross-coupling of small molecule heteroaryl boronate esters that are extremely sensitive to protodeboronation in their boronic acid form.<sup>17</sup> One particularly

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Scheme 1. Synthesis of Thienyl Cross-Coupled Products from Boronic Acids (Top) or MIDA Boronate Esters (Bottom)<sup>26</sup>Scheme 2. Two-Step Synthetic Route to Regio-Impure Monomer **M1** (Regioisomer Ratio of 9:1 As Indicated)

effective protecting group is the *N*-methyliminodiacetic acid (MIDA) boronate ester. The rigid tridentate chelate nature of the MIDA group binds boron strongly and affords exceptional stability to acidic conditions even for electron-rich heteroaryl boronate esters.<sup>24–26</sup> The slow hydrolysis of MIDA boronate esters proceeds under mild basic conditions to gradually unmask the active boron transmetallating agent. This minimizes the concentration of the sensitive boron species in solution and thus reduces undesired competitive reactions, such as protodeboronation, enabling high yielding cross-coupling. For example, thienyl MIDA boronate esters are highly effective reagents for small molecule Suzuki–Miyaura cross-coupling, in contrast to boronic acid analogues (Scheme 1).<sup>26</sup>

We have recently reported a novel route to thienyl MIDA boronate esters by direct electrophilic borylation in a one-pot, transition-metal-free synthesis that gives high-purity products in good yields.<sup>27</sup> This approach provides a simple route to the bifunctional monomers required for Suzuki–Miyaura polymerization and avoids the unstable boronic acids as intermediates during their synthesis. In this contribution we demonstrate the efficient synthesis of highly *rr*-P3HT by Suzuki–Miyaura polymerization in excellent yield with good polymer molecular weight ( $M_n$ ) and polydispersity ( $\mathcal{D}_M$ ) using a regioregular MIDA boronate ester monomer.

## RESULTS AND DISCUSSION

In a previous report,<sup>27</sup> the thiophene-derived MIDA boronate ester, **M1**, was synthesized in two steps and isolated in good yield (69%) as a 9:1 mixture of regioisomers (Scheme 2). In principle, polymerization of **M1** will lead to *rr*-P3HT if the major regioisomer is significantly more reactive in the polymerization reaction—reactivity previously seen for synthetic routes involving regio-impure Mg or Zn thienyl reagents.<sup>5,6,28</sup> Initial studies focused on understanding the rate of hydrolysis of the MIDA moiety of **M1** to discover appropriate slow release cross-coupling conditions for effective polymerization of **M1**.

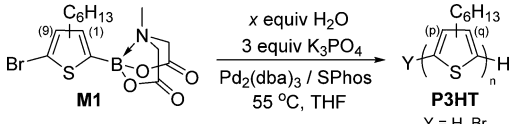
The Suzuki–Miyaura cross-coupling of small molecules using MIDA boronate esters shows a strong dependence on the number of equivalents of base and water added to the reaction mixture.<sup>26,29,30</sup> Initial investigations used reaction conditions

( $K_3PO_4$  base,  $H_2O$ :solvent 1:5 by volume/at 50–60 °C) that were effective for small molecule cross-couplings to determine if they were transferable to the polymerization of **M1**. However, the use of high ratios of water:monomer and 3 equiv of  $K_3PO_4$  led to rapid (<15 min) protodeboronation of **M1** and formation of 2-bromo-3-hexylthiophene (2Br3HT). In this reaction it is therefore important to minimize the  $H_2O$  content to disfavor protodeboronation of the unmasked boronic acid while maintaining sufficient water to slowly hydrolyze MIDA to access the active boron transmetallating reagent. The theoretical minimum required ratio of  $H_2O$ : $K_3PO_4$ :**M1** is 3:3:1 with 2 equiv of base required to hydrolyze MIDA and one to convert the intermediate boronic acid to the anionic boronate. In THF at 55 °C this ratio displayed the desired slow consumption of the B-MIDA moiety, although no evidence for the formation of the corresponding thienylboronic acid or anionic thienyl boronate species was detected, with only 2Br3HT and unreacted **M1** observed by  $^1H$  and  $^{11}B$  NMR spectroscopy. However, in polymerization studies this ratio of water:reactants only produced polymers of low to moderate molecular weights, using a range of precatalyst systems (see Supporting Information). A greater number of equivalents of water were explored in order to produce the key thienylboronic acid (or the anionic thienyl boronate) at an appreciable concentration. Increasing the quantity of water (to 30:3:1 ratio of  $H_2O$ : $K_3PO_4$ :**M1**) produced a completely homogeneous solution in THF ( $[M1] = 6.1 \times 10^{-2}$  M), and the presence of the thienylboronic acid was observed by  $^1H$  and  $^{11}B$  NMR spectroscopy confirming hydrolysis of the MIDA protecting group is proceeding. Under these conditions the hydrolysis of the B-MIDA protecting group was also still slow (14% remaining **M1** after 8 h). The polymerization of **M1** using this reagent ratios provided P3HT of higher molecular weight and significantly increased monomer conversion when compared to the 3:3:1 system. A range of precatalysts were tested, and the  $Pd_2(dba)_3/SPhos$  combination, widely used in the small molecule chemistry,<sup>26</sup> possessed superior catalytic efficiency (see Supporting Information).

