

**Investigation of Green and Sustainable Solvents for Direct  
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## Investigation of Green and Sustainable Solvents for Direct Arylation Polymerization (DARp)

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Direct arylation polymerization (DARp) is an emerging method for conjugated polymer synthesis. It alleviates typical synthetic routes from toxic, hazardous materials, such as pyrophosphoric organolithium or highly-toxic stannane reagents. The progress and development of synthetic methodologies for DARp have allowed for the preparation of conjugated polymers with a minimization or exclusion of undesired couplings, such as branching ( $\beta$ ) defects and donor-donor or acceptor-acceptor homocouplings. This has allowed for conjugated polymers prepared using DARp to converge upon or surpass the performance of polymers prepared using conventional polymerization methods, e.g. Stille or Suzuki, when integrated into polymer bulk-heterojunction solar cells. Considering that DARp has the potential to become the industrial-scale method for conjugated polymer synthesis, determining the compatibility of environmentally benign, non-hazardous, and low-cost solvents with DARp is imperative. Herein, we report the application of green and sustainable solvents, such as 2-methyltetrahydrofuran, cyclopentyl methyl ether, diethylcarbonate, and  $\gamma$ -valerolactone, for DARp towards the preparation of poly[(2,5-bis(2-hexyldecyloxy)phenylene)-alt-(4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole)] (PPDTBT) and poly(3-hexylthiophene) (P3HT), where optimal conditions are derived based on the molecular weight, yield, and characterization (NMR, XRD, and UV-vis) for the aforementioned polymers. We find that cyclopentyl methyl ether (CPME) provides the best polymerization products with an  $M_n$  up to 41 kDa for PPDTBT and with yields up to 98%, which is the highest reported to our knowledge for this polymer prepared using DARp. Application of CPME to P3HT resulted in  $M_n$  values of 12 kDa with 93% regio-regularity (RR) and no detectable  $\beta$ -defects.

### Introduction

Conjugated polymers have demonstrated significant potential as alternative materials to inorganic semiconductors, which can have energy intensive syntheses or contain highly toxic constituents, for applications including photovoltaics (PV), thin-film transistors (TFT), light-emitting diodes (LED), chemical sensors, and in the biomedical sector.<sup>1–6</sup> Unfortunately, the efforts to obtain high-performance with conjugated polymers, such as power conversion efficiency (PCE) in the case of PV applications, have seemingly clouded the focus of the field.<sup>7,8</sup> Rather than pursuing conjugated polymer targets that may offer a streamlined, low-cost synthetic pathway along with high-performance, the polymers pursued require numerous synthetic steps to yield the desired monomers. Likewise, of the numerous transition metal catalyzed polycondensations, such as Stille, Suzuki, or Negishi, most require the implementation of cryogenic conditions,

pyrophoric reagents, and the use of toxic, heavy-metals.

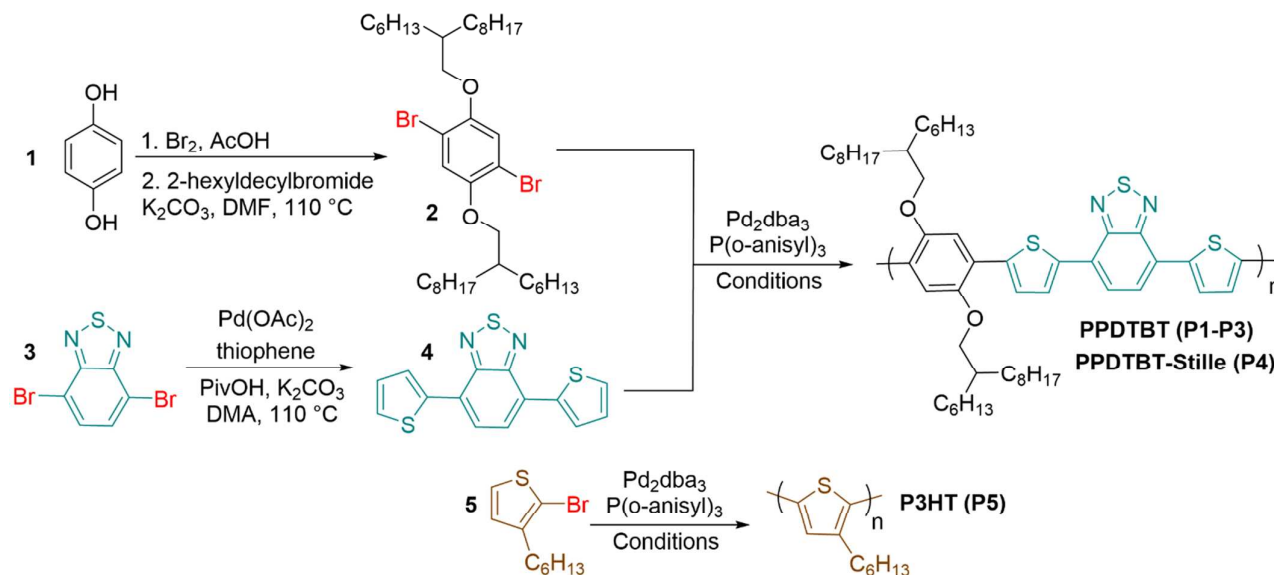
To contrast with most of the widely employed transition

