

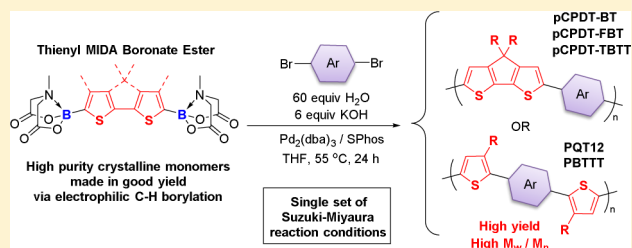
A General Protocol for the Polycondensation of Thienyl *N*-Methyliminodiacetic Acid Boronate Esters To Form High Molecular Weight Copolymers

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S Supporting Information

ABSTRACT: Thienyl di-*N*-methyliminodiacetic acid (MIDA) boronate esters are readily synthesized by electrophilic C–H borylation producing bench stable crystalline solids in good yield and excellent purity. Optimal conditions for the slow release of the boronic acid using KOH as the base in biphasic THF/water mixtures enables the thienyl MIDA boronate esters to be extremely effective homo-bifunctionalized (AA-type) monomers in Suzuki–Miyaura copolymerizations with dibromo-heteroarenes (BB-type monomers). A single polymerization protocol is applicable for the formation of five alternating thienyl copolymers that are (or are close analogues of) state of the art materials used in organic electronics. The five polymers were produced in excellent yields and with high molecular weights comparable to those produced using Stille copolymerization protocols. Therefore, thienyl di-MIDA boronate esters represent bench stable and low toxicity alternatives to highly toxic di-trimethylstannyl AA-type monomers that are currently ubiquitous in the synthesis of these important alternating copolymers.



INTRODUCTION

Thiophene moieties, including annulated derivatives, are key constituents of many polymers used in organic electronic devices.¹ While early studies were dominated by polythiophenes generated from a heterobifunctional (AB-type) monomer (e.g., P3HT, Figure 1),^{1,2} state of the art materials

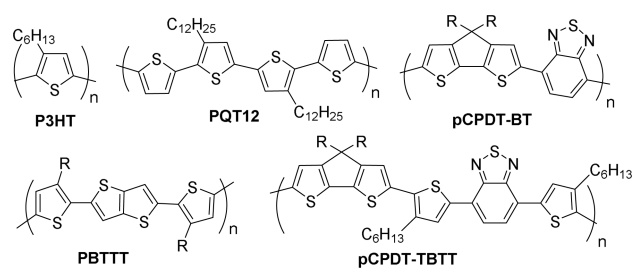


Figure 1. Selected thiophene containing polymers.

are based on alternating copolymers produced from two homo-bifunctional monomers (AA-/BB-type).² This approach allows access to more complex polythiophenes (e.g., PQT12, PBTTT, Figure 1) and to donor–acceptor (D–A) polymers. D–A polymers are ubiquitous active materials in organic electronic devices, and thienyl units, for example, 4,4′-bis(alkyl)-4*H*-cyclopenta-[2,1-*b*:3,4-*b'*]-dithiophene (CPDT), are privileged donor moieties in these materials.³

Homo-bifunctional CPDT monomers are copolymerized with bifunctional acceptors such as benzothiadiazole (BT) to form important D–A polymers (e.g., pCPDT-BT, pCPDT-

TBTT) that have desirable properties (e.g., high charge mobility).³ Indeed, thienyl containing alternating D–A polymers are among the state of the art active components in organic photovoltaic devices (enabling power conversion efficiencies (PCEs) of over 10%).^{2,3}

While parameters such as charge mobility and PCE are crucial markers of polymer performance in devices, another important but often overlooked criteria is the efficiency of monomer and polymer synthesis.⁴ Low toxicity monomers that are available in good yield and excellent purity via simple synthetic routes and that undergo highly effective polymerization are crucial for the large scale development of printed electronics.⁴ However, the copolymerization of an AA-type thienyl monomer with a BB-type acceptor monomer is dominated by the Stille cross-coupling reaction (Figure 2), which generally uses distannylated thienyl monomers.^{4d,5} This has drawbacks, including obtaining the distannylated thienyl monomer in sufficient purity (due to facile cleavage of thienyl–Sn bonds) making the precise control of stoichiometry in copolymerizations challenging.⁶ Furthermore, stoichiometric toxic tin waste is produced, which is particularly problematic with the Me₃Sn–thienyl derivatives (which generate volatile tin byproducts but are still widely used due to the crystalline nature of many Me₃Sn monomers).^{1,4d,5} Significant advances have been recently reported using direct (hetero)arylation polymerization (DHAP), which is a more efficient methodology (in terms of synthetic steps to produce the monomers and the