These results showed that the concentration of water is crucial to promote effective hydrolysis of the B-MIDA moiety at the optimal rate, while limiting protodeboronation. Hence, a

wide range of water:monomer ratios was screened in order to optimize the polymerization reaction. A direct relationship between the average molecular weight of the polymer and the number of equivalents of water employed in the reaction was observed (Table 1). The optimal balance for maximizing the

**Table 1. Polymerization of M1 as a Function of the Quantity of Water<sup>a</sup>**



entry <sup>b</sup>	H <sub>2</sub> O (equiv)	M <sub>n</sub> <sup>c</sup> (kDa)	M <sub>w</sub> <sup>c</sup> (kDa)	D <sub>M</sub> <sup>c</sup>	rr <sup>d</sup> (%)
1 <sup>c</sup>	3	5.9	11.5	2.0	72
2	10	9.8	21.6	2.2	75
3	20	11.4	25.1	2.2	75
4 <sup>f</sup>	30	11.5	29.1	2.5	75
5	40	14.3	37.2	2.6	75
6	80	14.6	36.6	2.5	74
7	120	14.0	49.5	3.5	75

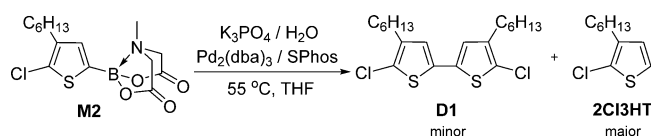
<sup>a</sup>Reaction conditions: T: 55 °C, [M1] = 6.1 × 10<sup>-2</sup> M, K<sub>3</sub>PO<sub>4</sub>: 3 equiv, Pd<sub>2</sub>(dba)<sub>3</sub>: 2.5 mol %, SPhos: 5 mol %, solvent: THF, t: 120 h, reaction quenched with MeCN. <sup>b</sup>Crude P3HT samples. <sup>c</sup>Determined by GPC (THF, PS calibration). <sup>d</sup>Regioregularity determined by integration of methylene signals (<sup>1</sup>H NMR spectroscopy, CDCl<sub>3</sub>, 400 MHz). <sup>e</sup>t: 168 h. <sup>f</sup>t: 48 h.

polymer molecular weight (*M<sub>w</sub>*) while minimizing the polydispersity (*D<sub>M</sub>*) under these conditions was found to be in the region of 40–80 equiv of H<sub>2</sub>O relative to the monomer M1.

The molecular weights of P3HT derived from this protocol were promising; however, all the polymer samples derived from M1 presented a HT regioregularity of 72–75% (Table 1). The aromatic region displayed four well-isolated singlets corresponding to HT–HT, HT–HH, HT–TT, and HH–TT couplings<sup>31</sup> (see Supporting Information), indicating that both M1 regioisomers participate in the polymerization, and are incorporated into the growing polymer chains. Therefore, to form highly rr-P3HT by polymerization of thienyl MIDA boronate esters a regioregular source of M1 is essential.

**Regiopure Monomer Synthesis.** A more efficient synthetic procedure than the previously reported one-step route to regiopure 5-bromo-4-hexylthien-2-yl-MIDA boronate ester (previous isolated yield of only 36%)<sup>27</sup> was required for the preparation of rr-P3HT. The low yields from the direct electrophilic borylation of 2Br3HT previously reported are in part due to AlCl<sub>3</sub> induced halide exchange with the C–Br functionality producing borylated thienyl chlorides and bromides (see Supporting Information).<sup>32</sup> The preclusion of any chloride containing monomer is essential for an effective preparation of rr-P3HT as while chloroaryl-MIDA boronates are commonly employed in Suzuki–Miyaura cross-coupling of small molecules<sup>26</sup> the performance of M2, the chloro-version monomer, in Suzuki–Miyaura polymerization is extremely poor. For example, under the optimal conditions found for M1 (Table 1, entry 5) M2 did not yield any P3HT, giving only protodeboronated 2-chloro-3-hexylthiophene (2Cl3HT), and a single tail-to-tail coupled dimer D1 (Scheme 3), identified by <sup>1</sup>H NMR spectroscopy and GC-MS (see Supporting Information). Although M2 undergoes hydrolysis of the MIDA group at rates comparable to the 5-bromo-4-hexylthien-2-yl-MIDA boronate ester

**Scheme 3. Attempted Polymerization of M2 under Reaction Conditions Developed for M1 (Table 1, Entry 5)**



(see Supporting Information), it appears unable to undergo oxidative addition to the palladium catalyst. Thus, only protodeboronation and a single homocoupling through the boronate functionality are observed.