Common Solvents for DARp	Xylenes	Toluene	THF	DMF	DMA
Energy Required for Production (MJ/kg)	72.5	80.0	270.8	91.1	N/A
Non-Toxic	X	X	X	X	X
Green Solvents Studied for Direct Arylation	2-MeTHF	CPME	GVL	DEC	

Figure 1. Commonly used solvents for DARp with the energy required for production (MJ/kg) and indication of toxicity (top). Green solvents in this study tested for efficacy in DARp (bottom).

catalyzed polymerizations, direct arylation polymerization (DARp) has become a successful method for the preparation of conjugated polymers, which circumvents the necessity for cryogenic conditions, pyrophoric reagents, and toxic tin byproducts.<sup>9–14</sup> This methodology has even been incorporated into continuous flow systems allowing for large-scale preparation of conjugated polymers in a safe, effective, and reproducible manner.<sup>15,16</sup> However, to firmly establish DARp as the most environmentally benign pathway for conjugated

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**Scheme 1.** Synthesis of PPDTBT from 1 and 3 using a variety of conditions listed in Table 1, and synthesis of P3HT (P5) using optimized conditions listed in Table 3.

polymer synthesis, the conditions themselves need to be assessed and more sustainable and benign alternatives for solvents and additives need to replace current reagents. Regarding this point, very little has been done. Many of the solvents used for DARP require energy intensive processes for their synthesis and purification, as shown in Figure 1 for xylenes, toluene, THF, DMF, and DMA, with all of those solvents possessing a high level of toxicity. To our knowledge, there are only a few examples of the implementation of green solvents in DARP. Illustrated in Figure 1, Sommer et al. introduced methyltetrahydrofuran (2-MeTHF) as a solvent, which was then used by Marks et al.<sup>17,18</sup> Also, Leclerc et al. showed that water with the addition of a phase-transfer agent can be incorporated into the reaction, but requires the presence of an organic co-solvent, such as toluene.<sup>19</sup> Ozawa et al. employed cyclopentylmethyl ether (CPME) for DARP, but did not obtain optimal results with this solvent.<sup>20</sup>

Conversely, there has been extensive study regarding the role of environmentally benign, green solvents for small-molecule direct arylation, but likely due to foreseen challenges in terms of polymer solubility there has been little application of such solvents to conjugated polymer synthesis.<sup>21–24</sup> Solvents studied for the preparation of biaryl compounds and the other small-molecule compounds include: ethyl acetate and water mixtures, carbonates, and cyclopentyl methyl ether (CPME).<sup>23–25</sup> Because of this apparent lack of research and focus in the field of DARP, we felt compelled to study solvents that can be considered more environmentally benign than those widely used, such as the ones listed in Figure 1. Solvents for this study were selected based on whether they can be considered as derived from renewable resources or if they require low-levels of processing and refinement for their production.<sup>26,27</sup>

A green, sustainable solvent that presents itself as a suitable replacement for the common solvents employed for conjugated polymer syntheses is cyclopentyl methyl ether

(CPME).<sup>20</sup> In comparison to many ethereal solvents, including 2-methyl tetrahydrofuran (2-MeTHF), CPME provides several merits furthering DARP's environmental compatibility.<sup>25,28,29</sup> For example, it can be manufactured by the addition of methanol to cyclopentene in a waste-free process. It also has a high hydrophobicity allowing for ease of water removal, a low-level of peroxide formation, a high stability under acidic/basic conditions, and a narrow explosion range.