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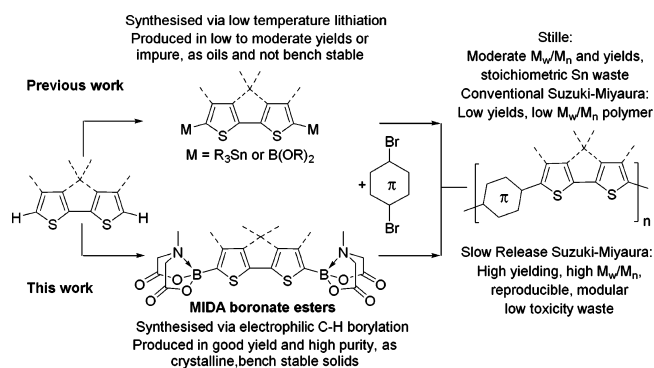


Figure 2. A comparison of previous routes to alternating thienyl copolymers and that reported herein using MIDA boronate esters.

quantity of waste byproducts).^{5,7} However, for producing D–A polymers such as pCPDT-BT, DHAP routes currently have a number of unsolved challenges (including low to moderate yields or homocoupling/branching defects) resulting in Stille cross-coupling polycondensation protocols still being the dominant method to access a range of important thienyl containing copolymers.^{4,c,d}

The Suzuki–Miyaura cross-coupling reaction utilizes organoboranes that have significantly lower toxicity than organostannanes. However, the utility of Suzuki–Miyaura polycondensation protocols in forming thienyl based copolymers is extremely challenging due to the propensity of thienyl boronic acids (and derivatives) to undergo protodeboronation.⁸ This generally leads to low yields of pure borylated thienyl monomer or significant impurities in the crude monomer. The latter when combined with premature chain termination events caused by protodeboronation during the polymerization often leads to a reduction in polymer yield and lower than required molecular weights.⁹ Using pCPDT-BT as a representative example, all the Suzuki–Miyaura polycondensation protocols reported to date have, to the best of our knowledge, drawbacks including: moderate monomer yields, complex monomer purifications (multiple flash chromatography cycles or recycling GPC), low to moderate polymer yields, and significantly lower molecular weights relative to pCPDT-BT generated by Stille cross-coupling polycondensation routes.¹⁰ Therefore, a general methodology for the Suzuki–Miyaura polycondensation of AA-/BB-type monomers to produce important thienyl containing alternating copolymers remains an outstanding goal. Key criteria for an ideal protocol are that high molecular weight polymers are formed in good yield from readily accessible, bench stable, crystalline thienyl boronate esters.

N-Methyliminodiacetic acid (MIDA) boronate esters are bench stable crystalline solids that can be produced on scale from inexpensive commodity chemicals.¹¹ The use of MIDA boronate esters was pioneered by Burke and co-workers who showed that under optimal hydrolytic cross-coupling conditions MIDA boronate esters slowly release the active boronic acid thus enabling high yielding Suzuki–Miyaura cross-coupling reactions even with challenging substrates such as 2-pyridyl MIDA boronate esters.^{8c} Furthermore, MIDA is biodegradable making the waste stream from cross-coupling using these boronate esters relatively easy to handle.^{11h} Since these seminal studies, MIDA boronate esters have become a well-established commercially available class of compounds that have enabled notable breakthroughs including automated iterative synthesis, access to >75% of polyene natural product frameworks by

Suzuki–Miyaura cross-coupling reactions, stereoselective coupling of sp³ moieties, and the formal homologation of aryl boronate esters.¹¹ While these are all impressive advances, a modular copolymerization protocol using thienyl di-MIDA boronate esters to form important conjugated copolymers is currently absent. An iterative coupling approach to oligothiophenes requires sequential deprotection, cross-coupling, and purification cycles and is thus not readily applicable to the formation of polymers, although a quaterthiophene has been made via this strategy.^{11b} Herein we report the facile synthesis of highly pure and crystalline AA-type thienyl di-MIDA boronate ester monomers and show that using these monomers a single polycondensation protocol is viable for the formation of a wide range of important alternating copolymers that are produced in excellent yield and with high molecular weights that are comparable to those afforded by Stille cross-coupling polymerization reactions.

RESULTS AND DISCUSSION

Due to the importance of fused thiophene building blocks in materials for organic electronic applications, studies commenced with the extremely electron rich donor moiety CPDT. Previously, we reported the synthesis of 5-bromo-4-hexylthien-2-yl-MIDA boronate ester, **1** (Figure 3 inset bottom left), by

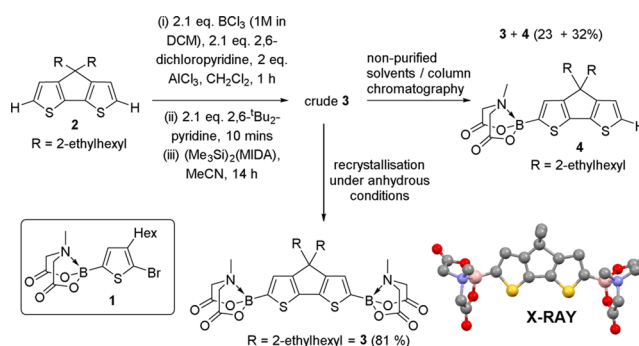


Figure 3. Synthesis (and partial solid state structure) of **3**.