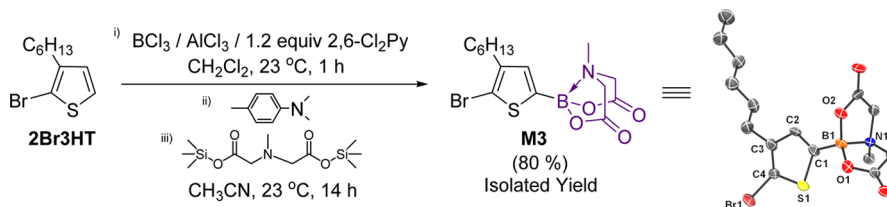
Chlorine-free and regio-pure 5-bromo-4-hexylthien-2-yl-MIDA boronate ester, M3, was synthesized on a multigram scale in high yield (80%) using an optimized one-pot procedure. The electrophilic borylation of 2Br3HT is fast and efficient at room temperature (>90% conversion after 1 h, by <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy) provided the noncoordinating base 2,6-dichloropyridine (2,6-Cl<sub>2</sub>Py) is used. A slight excess (20 mol %) of 2,6-Cl<sub>2</sub>Py was also required to reduce the reactivity of highly Lewis acidic “AlCl<sub>3</sub>” species and therefore avoid halogen scrambling between the thienyl bromide substrate and AlCl<sub>3</sub>.<sup>32</sup> Addition of 1 equiv of *N,N*-dimethyl-*p*-toluidine (Me<sub>2</sub>NTol) as a proton scavenger post-borylation but prior to installation of the MIDA group was found to be necessary, presumably to prevent undesired side reactions involving the strongly Brønsted acidic [H(2,6-Cl<sub>2</sub>Py)]<sup>+</sup> byproduct from S<sub>E</sub>Ar. The final product M3 is a highly pure crystalline air-stable solid that is soluble in many organic polar and nonpolar solvents (Scheme 4).

**Polymer Synthesis.** Initial polymerization reactions with M3 were performed using the conditions optimized for M1, i.e., 40 and 80 equiv of water relative to monomer and 3 equiv of K<sub>3</sub>PO<sub>4</sub> at 55 °C in THF. These two systems (Table 2, entries 1 and 2) produced polymers with average molecular weights comparable to those derived from M1. The higher concentration of water (Table 2, entry 2, 80 equiv of H<sub>2</sub>O) resulted in higher polydispersities (see Supporting Information), and the polymerization was faster than those with lower concentrations (Table 2, entry 1, 40 equiv of H<sub>2</sub>O). This was shown by the higher molecular weight of the P3HT at 4 h of reaction (*M<sub>n</sub>* = 12.8 kDa, *D<sub>M</sub>* = 2.8) and was consistent with the reaction mixture turning purple over the first hour of reaction. However, Soxhlet purification using hexane removed a larger fraction of the P3HT than Soxhlet extraction of polymers prepared using 40 equiv of H<sub>2</sub>O. This indicates that more short chains are produced with 80 equiv of H<sub>2</sub>O presumably due to the greater concentration of water, resulting in more protodeboronation. Thus, the 40:3:1 ratio of H<sub>2</sub>O:K<sub>3</sub>PO<sub>4</sub>:M3 was chosen to investigate the effect of varying the polymerization parameters on the properties of the generated P3HT.

Gel permeation chromatography (GPC) traces of the crude polymer produced where the solvent volume had been halved (Table 2, entry 3) revealed that lower polymer molecular weights (*M<sub>n</sub>*) were produced. Precipitation of solid from this reaction suggested that the polymer molecular weight is limited by solubility of the growing chains due to the lower quantity of THF employed. Furthermore, when THF was replaced with toluene, with or without Aliquat 336, only traces of P3HT were isolated, while the use of 2-Me-THF was also inferior to THF. Halving the catalyst loading gave P3HT with only marginally lower average molecular weight (Table 2, entry 4). Burke et al.<sup>25,26</sup> and others<sup>33–35</sup> routinely use ≥6 equiv of K<sub>3</sub>PO<sub>4</sub> base:MIDA boronate ester for small molecule cross-couplings, and therefore



**Scheme 4. One-Pot Synthetic Route to M3 by Direct Electrophilic Borylation and Esterification with TMS<sub>2</sub>-MIDA; Crystal Structure of M3 (Ellipsoids at 50% Probability, Structural Metrics Consistent with Other MIDA Boronate Esters<sup>26</sup>)**