A conjugated polymer that coincides with the tenets of sustainable chemistry is poly[2,5-bis(2-hexyldecyloxy)phenylene-alt-(4,7-dithiophen-2-yl)benzo[c][1,2,5]thiazole] (PPDTBT), shown in Scheme 1.<sup>30</sup> This polymer can be easily prepared in only a few steps from commercially available reagents, and has shown great promise for solar-cell applications with a power conversion efficiency (PCE) of 3.5% in large-area, roll-to-roll (R2R) processed devices.<sup>15</sup> It offers a stark contrast to many of the high-performing conjugated polymers currently being studied for PV applications, which require stringent, air and moisture free processing conditions and toxic additives to achieve high-efficiency in only small-area solar cell devices. Thus, PPDTBT is the perfect candidate for study in regard to applying green solvents to DARP reaction conditions. Another polymer that shares these attributes is poly(3-hexylthiophene) (P3HT), shown in Scheme 1. P3HT has shown great promise in numerous applications outside of PV, making it a ubiquitous material for the organic electronics community. Also, P3HT has been well characterized spectroscopically allowing for a direct analysis for branching ( $\beta$ ) defects.<sup>31,32</sup>

Herein, we report the synthesis and optimization of PPDTBT using the green, sustainable solvents CPME, 2-MeTHF,  $\gamma$ -valerolactone (GVL), and diethylcarbonate (DEC). Other carboxylate additives other than neodecanoic acid (NDA) are

also explored, including the industrially relevant naphthenic acid (NPA) and bismuth neodecanoate (BiNDA). Although they are not necessarily more green or sustainable than the commonly employed NDA or pivalic acid, additives such as NPA require much less refinement.<sup>33</sup> Also, BiNDA offers an interesting opportunity to investigate carboxylate derivatives as an additive, something which has not broadly pursued for DARp, to our knowledge.<sup>34</sup> We found that CPME provided optimum results affording PPDTBT with a  $M_n$  of 41 kDa and a yield of 78%, vastly improving upon the high-pressure THF conditions previously reported (15 kDa and 78%).<sup>30</sup> Application of CPME towards the synthesis of P3HT via DARp was then performed, affording a polymer product with 93% regio-regularity (RR), a  $M_n$  of 12 kDa, and no detected  $\beta$ -defects. We believe based on these results CPME has great potential to overtake the common, hazardous solvents employed for DARp, allowing this methodology to become a truly competitive alternative for conventional conjugated polymer synthetic methods. Structural analysis for the polymers was performed using <sup>1</sup>H NMR spectroscopy, absorbance spectroscopy, and GIXRD for which all information is provided in the electronic supporting information (ESI).

## Experimental

All reactions were performed under dry N<sub>2</sub> in oven dried glassware. Unless otherwise noted, all reagents were purchased and used as received from commercial sources. Solvents were purchased from VWR and used without purification. Anhydrous, unstabilized cyclopentyl methyl ether (CPME) was purchased and used as received. Cs<sub>2</sub>CO<sub>3</sub> was ground into a fine powder and dried at 120 °C in a vacuum oven before use. Tetrahydrofuran (THF) was dried over sodium/benzophenone before distillation. 2-MeTHF was dried over CaH<sub>2</sub> and distilled onto activated molecular sieves (3 Å) prior to use. Diethylcarbonate (DEC) and  $\gamma$ -Valerolactone (GVL) were stirred with K<sub>2</sub>CO<sub>3</sub> and distilled onto activated molecular sieves (3 Å) prior to use. 1,4-dibromo-2,5-bis[(2-hexyldecyl)oxy]-benzene (2), 4,7-di-2-thienyl-2,1,3-benzothiadiazole (4), and 2-bromo-3-hexyl-thiophene (5) were prepared following literature procedures. All NMR were recorded at 25 °C using CDCl<sub>3</sub> on either a Varian Mercury 400 MHz, Varian VNMRS-500 MHz, or a Varian VNMR-600 MHz. All spectra were referenced to CHCl<sub>3</sub> (7.26 ppm), unless otherwise noted. PPDTBT prepared using Stille polycondensation (P4) was previously synthesized following literature procedure ( $M_n$  = 65 kDa and  $\bar{D}$  = 1.98).<sup>30</sup>