electrophilic C–H borylation of 2-bromo-3-hexylthiophene.^{12,13} A related procedure enabled the double electrophilic borylation of CPDT (Figure 3) with subsequent MIDA protection leading to crude monomer **3** in high conversion (by *in situ* NMR spectroscopy). The isolation of this monomer in high yield required purification under anhydrous conditions, with standard purification by silica gel column chromatography using nonpurified “wet” solvents leading to protodeboronation and the formation of significant quantities of monoborylated product **4**. The crystalline nature of **3** facilitated isolation under anhydrous conditions in 81% yield on a multigram scale with single crystals obtained from MeCN/Et₂O (a partial connectivity map from X-ray diffraction studies for **3** is shown in Figure 3, multiple attempts with a number of crystals only produced low quality data). It is noteworthy that the formation of **3** proceeds at ambient temperature using electrophilic borylation and does not require column chromatography during purification, thus being readily amenable to large scale synthesis. Compound **3** is stable as a solid for at least 12 months under an inert atmosphere, and in the solid state **3** can be handled on the bench for several hours without any special precautions. While the di-MIDA thienyl monomers reported herein can be stored under ambient atmosphere as a solid for at

least 1 week with no observable decomposition (by NMR spectroscopy) prolonged storage leads to slow protodeboronation (e.g., after 18 months pristine **3** had converted to a mixture of 86% **3**/14% **2**).

Hydrolysis Studies. The protodeboronation of **3** during silica gel chromatography with “wet solvents” warranted investigation because it is essential to prevent this process during step growth polymerization reactions if high molecular weight polymers are to be obtained. Heteroaryl MIDA boronate esters are generally compatible with column chromatography and even stable toward strong Brønsted acids (e.g., triflic acid), with the stability attributed to the rigid tridentate chelation of boron by the MIDA dianion.^{11f} NMR studies on **3** confirmed that the rigid tridentate chelation of MIDA²⁻ to boron persists to at least 100 °C with the CH₂ groups of MIDA remaining diastereotopic over this temperature range. Furthermore, compound **3** proved stable toward protodeboronation by DCl (in Et₂O) in anhydrous THF (for at least 1 h) indicating that it is not **3** but a different compound derived from **3** that is undergoing protodeboronation under standard workup conditions using “wet” (nonpurified) solvents and silica gel chromatography. This suggests that BMIDA hydrolysis in **3** must be occurring in the absence of base (since workup conditions are base free), and it is a hydrolyzed boron species derived from **3** that is undergoing protodeboronation. This was confirmed by dissolution of **3** in *d*₈-THF containing D₂O (60 equiv relative to **3**) resulting in the slow hydrolysis of **3** at 23 °C and formation of the boronic acid **5** (15% of **3** is consumed after 24 h with the rate of hydrolysis accelerated at 55 °C, with 86% consumed after 24 h at 55 °C).

Probing the hydrolysis of **3** in THF containing ¹⁷O labeled water revealed that **5** contained labeled oxygen but the isolated diacid of MIDA produced from **3** did not (by ¹⁷O NMR spectroscopy). While isotopic scrambling of boronic acids in the presence of H₂¹⁷O has been previously reported (thus incorporation of ¹⁷O into **5** is mechanistically inconclusive),¹⁴ the absence of any ¹⁷O in the MIDA diacid indicates that water is hydrolyzing the B–O bonds in **3** and not the C–O bonds of the ester moiety. This observation is consistent with the recent detailed mechanistic study into the hydrolysis of MIDA boronate esters, which also observed only B–O heterolysis under neutral conditions.¹⁵ Thus, during the work up water is hydrolyzing the B–O bonds in **3** and a compound containing a partially dechelated MIDA (e.g., **A**, Scheme 1, although only **3**

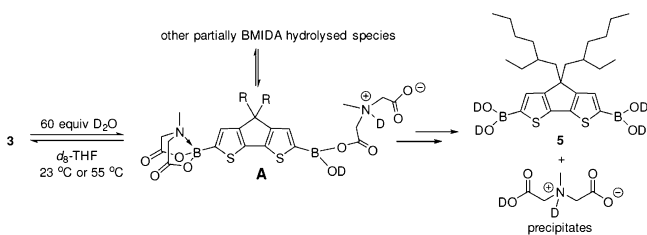
when exposed to Brønsted acids such as DCl (and presumably silica gel or H₂MIDA).