**Table 2. Selected Results from the Polymerization of M3 under Different Reaction Conditions (for Full Data See Supporting Information)<sup>a</sup>**

entry <sup>b</sup>	H <sub>2</sub> O (equiv)	K <sub>3</sub> PO <sub>4</sub> (equiv)	<i>M<sub>n</sub></i> <sup>c</sup> (kDa)	<i>M<sub>w</sub></i> <sup>c</sup> (kDa)	<i>Đ<sub>M</sub></i> <sup>c</sup>	rr <sup>d</sup> (%)
1	40	3	13.4	37.7	2.8	≥98
2	80	3	14.3	45.0	3.2	≥98
3 <sup>e</sup>	40	3	8.2	22.1	2.7	≥98
4 <sup>f</sup>	40	3	12.3	32.7	2.7	≥98
5	40	6	7.8	18.1	2.3	97
6	40	2	10.2	31.2	3.1	≥98

<sup>a</sup>Reaction conditions: *T*: 55 °C, [M3] = 6.1 × 10<sup>−2</sup> M, Pd<sub>2</sub>(dba)<sub>3</sub>: 2.5 mol %, SPhos: 5 mol %, Solvent: THF, *t*: 72 h, reaction quenched with MeCN. <sup>b</sup>Crude P3HT samples. <sup>c</sup>Determined by GPC (THF, PS calibration). <sup>d</sup>Regioregularity determined by integration of methylene signals (<sup>1</sup>H NMR spectroscopy, CDCl<sub>3</sub>, 400 MHz). <sup>e</sup>[M3] = 12.2 × 10<sup>−2</sup> M. <sup>f</sup>Pd<sub>2</sub>(dba)<sub>3</sub>: 1.25 mol %, SPhos: 2.5 mol %.

the importance of the base concentration was examined. Increasing the concentration to 6 equiv of base per monomer (Table 2, entry 5) showed a detrimental effect on the molecular weight possibly caused by a combination of more rapid protodeboronation of the growing chains and the heterogeneous nature of the reaction mixture. Reducing the content of base to 2 equiv (Table 2, entry 6) also proved inferior to that with 3 equiv. Finally, polymerization of M3 at 40 °C or at reflux in THF proved inferior to reactions conducted at 55 °C (Table 2, entry 1) in terms of the P3HT molecular weight and the polymer yields (see Supporting Information). Therefore, all remaining polymerization reactions were performed with 3 equiv of base at 55 °C in THF.