Number average molecular weight ( $M_n$ ) and polydispersity ( $\bar{D}$ ) were determined by size exclusion chromatography (SEC) using a Viscotek GPC Max VE 2001 separation module and a Viscotek Model 2501 UV detector, with 70 °C HPLC grade 1,2-dichlorobenzene (o-DCB) as eluent at a flow rate of 0.6 mL/min on one 300 × 7.8 mm TSK-Gel GMHHR-H column (Tosoh Corp). The instrument was calibrated vs. polystyrene standards (1050–3,800,000 g/mol), and data were analysed using OmniSec 4.6.0 software. Polymer samples were dissolved in HPLC grade o-dichlorobenzene at a concentration of 0.5 mg

mL<sup>-1</sup>, stirred at 65 °C until dissolved, cooled to room temperature, and filtered through a 0.2  $\mu$ m PTFE filter.

For polymer thin-film measurements, solutions were spin-coated onto pre-cleaned glass slides from o-dichlorobenzene (o-DCB) solutions at 7 mg/mL, which were then annealed at 150 °C for 30 minutes under N<sub>2</sub>. UV-vis absorption spectra were obtained on a Perkin-Elmer Lambda 950 spectrophotometer. Thicknesses of the samples and grazing incidence X-ray diffraction (GIXRD) measurements were obtained using Rigaku diffractometer Ultima IV using a Cu K $\alpha$  radiation source ( $\lambda$  = 1.54 Å) in the reflectivity and grazing incidence X-ray diffraction mode, respectively. Crystallite size was estimated using Scherrer's equation:

$$\tau = K\lambda/(\beta \cos\theta) \quad (1)$$

where  $\tau$  is the mean size of the ordered domains,  $K$  is the dimensionless shape factor ( $K$  = 0.9),  $\lambda$  is the x-ray wavelength,  $\beta$  is the line broadening at half the maximum intensity (FWHM) in radians, and  $\theta$  is the Bragg angle.

### General procedure for PPDTBT synthesis using a high-pressure vessel.

An oven-dried 15 mL high pressure vessel equipped with a stir-bar was stoppered with a rubber-septum and cooled under a flow of N<sub>2</sub>. 2 (0.25 mmol), 4 (0.25 mmol), carboxylic acid additive (1 equiv.), Cs<sub>2</sub>CO<sub>3</sub> (3 equiv.), and P(o-anisyl)<sub>3</sub> (8 mol %) were added to the vessel. The solvent was then added to the vessel via syringe to achieve the appropriate monomer concentration, and it was degassed for 15 min. using N<sub>2</sub>. Pd<sub>2</sub>dba<sub>3</sub> (2 mol %) was then added quickly and the rubber septum replaced with a Teflon screw-cap with a rubber o-ring. The vessel was then submerged in a pre-heated oil bath (120 °C). After the polymerization (16 hours), the reaction mixture was cooled to room temperature, the product was dissolved in dichlorobenzene, and then precipitated into cold MeOH. The polymer product was filtered off and purified using Soxhlet extraction with MeOH, hexanes, and CHCl<sub>3</sub>. The chloroform fraction was concentrated and precipitated into cold methanol, the solid filtered off, and then dried overnight under vacuum.

### General procedure for PPDTBT synthesis using a Schlenk-tube.

An oven-dried 15 mL Schlenk-tube equipped with a stir-bar was stoppered with a rubber-septum and cooled under a flow of N<sub>2</sub>. 2 (0.25 mmol), 4 (0.25 mmol), carboxylic acid additive (1 equiv.), Cs<sub>2</sub>CO<sub>3</sub> (3 equiv.), and P(o-anisyl)<sub>3</sub> (8 mol %) were added to the vessel. The vessel was then vacuum-backfilled with N<sub>2</sub> 3 times. The solvent was then added to the vessel via syringe to achieve the appropriate monomers' concentration, and it was degassed for 15 min. using N<sub>2</sub>. Pd<sub>2</sub>dba<sub>3</sub> (2 mol %) was then added quickly. The vessel was then submerged in a pre-heated oil bath (120 °C). After the polymerization, the reaction mixture was cooled to room temperature, the product was dissolved in dichlorobenzene, and then precipitated into cold MeOH. The polymer product was filtered

off and purified using Soxhlet extraction with MeOH, hexanes, and CHCl<sub>3</sub>. The chloroform fraction was concentrated and precipitated into cold methanol, the solid filtered off, and then dried overnight under vacuum.