The hydrolysis of **3** under conditions more relevant to cross-coupling was also examined. It is essential for high fidelity cross-coupling that the formation of the active boron transmetallating reagent derived from **3** (**5** or [thienylB(OH)₃]⁻) proceeds under optimal slow release conditions.^{8c} Previously, optimal rates of hydrolysis of MIDA boronate esters were achieved using K₃PO₄ as base, with complete BMIDA hydrolysis generally requiring 3–6 h at 60 °C in etherate/H₂O mixtures.^{8c,11} However, monomer **3** undergoes slow hydrolysis at 55 °C in *d*₈-THF containing 60 equiv of D₂O and 6 equiv of K₃PO₄ to produce **5**, with only 50% consumption of **3** observed after 24 h at 55 °C. This is notably slower than the hydrolysis of **3** in the absence of K₃PO₄ (under otherwise identical conditions). These basic THF/water solutions are biphasic, with a minor base rich aqueous phase.^{11d,e,16} The presence of a basic aqueous biphasic system will lower the concentration of water in the organic phase leading to a slower hydrolysis of the BMIDA moieties by water.¹⁵ These in situ hydrolysis studies were performed in NMR tubes fitted with J. Young valves that were not effectively stirred (either rotated at a frequency of 10 rpm for 23 °C reactions or not agitated for studies at 55 °C). The low interfacial area between the two phases and poor mixing limit mass transport between the phases¹⁷ slowing the BMIDA hydrolysis. Repeating the hydrolysis of **3** at 55 °C in *d*₈-THF/water (60 equiv of D₂O, 6 equiv of K₃PO₄) in a Schlenk tube with stirring (900 rpm) to increase the interfacial area between phases led to more rapid BMIDA hydrolysis, consistent with improved mass transport between the two phases. However, even with stirring ca. 5% of **3** remained after 24 h at 55 °C under these conditions. Incomplete hydrolysis of **3** during polymerization is highly undesirable since in step-growth polymerizations this would prevent the formation of high molecular weight polymers.

The hydrolysis of the BMIDA groups in extremely electron rich **3** is slower than BMIDA hydrolysis in **1**.¹² For a direct comparison under identical conditions **1** and **3** (in a 2:1 ratio to obtain a 1:1 ratio of the respective thienyl-BMIDA moieties) were combined with 3 equiv of K₃PO₄ (per BMIDA moiety) in *d*₈-THF/water (30 equiv of D₂O per BMIDA moiety), and the hydrolysis was monitored by NMR spectroscopy at 55 °C. This confirmed that the BMIDA groups in **1** are hydrolyzed approximately twice as fast as those in **3** under pseudo-first-order kinetics (Figure 4). The slower hydrolysis of the BMIDA groups in the more electron rich heteroaromatic **3** relative to **1** suggests a buildup of negative charge at boron during the hydrolysis process¹⁵ and is consistent with studies on the rate of ester hydrolysis where more electron rich aromatic esters undergo slower ester hydrolysis.¹⁹ It should be noted that the rate of hydrolysis of **1** is not changed by the presence (or absence) of **3** under otherwise identical conditions indicating that **3** does not significantly affect the phase separation or concentration of H₂O (or base) in the THF phase.

Effective Suzuki–Miyaura polymerization reactions require faster hydrolysis of the BMIDA groups in **3** than that possible with K₃PO₄ as the base under these conditions. Metal hydroxide salts have been previously reported to give extremely rapid hydrolysis of BMIDA groups in aryl and heteroaryl MIDA boronate esters.^{8c} Replacing K₃PO₄ with KOH produced a biphasic system and importantly led to faster hydrolysis of the BMIDA groups in **3** under identical reaction conditions. Boronic acid **5** was cleanly produced from **3** (e.g., 84%

Scheme 1. Hydrolysis of **3 in THF/Water To Form **5****



and **5** are observed by multinuclear NMR spectroscopy) or the boronic acid **5** is formed and then undergoes protodeboronation. It is notable that **5** ($\delta_{11B} +26.4$ ppm, which is characteristic for a thienyl boronic acid) is stable in *d*₈-THF/D₂O solutions for days (by ¹H NMR spectroscopy); this is consistent with the enhanced stability of 2-thienyl boronic acids at neutral pH.^{8c} However, electron rich **5** undergoes rapid protodeboronation