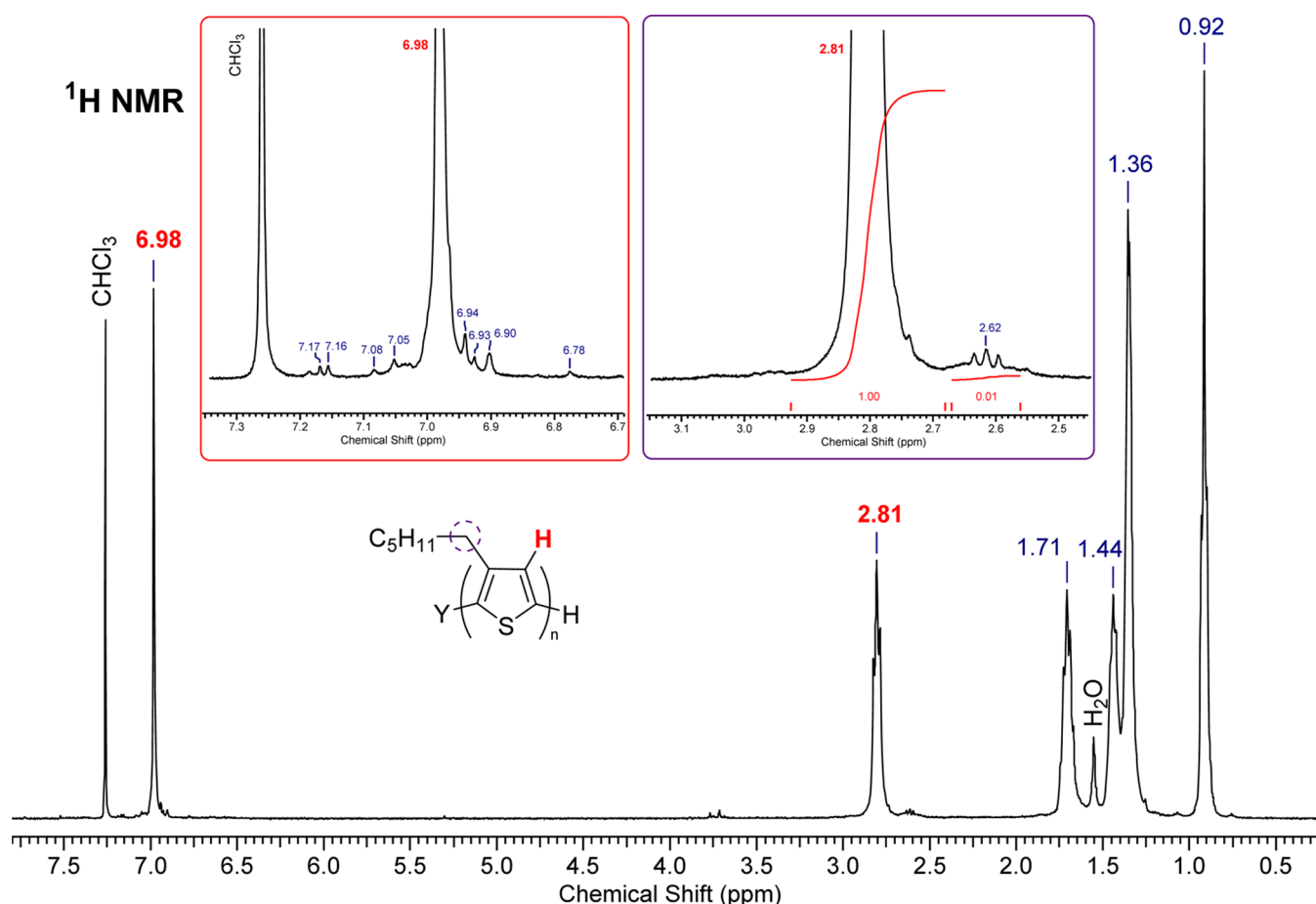
The regioregularity of the crude polymers was >97% for all reactions (determined by <sup>1</sup>H NMR spectroscopy). This indicates that the regiopure monomer M3 ensures exclusively HT couplings. The aliphatic region in the <sup>1</sup>H NMR spectrum (Figure 1) showed the main triplet at 2.81 ppm and a small triplet at 2.62 ppm that corresponds to the α-methylene hydrogens of the hexyl group on the terminal thiophene, the intensity of which is dependent on the length of the polymeric chains.<sup>31,36,37</sup> The aromatic region showed the main singlet at 6.98 ppm plus other extremely minor signals. No evidence was found for regioirregular couplings other than a small singlet at 7.05 ppm which was more prominent when using regioimpure M1 (*vide supra*). The small doublet at 7.16 ppm is attributed to a protodeboronated end group originally corresponding to the B-MIDA moiety, and the small singlet at 6.90 ppm is attributed to the H/H terminated chains that have undergone

protodehalogenation (see Supporting Information), while the minor resonance at 6.94 ppm cannot currently be assigned. In addition, <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy only revealed carbon signals corresponding to HT couplings in all cases.<sup>31</sup>

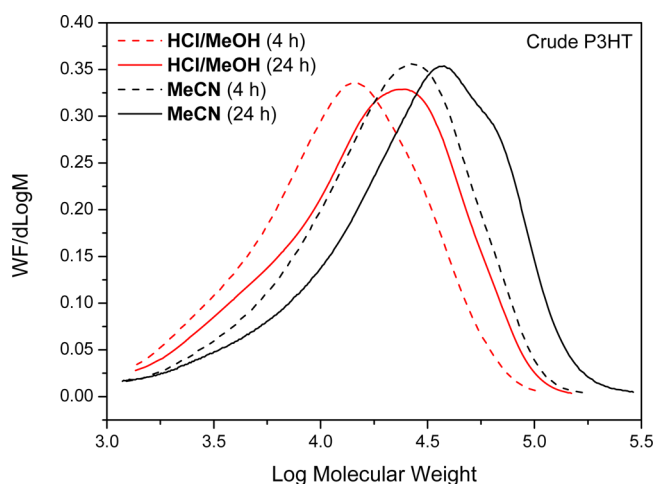
The most notable effect on the polymer molecular weight was found to be variation in the quenching method. High molecular weights were achieved when polymerizations are terminated by addition of the THF solution into MeCN to precipitate the polymer. Polymers isolated in this manner displayed a shoulder or second peak (in both the crude and Soxhlet-fractionated polymer) in the GPC traces that approximately corresponds to a distribution with double the molecular weight of the first peak. Previous work employing Ni-catalyzed GRIM polymerization for the synthesis of P3HT reported the appearance of a second peak of twice the molecular weight of the first one in the GPC traces, when the polymerization was quenched with H<sub>2</sub>O. Quenching the GRIM polymerization with acid stopped the chain doubling, an effect attributed to more rapid protodemetalation of the polymer chain.<sup>38</sup> Analogously, we found that the use of HCl-acidified MeOH in place of MeCN to quench the polymerization of M3 led to a unimodal polymer (Figure 2) as evidenced by decreased *M<sub>w</sub>* and narrower *Đ<sub>M</sub>* with respect to that precipitated in MeCN (Table 3, entries 1–8). This is consistent with a more effective termination that prevents chain doubling events at the end of the polymerization.

