




CHEMISTRY

SUPPLEMENTARY-RESULT

# Cyclopentadithiophene polymers synthesised *via* Suzuki-Miyaura polymerisation of MIDA boronate esters

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## Abstract

Cyclopentadithiophene (CPDT), a  $C_{sp^3}$ -bridged bithiophene heteroaromatic unit, displays interesting properties when it is embedded in the repeating units of  $\pi$ -conjugated polymers, and they are applied in organic electronics devices. Common synthetic routes to CPDT-derived polymers rely on toxic methodologies whilst alternative non-toxic strategies such as the Suzuki-Miyaura reaction have been less studied. In this report we demonstrate that the use of a *N*-methyliminodiacetic acid (MIDA) boronate ester-derived CPDT monomer allows the efficient formation of poly(cyclopentadithiophene) homopolymer under Suzuki-Miyaura cross-coupling reaction conditions. Thus, the use of MIDA boronate esters might be extended to other organic units to design and construct a plethora of  $\pi$ -conjugated polymers.

**Keywords:** cyclopentadithiophene; MIDA boronates; Suzuki-Miyaura polymerisation

## Introduction

$\pi$ -conjugated polymers are important materials for organic electronic applications, and thienyl-derived moieties possess excellent electronic properties. A number of synthetic routes and physical properties of soluble poly(dialkylcyclopentadithiophene) polymers, **pCPDT**, a  $C_{sp^3}$ -bridged bithiophene framework, have been extensively studied (Coppo & Turner, 2005). Current use of **pCPDT** homopolymer is far less extended than its donor-acceptor copolymer analogue, *e.g.*, cyclopentadithiophene-benzothiadiazole, due to its high HOMO energy level which makes it sensitive to oxidation. Nonetheless, since the first chemical polymerisation report of dialkyl-substituted cyclopentadithiophenes to form soluble **pCPDT** (Asawapirom & Scherf, 2001) its use as active layer in organic field-effect transistors (Horie et al., 2010), organic photovoltaics (Bijleveld et al., 2010), and tuning of its bandgap *via* protonation of terminal  $\alpha$ -positions with trifluoroacetic acid (Tang et al., 2015) suggest there is room for novel applications.

Despite its non-toxic reagents and by-products, among other advantages, the Suzuki-Miyaura cross-coupling (Suzuki, 2011) remains under explored for the synthesis of thienyl-derived polymers, compared to other transition-metal catalysed cross-coupling reactions such as Kumada and Stille methodologies, partly due to the difficulty in synthesising the required organoboryl-containing monomers and their undesired protodeborylation during the cross-coupling polymerisation reaction. In this regard, *N*-methyliminodiacetic acid (MIDA) boronate esters have proven to be excellent nucleophilic partners for the Suzuki-Miyaura reaction because they can slowly deliver the reactive boronic acid under mild conditions (Burke & Gillis, 2009).

## Objective

To synthesise cyclopentadithiophene homopolymers, **pCPDT**, *via* Suzuki-Miyaura polymerisation using MIDA boronate esters as the key boron masking group in AB-type monomers, and thus demonstrate their potential as efficient substrates for the formation of thienyl-derived conjugated polymers in high yields and high polymer molecular weights.

## Methods

The Direct C-H Electrophilic Borylation synthetic methodology (Bagutski et al., 2013) was employed for the preparation of the MIDA boronate ester monomer, **1**, according to the procedure previously reported (Ayuso Carrillo et al., 2015). **pCPDT** homopolymer was prepared *via* Suzuki-Miyaura polymerisation methodology (Suzuki, 2011). Further details are provided in the Supplementary Materials.

## Results

Monomer **1** quantitatively produces **pCPDT** (99% isolated yield, crude polymer) under identical polymerisation reaction conditions that were optimised for poly(3-hexylthiophene), P3HT (Ayuso Carrillo et al., 2015). Table 1 shows polymer molecular weights recorded at different reaction times.

Suzuki-Miyaura polymerisation of **1** displayed reaction features analogously to other MIDA boronate esters, *e.g.*, slow release of the corresponding thienyl boronic acid, step-growth of polymer chains over time, high yield and high molecular weight of isolated polymer. For example, Figure 1 shows the increase of polymer molecular weights of **pCPDT** over time (Ayuso Carrillo et al., 2015; 2016; Foster et al., 2017). Likewise, the <sup>1</sup>H NMR spectra of the filtered solutions after polymer precipitation (Figure S1) showed evidence of **1** only but no deboronated monomer, after 4 h and 8 h of reaction.