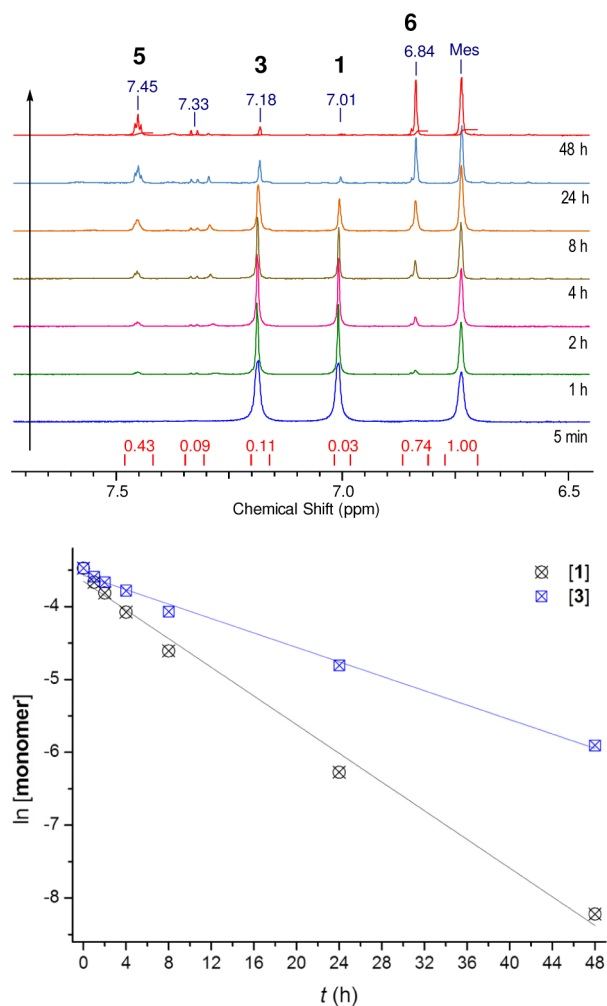


Figure 4. Hydrolysis of a 2:1 mixture of **1**/**3** in d_8 -THF/ D_2O (30 equiv relative to BMIDA)/3 equiv of K_3PO_4 (relative to BMIDA) at 55 °C. (top) 1H NMR spectra at various times; (bottom) pseudo-first-order BMIDA hydrolysis kinetics. Compound **6** is the boronic acid derived from **1**. The resonance at 7.33 ppm is 2-Br-3-hexylthiophene produced from protodeboronation of **6**.¹⁸

conversion after 3 h at 55 °C) with no protodeboronation products observed (**2** is not observed after 3 h). This indicates that KOH is a more appropriate base than K_3PO_4 for enabling release of the boronic acid from **3** at a suitable rate for polymerization under these specific biphasic conditions.

pCPDT-BT Polymerization Studies. The synthesis of pCPDT-BT from **3** and 4,7-dibromo-benzo[*c*]-1,2,5-thiadiazole, **7**, was initially attempted utilizing K_3PO_4 as base. This resulted in no significant polymer formation after 24 h at 55 °C (Table 1, entry 1) consistent with the aforementioned BMIDA hydrolysis studies. The absence of significant polymer was not due to pervasive chain termination by protodeboronation since CPDT-BMIDA groups were still present after 24 h of reaction (by NMR spectroscopy). Based on the BMIDA hydrolysis studies 2 equiv of KOH was added to this reaction mixture to accelerate the hydrolysis of the BMIDA groups, and subsequent heating for an additional 24 h now led to more effective polymerization (pCPDT-BT formed with $M_n/M_w = 10.2/21.4$ kDa). In contrast, no significant pCPDT-BT is produced in the absence of KOH even on further heating (72 h). This indicates that under these conditions (i) active thienyl boronic species derived from **3** are still present even after prolonged heating at 55 °C (with stirring at 900 rpm) in the presence of K_3PO_4/H_2O and (ii) K_3PO_4 is not an effective base for the polymerization of **3** to form high molecular weight polymer due to the slow hydrolysis of the BMIDA moieties in **3**.

Replacing K_3PO_4 with KOH under otherwise identical polymerization conditions leads to highly effective polymerization and formation of high molecular weight pCPDT-BT (entry 2), with the polymerization complete within 24 h. Investigations into the effect of KOH stoichiometry confirm that 6 equiv of KOH (relative to **3**) is optimal. Notably, changing the hydroxide salt to nBu_4NOH , which contains a cation that facilitates the phase transfer of salts into the organic phase,¹⁷ leads to significantly lower molecular weight polymer being formed in lower yield (entry 3) than that with KOH as base. Analysis of the polymerization reaction mixture containing nBu_4NOH indicated more rapid hydrolysis of BMIDA groups in **3** (relative to that with K_3PO_4 and KOH) with no BMIDA moieties remaining after 4 h of reaction, with

Table 1. Polymerization of CPDT Monomers and **7**

	method/monomer (base)	yield ^b (%)	M_n (kDa)	M_w (kDa)	ref
1 ^a	Suzuki/M = BMIDA (K_3PO_4)	12	1.5 ^c	2.7 ^c	this work
2 ^a	Suzuki/M = BMIDA (KOH)	98	42.5 ^d (21.5) ^c	130.0 ^d (40.4) ^c	this work
3 ^a	Suzuki/M = BMIDA (nBu_4NOH)	75	3.0 ^e	5.7 ^c	this work
4	Stille/M = Me_3Sn^e	80	34.0	58.0	6
5	DHAP/M = C-H ^f	40	38.2	80.0	7c
6	Suzuki/M = BPin	56	14.1	47.2	10
7	Suzuki/M = BPin	72	15.0	22.0	10
8	Suzuki/M = BPin	63	11.7	31.0	10

^a $T = 55$ °C, $[3] = 3.5 \times 10^{-2}$ M, base 6 equiv, H_2O 60 equiv, $Pd_2(dba)_3$ 2.5 mol %, SPhos 5 mol %, solvent THF, $t = 24$ h, 900 rpm stirring. ^bIsolated. ^cDetermined by GPC (THF at 35 °C, PS calibration). ^dDetermined by GPC (1,2,4-trichlorobenzene at 160 °C, PS calibration). ^eThis is a representative high M_w polymer from a Stille coupling polymerization procedure. ^fPolymer with the minimum level of homocoupling/other defects chosen.