From the parameter variation studies two optimal systems for the polymerization of M3 were developed with maximum *M<sub>w</sub>*, or minimum *Đ<sub>M</sub>*, i.e., the reaction quenched with MeCN and that quenched with HCl-acidified MeOH, respectively. P3HT with *M<sub>w</sub>* in the region of 20–30 kDa has been determined to give optimal performance in P3HT/PCBM solar cells.<sup>39</sup> Thus, the high yielding nature of monomer and polymer formation (the overall isolated yield of P3HT from 2Br3HT was 72% for Table 3, entry 8) combined with the useful *M<sub>w</sub>* of P3HT produced indicates that thienyl MIDA boronate esters are highly attractive monomers for the production of polythiophenes.

It was important to benchmark the MIDA boronate esters to other widely used boronate esters under identical polymerization conditions. Previous Suzuki–Miyaura polymerization of boronate esters has used predominantly either neopentylglycol or pinacol (Pin) derived alkylthienyl derivatives.<sup>18–21</sup> Thus, M4, the pinacol boronate ester version of M3, was synthesized regiopure by electrophilic borylation and tested under exactly the same polymerization reaction conditions to that used for M3 (Table 3, entries 9–14). The two different methods of quenching showed no effect on the shape of the GPC traces of P3HT derived from M4 (Figure 3). Most notable, however, was the fact that the polymers produced from M4 displayed virtually half the average molecular weight of the P3HT derived from M3 quenched with HCl-acidified MeOH (Table 3, compare entries 7–8 and 13–14) and a third of the M3 polymerization



**Figure 1.**  $^1\text{H}$  NMR spectrum (400 MHz) of the rr-P3HT ( $\text{CHCl}_3$  fraction after Soxhlet extraction) derived from **M3** (Table 2, entry 1). Insets: aromatic region showing the singlet at 6.98 ppm corresponding to HT couplings (left). Methylene signal at 2.81 ppm corresponding to HT couplings; signal at 2.62 ppm overlaps  $^{13}\text{C}$  satellite signals of the former (right).



**Figure 2.** GPC traces of crude **M3**-derived rr-P3HT comparing different quenching methods: with HCl-acidified MeOH or with MeCN.

quenched with MeCN (Table 3, compare entries 3–4 and 11–12), respectively. In further contrast to polymerizations with **M3**, where considerable increase in  $M_w$  occurs after 4 h (Table 3, entries 2 and 4), there is a negligible increment in polymer chain length beyond 4 h using **M4** (Table 3, entries 10 and 12). Analysis of aliquots taken from the polymerization

mixtures using **M4** at different times showed only 2Br3HT and P3HT, in contrast with the polymerization experiments employing **M3**, where **M3** but no 2Br3HT is observed alongside P3HT. The termination of polymerization within 4 h using **M4** is due to protodeboronation under these conditions as **M4** is thermally stable at 55 °C in THF for at least 24 h (by multinuclear NMR spectroscopy). The MIDA protecting group is therefore essential, with the protodeboronation of **M4** and consequently chain termination of the growing polymer leading to lower molecular weights and yields relative to **M3**-derived P3HT. This is also consistent with polymerization being complete within 4 h with **M4** but requiring up to 24 h for monomer **M3** (see Supporting Information).

Further evidence for the disparate behavior of MIDA versus pinacol protecting groups under these conditions was obtained by addition of *p*-iodotoluene to the polymerization reactions at 4 h. This resulted in the incorporation of tolyl groups into one terminus of the polymer chains in P3HT derived from **M3** but not for the polymers derived from **M4** (Figure 4). The high degree of tolyl incorporation into **M3** derived polymers (by  $^1\text{H}$  NMR spectroscopy) demonstrates that a significant fraction of the growing polymer chains retain an intact B-MIDA moiety after 4 h under these reaction conditions. In contrast, no thienyl-B-Pin moieties persist at 4 h, indicating premature polymer chain termination by protodeboronation—an outcome minimized using the MIDA protecting group and the slow release strategy.