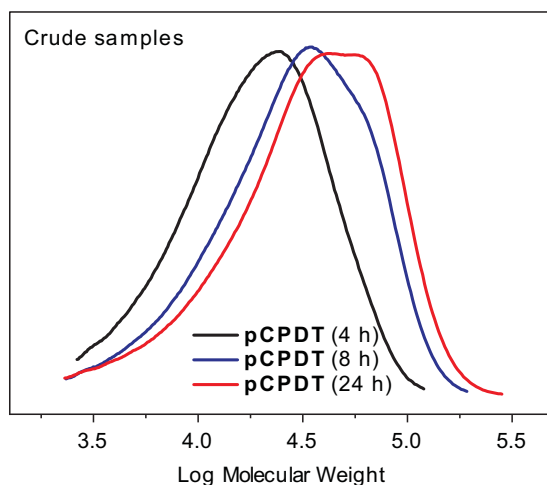
## Discussions

Combination of highly active phosphines and palladium precatalysts with cyclopentadithiophene-derived MIDA boronate ester AB-type monomers afforded **pCPDT** under mild reaction conditions. The molecular weights of isolated polymers after Soxhlet fractionation (typically producing ≥90% yield of the chloroform fraction) are superior to those reported in the literature synthesised by Yamamoto

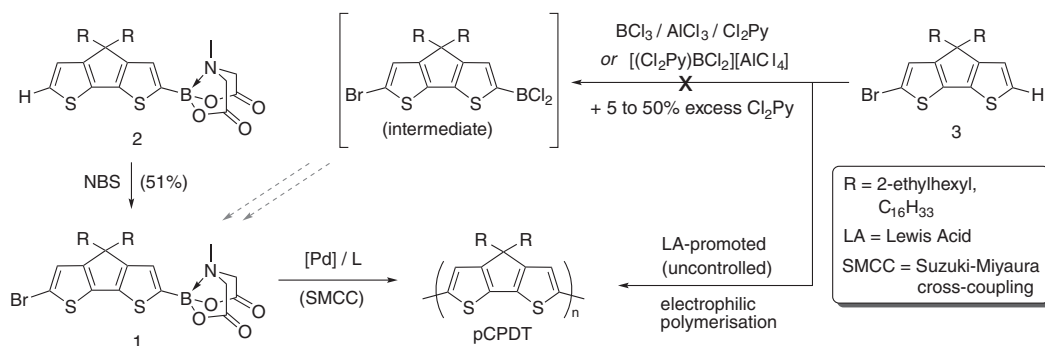
**Table 1.** Selected results from the Suzuki-Miyaura polymerisation of **1** to form **pCPDT**.<sup>a</sup>

Entry	<i>t</i> (h)	<i>M<sub>n</sub></i> <sup>b</sup> (kDa)	<i>M<sub>w</sub></i> <sup>b</sup> (kDa)	<i>D<sub>M</sub></i> <sup>b</sup>
1	4	24.6 (12.9) <sup>c</sup>	40.0 (22.7)	1.6 (1.8)
2	8	29.1 (17.4)	47.2 (35.1)	1.6 (2.0)
3	24	30.6 (19.6)	49.9 (42.5)	1.6 (2.2)

<sup>a</sup>Reaction conditions: *T*: 55 °C, [**1**] = 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 (CAS 657408-07-6): 5 mol%, Solvent: THF. <sup>b</sup>Determined by Gel Permeation Chromatography (THF at 35 °C, polystyrene calibration). Quoted values corresponding to Soxhlet-fractionated chloroform fraction after sequential extractions with methanol, and *n*-hexane, for 14 h each. <sup>c</sup>Numbers in parenthesis correspond to crude samples.



**Figure 1.** GPC traces at different times of **1**-derived pCPDT. Crude samples. Reaction conditions as in Table 1.



**Scheme 1.** Possible synthetic routes for cyclopentadithiophene-derived AB-type monomers for Suzuki-Miyaura polymerisation.

reductive polymerisation (e.g.,  $M_n = 5\text{--}9\text{ kDa}$ ,  $D_M = 1.8\text{--}2.6$ ) (Asawapirom & Scherf, 2001), oxidative polymerisation with  $\text{FeCl}_3$  (e.g.,  $M_n = 10.5\text{ kDa}$ ,  $D_M = 3.9$ ) (Horie et al., 2010), and comparable to those obtained by Kumada catalyst-transfer polymerisation (e.g.,  $M_n = 31.2\text{ kDa}$ ,  $D_M = 2.0$ ) (Willot et al., 2013).