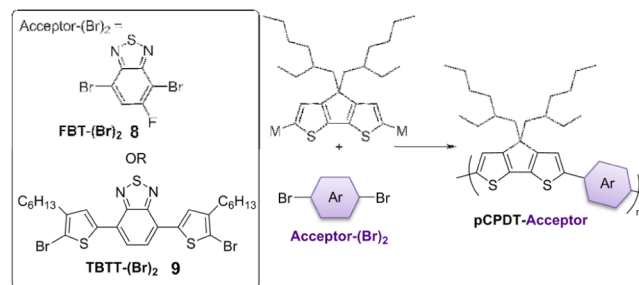
protodeboronation products also observed at this point (by multinuclear NMR spectroscopy). This disparity is presumably due to a greater concentration of base being present in THF when using $n\text{Bu}_4\text{NOH}$, with hydroxide documented to lead to rapid BMIDA hydrolysis.¹⁵ Thus, in the polymerization of **3** under these conditions hydrolysis of the BMIDA groups with K_3PO_4 as base is too slow (and incomplete even after 24 h), while with $n\text{Bu}_4\text{NOH}$ hydrolysis it is too rapid leading to competitive protodeboronation and chain termination. In contrast, the use of KOH and biphasic mixtures provides an appropriate BMIDA hydrolysis rate leading to high molecular weight pCPDT-BT in high yield.

Using 6 equiv of KOH (relative to **3**) as base, the formation of high molecular weight pCPDT-BT is essentially quantitative (entry 2) and does not require an excess of **3**, with a 1:1 ratio of monomers being effective (in contrast to Stille protocols).⁶ The $\text{C}_6\text{H}_5\text{Cl}$ Soxhlet fraction was isolated in 98% yield as a dark green solid that was not fully soluble in THF even at raised temperatures (hence M_n/M_w determined by GPC in THF at 35 °C are not representative of the actual molecular weight distribution of this polymer, whereas pCPDT-BT produced using K_3PO_4 or $n\text{Bu}_4\text{NOH}$, entries 1 and 3, are fully soluble in THF at 35 °C). Subsequent analysis in 1,2,4-trichlorobenzene at 160 °C revealed that extremely high molecular weight pCPDT-BT is formed using this methodology (entry 2). Extremely high molecular weight pCPDT-BT was obtained from several separate polymerizations run under identical conditions, confirming the reproducibility of this process. This is significant because high molecular weight pCPDT-BT ($M_n > 20$ kDa) is essential for good hole mobility.²⁰ The ^1H NMR spectrum (70 °C, $\text{C}_6\text{D}_5\text{Br}$) of this pCPDT-BT does not display any observable resonances corresponding to homocoupling linkages indicating that the polymer has extremely low defect levels. Further analysis of this polymer (and the other thienyl polymers discussed below) by MALDI-TOF spectroscopy revealed only H/H, H/Br, or Br/Br end groups, with no residual BMIDA groups observed; presumably these undergo hydrolysis and protodeboronation during quenching of the polymerization (using acidified MeOH). The UV-vis spectrum of this high molecular weight pCPDT-BT in chlorobenzene at room temperature (λ_{max} of absorption at 416 and 730 nm) was closely comparable to that reported for pCPDT-BT produced via other protocols,⁶ indicating comparable electronic properties (the other polymers discussed below also have UV-vis absorption spectra comparable to that reported for the analogous polymer produced by other synthetic methods). The formation of high molecular weight pCPDT-BT from **3** is higher yielding than that reported for producing pCPDT-BT by Stille polycondensation, which also required superstoichiometric quantities of the Me_3Sn stannylated monomer due to protodestannylation (entry 4).⁶ Furthermore, the yield of pCPDT-BT produced via **3** is higher than that of low defect pCPDT-BT made via DHAP (entry 5)^{7c} and higher than pCPDT-BT made via other Suzuki-Miyaura cross-coupling protocols from diborylated CPDT monomers (entries 6 to 8).¹⁰ Therefore, the copolymerization of **3** is an extremely effective methodology for producing pCPDT-BT of useful molecular weight, which combined with the high yielding formation of crystalline monomer **3** make this an attractive alternative to the established Stille protocols.