Table 3. Results from the Polymerization of M3 or M4<sup>a</sup>

entry	M	<i>t</i> (h)	<i>M</i> <sub>n</sub> <sup>b</sup> (kDa)	<i>M</i> <sub>w</sub> <sup>b</sup> (kDa)	<i>D</i> <sub>M</sub> <sup>b</sup>	rr <sup>c</sup> (%)	yield <sup>d</sup> (%)	quench	Soxhlet fraction <sup>e</sup>
1	M3	4	11.1	24.9	2.3	—	—	MeCN	crude
2	M3	4	13.4	32.4	2.4	—	—	MeCN	CHCl <sub>3</sub>
3	M3	24	13.4	36.2	2.7	≥98	99	MeCN	crude
4	M3	24	18.7	42.7	2.3	≥98	94	MeCN	CHCl <sub>3</sub>
5	M3	4	7.9	15.9	2.0	—	—	HCl/MeOH <sup>g</sup>	crude
6	M3	4	12.1	20.9	1.7	—	—	HCl/MeOH	CHCl <sub>3</sub>
7	M3	24	9.6	21.8	2.3	≥98	95	HCl/MeOH	crude
8	M3	24	13.8	24.1	1.8	≥98	90	HCl/MeOH	CHCl <sub>3</sub>
9	M4	4	4.3	10.8	2.6	—	—	MeCN	crude
10	M4	4	8.2	13.5	1.6	—	—	MeCN	CHCl <sub>3</sub>
11	M4	24	4.8	11.3	2.4	—	69	MeCN	crude
12	M4	24	8.6	13.8	1.6	96	36	MeCN	CHCl <sub>3</sub>
13	M4	24	5.2	12.2	2.4	—	69	HCl/MeOH	crude
14	M4	24	9.6	15.4	1.6	97	58	HCl/MeOH	CHCl <sub>3</sub>

<sup>a</sup>Reaction conditions: *T*: 55 °C, [**M**] = 6.1 × 10<sup>−2</sup> M, K<sub>3</sub>PO<sub>4</sub>: 3 equiv, H<sub>2</sub>O: 40 equiv, Pd<sub>2</sub>(dba)<sub>3</sub>: 2.5 mol %, SPhos: 5 mol %, solvent: THF.

<sup>b</sup>Determined by GPC (THF, PS calibration). <sup>c</sup>Regioregularity determined by integration of methylene signals (<sup>1</sup>H NMR spectroscopy, CDCl<sub>3</sub>, 400 MHz). <sup>d</sup>Isolated. <sup>e</sup>Soxhlet-fractionated chloroform fraction after sequential extractions with methanol, and *n*-hexane, for 14 h each.

<sup>f</sup>Regioregularity and yield at 4 h not determined, GPC run on aliquots extracted from reaction mixture. <sup>g</sup>[HCl] = 5 × 10<sup>−4</sup> M.

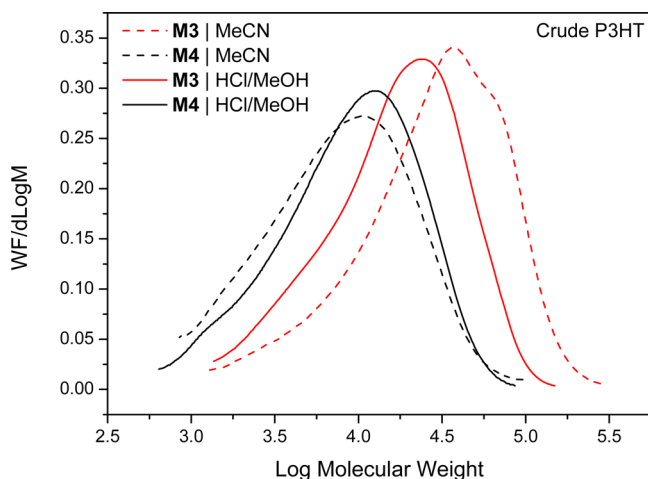


Figure 3. GPC traces of crude P3HT derived from **M3** or **M4** quenched at 24 h with MeCN or HCl-acidified MeOH.