It is noteworthy that **1** was prepared *via* a two-step synthesis (Scheme 1, left) where **2** was obtained during the purification of the diborylated cyclopentadithiophene unit *via* chromatographic column. In contrast, as shown in Scheme 1, top-right, multiple attempts to borylate **3** in a controlled fashion were unsuccessful, leading to *in situ* deborylation and uncontrolled electrophilic polymerisation of the cyclopentadithiophene fragment (see Supplementary Materials).

## Conclusions

The synthesis of soluble poly(cyclopentadithiophene) polymers employing *N*-methyliminodiacetic acid boronate ester/bromo heterobifunctionalised AB-type monomers was demonstrated. Thus, the use of MIDA boronate esters in Suzuki-Miyaura polymerisations holds a promising future for the efficient and non-toxic preparation of  $\pi$ -conjugated polymers relevant for organic electronics applications.

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**Author Contributions.** JA-C designed, performed the experiments, collected and analysed the data, and wrote the manuscript.

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**Conflict of Interest.** JA-C declares none.

**Data Availability Statement.** The data that support the findings of this study are openly available in Zenodo at <http://doi.org/10.5281/zenodo.3735473>

**Supplementary Materials.** To view supplementary materials for this article, please visit <http://dx.doi.org/10.1017/exp.2020.30>.

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# Peer Reviews

**Reviewing editor:** Dr. Feng Yan

The University of Alabama College of Engineering, Tuscaloosa, Alabama, United States, 35487-0200

Minor revisions requested

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## Review 1: Cyclopentadithiophene polymers synthesised via Suzuki-Miyaura polymerisation of MIDA boronate esters

**Reviewer:** Dr. Ullrich Scherf 

Date of review: 02 April 2020

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**Conflict of interest statement.** Reviewer declares none

*Comments to the Author:* The authors report an original and new PCPDT synthesis via Suzuki-Miyaura polymerisation of MIDA boronate esters. The method is well outlined and explained. The results will be of interest and significant benefit for the community working in the synthesis of conjugated polymers especially polythiophenes. The report is, therefore, recommended for publication after some minor revision:

- (1) PCPDT synthesis via Yamamoto-type homocoupling that starts from dibromoCPDT monomers should be included into the discussion of advantages and shortcomings of the several methods that have been applied for PCPDT generation until now (see e.g. Udom Asawaprom et al. 2001, DOI: 10.1002/1521-3927(20010701)22:10<746::AID-MARC746>3.0.CO;2-H).
- (2) Please add the solution UV-vis spectra of the PCPDTs of entries 1-3.

### Score Card

#### Presentation



Is the article written in clear and proper English? (30%)

5/5

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5/5

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Does the introduction give appropriate context? (25%)

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Is the objective of the experiment clearly defined? (25%)

5/5

## Analysis



Does the discussion adequately interpret the results presented? (40%)

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5/5

Is the conclusion consistent with the results and discussion? (40%)

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4/5

Are the limitations of the experiment as well as the contributions of the experiment clearly outlined? (20%)

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5/5

## Review 2: Cyclopentadithiophene polymers synthesised via Suzuki-Miyaura polymerisation of MIDA boronate esters

Reviewer: Dr. Andrew Foster 

The University of Manchester, Manchester, United Kingdom of Great Britain and Northern Ireland, M13 9PL

Date of review: 22 June 2020

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**Conflict of interest statement.** Reviewer has written paper with author on the use of N -methyliminodiacetic acid boronate esters in Suzuki-Miyaura cross-coupling polymerizations of triarylamine and fluorene monomers.

*Comments to the Author:* Author has presented a further utilisation of MIDA boronate esters in Suzuki Miyaura polymerizations to produce poly(cyclopentadithiophene) homopolymer. The use of MIDA boronate esters could be applicable to creating a range of pi-conjugated polymers. It would be worthwhile to reference in the introduction the other non-thienyl publication which has made use of MIDA boronate esters in Suzuki Miyaura polymerizations. There was also one minor error in text of the manuscript. Line 9. I think it should read 'when it is embedded' or alternatively 'when embedded'.

### Score Card

#### Presentation



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5/5

Is the data presented in the most useful manner? (40%)

5/5

Does the paper cite relevant and related articles appropriately? (30%)

4/5

#### Context



Does the title suitably represent the article? (25%)

5/5

Does the abstract correctly embody the content of the article? (25%)

5/5

Does the introduction give appropriate context? (25%)

4/5

Is the objective of the experiment clearly defined? (25%)

5/5

#### Analysis



Does the discussion adequately interpret the results presented? (40%)

5/5

Is the conclusion consistent with the results and discussion? (40%)

5/5

Are the limitations of the experiment as well as the contributions of the experiment clearly outlined? (20%)

5/5