Extension To Form Other CPDT Copolymers. To be truly modular, a new polymerization methodology needs to be effective for a range of nucleophilic and electrophilic coupling

partners using a single set of polymerization conditions. If the rate of hydrolysis of the BMIDA moieties in **3** is the key factor in enabling effective polymerization, then the same polymerization conditions should be viable for copolymerizing **3** with different comonomers. To demonstrate this, monomer **3** was copolymerized with monomer **8**, which was selected because the resulting pCPDT-FBT polymers give excellent performance as the active component in bulk heterojunction solar cells.²¹ Analogous to the formation of pCPDT-BT, monomer **8** is polymerized effectively quantitatively to form pCPDT-FBT (Table 2, entry 1) using identical polymerization conditions to

Table 2. Copolymerization of **3 and Acceptor-(Br)₂**



	acceptor (M)	yield ^c (%)	M_n (kDa)	M_w (kDa)	ref
1 ^{a,b}	FBT (BMIDA)	95	19.4 ^d	38.2 ^d	this work
2	FBT (Me_3Sn)	67	10.1	21.5	21
3 ^{a,b}	TBTT (BMIDA)	97	35.6 ^e	63.7 ^e	this work
4	TBTT (Me_3Sn)	86	9.0	11.7	23

^a $T = 55$ °C, $[\mathbf{3}] = 3.5 \times 10^{-2}$ M, KOH 6 equiv, H_2O 60 equiv, $\text{Pd}_2(\text{dba})_3$ 2.5 mol %, SPhos 5 mol %, solvent THF, $t = 24$ h, 900 rpm stirring. ^b $\text{C}_6\text{H}_5\text{Cl}$ fraction. ^cIsolated. ^dDetermined by GPC (1,2,4-trichlorobenzene at 160 °C, PS calibration). ^eDetermined by GPC (THF at 35 °C, PS calibration).

that used for pCPDT-BT. The molecular weight of the resultant pCPDT-FBT polymer is lower than that achieved for pCPDT-BT derived from **3** possibly due to the lower solubility of pCPDT-FBT, which may lead to premature polymer precipitation during the reaction.²² Nevertheless, the molecular weight of pCPDT-FBT formed from **3** is still sufficiently high for applications, and it is formed in superior yield to that produced by Stille cross-coupling polymerization protocols (95% using **3** vs 40–67% by Stille; entry 2 is a representative example).^{21,22}

Copolymerization of **3** with monomer **9** was examined because the latter is a dibromo-heteroarene electronically distinct from **7** and **8** (an electron rich thienyl-bromide versus electron poor dibromo-benzothiadiazoles) while still being relevant for the production of high performing D–A polymers.² Furthermore, pCPDT-TBTT is a highly soluble polymer precluding any premature polymer precipitation that may have limited the molecular weight of pCPDT-FBT derived from **3**. Using identical conditions to that successful for forming high molecular weight pCPDT-BT from **3**, pCPDT-TBTT was produced in excellent yield and high molecular weight (entry 3) with both being greater than those reported for polymers produced by Stille cross-coupling reactions (entry 4 is a representative example).²³ Therefore, this polymerization protocol using monomer **3** is applicable to copolymerization reactions with a range of electronically distinct dibromo comonomers. The importance of KOH as base in achieving

appropriate slow release of the boronic acid again was confirmed using K_3PO_4 as base instead of KOH under otherwise identical polymerization conditions. This produced pCPDT-TBTT in low yield (10%) and with low M_n/M_w (4.3/5.6 kDa) after 24 h. *In situ* NMR spectroscopy at this point revealed that thienyl BMIDA moieties remained; thus slow BMIDA hydrolysis was again limiting polymerization when using K_3PO_4 under these conditions.

Extension to Other Thienyl Di-MIDA Boronate Esters.

For the formation of high molecular weight polymers derived from other thienyl MIDA boronate esters, conditions enabling an appropriate rate of BMIDA hydrolysis have to be identified. For example, the hydrolysis of BMIDA in **1** is more rapid than that in **3** and thus optimal hydrolysis conditions for **1** required K_3PO_4 and not KOH (in basic THF/water mixtures). This is exemplified by the Suzuki–Miyaura polymerization of **1** using KOH as base (under otherwise identical conditions) giving significantly poorer outcomes due to BMIDA hydrolysis being too fast and protodeboronation of the thienylboronic acid becoming a significant factor (P3HT produced from **1** with K_3PO_4 as base yield = 90%, M_n/M_w = 13.8/24.1 kDa,¹² with KOH as base yield = 47%, M_n/M_w = 10.0/14.1 kDa). Nevertheless, excluding the change in base, the polymerization of **1** and **3** both proceed under otherwise identical conditions. Therefore, the identification of highly effective polymerization conditions for any new thienyl-MIDA boronate ester monomer should only require the identification of conditions that result in appropriate BMIDA hydrolysis rates using either K_3PO_4 or KOH (at 55 °C in THF/water).