## CONCLUSIONS

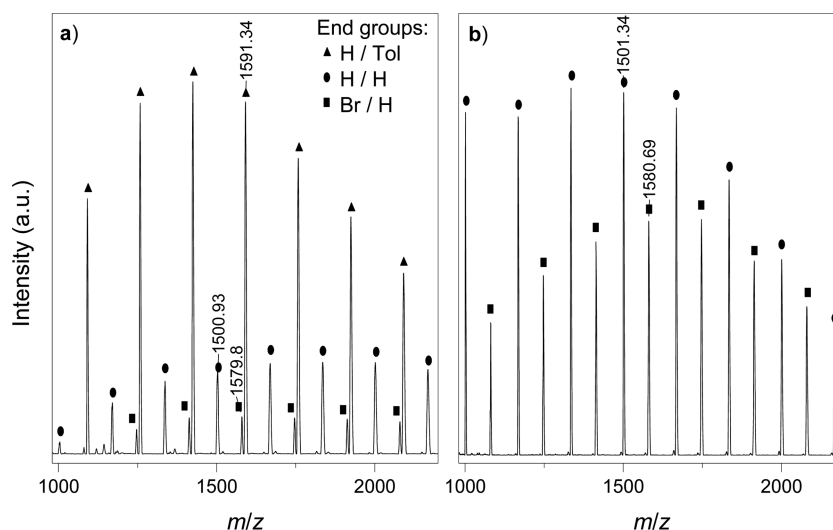
A novel synthetic route to a highly pure bromothieryl MIDA boronate ester monomer (**M3**) by direct electrophilic borylation is reported. The performance of this monomer under a range of polymerization reaction conditions showed that the slow hydrolysis of the B-MIDA moiety enables highly effective Suzuki–Miyaura polymerization. **M3** yields superior P3HT in terms of higher regioregularity, higher yield, higher molecular weight, and complete conversion of the monomer relative to the pinacol boronate ester congener. Depending on the quenching method employed, P3HT of molecular weight up to *M*<sub>n</sub> = 18.7 kDa and *M*<sub>w</sub> = 42.7 kDa were obtained in excellent yield, 94%, and with excellent regioregularity (>98%). MIDA boronate esters thus are a highly attractive boron protecting group for Suzuki–Miyaura polymerization of thienyl monomers due to the monomer's accessibility in high yield and purity coupled with the stability of the B-MIDA moiety to

protodeboronation and its slow release ability. This opens up the possibility of avoiding air-sensitive organometallic reagents and toxic tin byproducts in the preparation of many thiophene-containing polymers.

## EXPERIMENTAL SECTION

**Monomer Synthesis.** An oven-dried Schlenk ampule fitted with a J. Young's tap containing a stirrer bar was heated under reduced pressure and backfilled with N<sub>2</sub>. The ampule was charged under inert atmosphere with 2,6-dichloropyridine (7.13 g, 48.2 mmol, 1.20 equiv) and AlCl<sub>3</sub> (5.35 g, 40.1 mmol, 1.01 equiv). Then, anhydrous CH<sub>2</sub>Cl<sub>2</sub> (120 mL) was added, and the mixture was stirred until the solids completely dissolved. This was followed by addition of BCl<sub>3</sub> (40.1 mL, 1.01 equiv, 1.0 M solution in CH<sub>2</sub>Cl<sub>2</sub>), cooling to 0 °C, and then 2-bromo-3-hexylthiophene (9.92 g, 1.00 equiv) was added. After stirring at ambient temperature for 1 h, *N,N*-dimethyl-*p*-toluidine (5.43 g, 40.1 mmol, 1.01 equiv) was injected into the solution. The reaction mixture was then immediately added to a mixture of TMS<sub>2</sub>-MIDA (12.28 g, 42.1 mmol, 1.05 equiv) in anhydrous MeCN (100 mL) at 0 °C, and the stirring was continued at ambient temperature for 14 h. The reaction mixture was dried under reduced pressure at ambient temperature to remove TMSCl and solvents. The crude product was washed with water and brine and extracted with CH<sub>2</sub>Cl<sub>2</sub>. Further purification by dry column vacuum chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate afforded 13 g (80%) of pure **M3** as a pale yellow crystalline solid.

**Polymer Synthesis.** An oven-dried Radley's carousel tube containing a stirrer bar was charged under an inert atmosphere with **M3** (1.0 equiv) and K<sub>3</sub>PO<sub>4</sub>·H<sub>2</sub>O (3.0 equiv). Dry and degassed THF was added, and the reaction mixture was stirred until **M3** completely dissolved. Then, the appropriate quantity of degassed H<sub>2</sub>O was added, and the system was heated to the reaction temperature. Subsequently, a palladium precatalyst solution (5.0 mol %) was injected, and the polymerization was carried out under vigorous stirring and constant flow of N<sub>2</sub> gas. At the end of the reaction, the crude mixture was quenched by precipitating it into an excess (50-fold by volume) of vigorously stirred MeCN or HCl-acidified MeOH. The dark purple solid material was collected and dried overnight at ambient temperature under reduced pressure (1 × 10<sup>−2</sup> mbar) for further analyses. Sequential MeOH, *n*-hexane, and chloroform fractions were collected by Soxhlet extraction, for 14 h at each stage.



**Figure 4.** MALDI-TOF spectra of rr-P3HT derived from (a) **M3** and (b) **M4**. Both samples are the hexane fraction after Soxhlet extraction.

## ■ ASSOCIATED CONTENT

### Supporting Information

Full experimental details, NMR, MALDI-TOF spectra, and GPC data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*E-mail [michael.ingleson@manchester.ac.uk](mailto:michael.ingleson@manchester.ac.uk) (M.J.I.).

\*E-mail [michael.turner@manchester.ac.uk](mailto:michael.turner@manchester.ac.uk) (M.L.T.).

### Notes

The authors declare no competing financial interest.

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