To validate this hypothesis, the synthesis of PQT12 from a thienyl di-MIDA boronate ester was investigated. PQT12 is a well-studied polymer with a number of synthetic routes previously reported; however, these generally proceed from the preformed quaterthiophene (often made via Stille cross-couplings) or from copolymerization of Me_3Sn -functionalized bithiophenes.^{7a,24–27} The required di-MIDA boronate ester monomer **10** can be synthesized and isolated as a crystalline solid (a partial connectivity map from X-ray diffraction studies for **10** is shown in Figure 5) on a multigram scale using an analogous electrophilic borylation methodology to that successful for **3**. Anhydrous work up conditions are again essential due to the hydrolysis and protodeboronation of **10** using standard isolation procedures and “wet” (nonpurified) solvents.

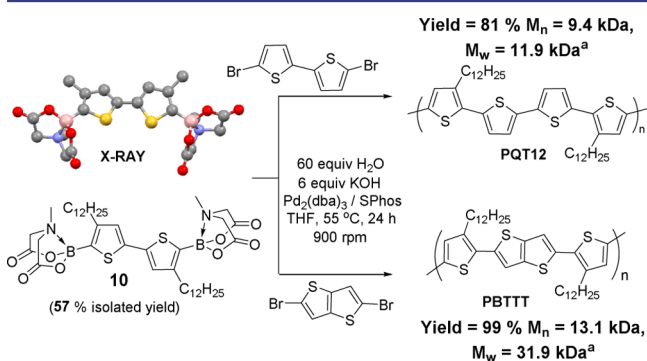


Figure 5. (left) Compound **10** (including partial solid state structure) and (right) formation of PQT12 and PBTTT from **10**; a indicates molecular weight determined by GPC at 70 °C in C_6H_5Cl , PS calibration.

Prior to commencing polymerization studies, the hydrolysis of the BMIDA moieties in **10** was explored in d_8 -THF/ D_2O (60 equiv relative to **10**) using both K_3PO_4 and KOH as the base (6 equiv relative to **10**). As expected both bases led to faster hydrolysis of the BMIDA moieties in **10** relative to those in the more electron rich **3**. Again, K_3PO_4 led to undesirably slow hydrolysis of the BMIDA moieties with a significant amount of **10** still remaining after 18 h at 55 °C. Using KOH as base led to a more desirable BMIDA hydrolysis rate for subsequent slow release polymerization applications. The copolymerization of **10** with 5,5'-dibromobithiophene (in a 1:1 monomer ratio) was explored using identical polymerization conditions as previously utilized. This resulted in a higher yield and a higher molecular weight PQT12 using KOH as the base (Figure 5) relative to PQT12 formed using K_3PO_4 as the base, fully consistent with the studies into the hydrolysis of BMIDA groups in **10**. The molecular weight of PQT12 formed from **10** using KOH as base is good for PQT12 produced by the copolymerization of two homobifunctionalized (AA/BB type) monomers. Importantly, the PQT12 produced from **10** contains significantly more thiophene units than required to exhibit key desirable properties, with the effective conjugation length for PQT12 determined to be in the range of 22 thiophene units.²⁸ Furthermore, we reiterate that the UV–vis spectra of the thienyl polymers produced using di-MIDA boronate ester monomers are effectively identical to that reported for the analogous polymer produced by other methodologies confirming comparable electronic properties of the polymers (e.g., for PQT12 made from **10** λ_{max} = 470 nm, for PQT12 made via Stille coupling protocols λ_{max} = 470 nm, both in $CHCl_3$).²⁸

Finally, with the standard polymerization conditions demonstrated to be viable for PQT12 formation from monomer **10** the synthesis of PBTTT was investigated. PBTTT exhibits desirable properties for organic electronic applications, for example, good charge mobilities, but is generally synthesized by Stille copolymerization protocols using Me_3Sn -substituted bithiophenes.²⁹ The copolymerization of **10** with 2,5-dibromo-thieno[3,2-*b*]thiophene under identical polymerization conditions used with monomer **3** and for forming PQT12 from **10** was effective for producing PBTTT in excellent yield and good molecular weight (Figure 5).³⁰ The PBTTT produced from **10** is comparable to that produced from Stille protocols;²⁹ this further confirms the generality of this Suzuki–Miyaura polycondensation procedure.

CONCLUSIONS

In conclusion, a scalable synthesis of thienyl-di MIDA boronate esters that can be isolated as highly pure crystalline solids in good to excellent yields is reported. Reaction conditions that enable desirable BMIDA hydrolysis rates have been identified, and these have been applied for the synthesis of a range of important and electronically distinct thienyl containing alternating copolymers. The copolymers are all produced in excellent yield, have low defect levels and have high molecular weights that are comparable to the analogous copolymers produced by Stille cross-coupling protocols. Thus, thienyl di-MIDA boronate esters represent a general, environmentally benign class of monomers useful for forming a range of important alternating copolymers widely utilized in state of the art plastic electronic applications that are currently made using highly toxic trimethylstannyl functionalized monomers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b07666. Additional research data supporting this publication are available as supplementary information accompanying this publication.

Full experimental, characterization, and crystallographic details for all compounds (PDF)

Crystallographic information for 10 (CIF)

Crystallographic information for 3 (CIF)

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Notes

The authors declare no competing financial interest.

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