### General procedure for P3HT synthesis using a High-Pressure Vessel.

Similar to that of PPDTBT, but with 0.8 mmol of 5, 4 mol % Pd<sub>2</sub>dba<sub>3</sub>, 16 mol % P(o-anisyl)<sub>3</sub>, carboxylic acid additive (1 equiv.) and 3 equiv. of Cs<sub>2</sub>CO<sub>3</sub>.

## Results and Discussion

Depicted in Scheme 1, PPDTBT was synthesized under a variety of different conditions from 2 and 4 with the outcomes reported in Table 1. For every entry in Table 1, the palladium source (Pd<sub>2</sub>dba<sub>3</sub>), the phosphine ligand (P(o-anisyl)<sub>3</sub>), and the base (Cs<sub>2</sub>CO<sub>3</sub>) remained constant throughout this study.<sup>20,30,31,35,36</sup> Variations in the conditions include solvent, temperature, reaction vessel, and carboxylate/carboxylic acid additive. The purpose of these variations was to find the optimal condition set, in terms of providing a high value for molecular weight (M<sub>n</sub>) and yield (%).

We have previously reported on the high-pressure conditions using THF for the synthesis of PPDTBT (Entry 1), which were originally described by Ozawa et al.<sup>20</sup> While these conditions have proven successful for a variety of substrates, a pressurized reaction vessel with THF presents a toxic, hazard not amenable to a large-scale, industrial setting.<sup>37</sup> Shown with entries 2-4 of Table 1, we initially investigated the effect of changing the solvent, in reference to the original high-pressure THF conditions that afforded PPDTBT in 78% and M<sub>n</sub> of 15 kDa (entry 1) with NDA as the additive. We found that 2-MeTHF (entry 2) provided satisfactory results with a slight improvement to THF with a yield of 81 % and an M<sub>n</sub> of 17 kDa. For CPME, which has a boiling point of 106 °C, it was found that a high-pressure setting (120 °C in a high-pressure vessel for 16 hours) was unsuccessful and no polymer product was obtained. It is possible that the temperature employed (120 °C) and reaction time (16 hours) are not adequate for CPME in a high-pressure setting to provide isolable polymer product via precipitation. Any temperatures excessively higher than 120 °C are likely to result in decomposition of the catalyst.<sup>20,38,39</sup> We found that CPME at 120 °C can provide a higher M<sub>n</sub> (30 kDa) and yield (94%) when a Schlenk-tube is employed as the reaction flask and the reaction time extended to 72 hours (entry 4). With both THF and 2-MeTHF, significant amounts of polymer precipitate from the reaction after only 16 hours and so it is not believed that extending the reaction time for those solvents will improve the M<sub>n</sub> or yield significantly. Unfortunately, the carbonate-based solvents GVL and DEC did not provide any polymer product (entries 3 and 5). This is perhaps due to incompatibility with the catalytic system or monomers employed. At the time of study, it was reported that GVL can undergo ring-opening polymerizations with alkaline earth metal carboxylate salts.<sup>40</sup> This was indeed

observed with Cs<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>, but not with Na<sub>2</sub>CO<sub>3</sub>. However, no polymerization occurred to afford PPDTBT with Na<sub>2</sub>CO<sub>3</sub> as the base and GVL as the solvent, likely in part due to the low basicity of Na<sub>2</sub>CO<sub>3</sub>.

**Table 1.** Conditions explored for PPDTBT synthesis. All polymerizations used Pd<sub>2</sub>dba<sub>3</sub> as the palladium source, P(o-anisyl)<sub>3</sub> as the phosphine ligand, and Cs<sub>2</sub>CO<sub>3</sub> as the base. Concentrations were 0.4 M and performed in a high-pressure vessel unless otherwise noted.

Entry	Solvent (M)	Additive	Yield (%) <sup>[a]</sup>	M <sub>n</sub> (Đ) <sup>[a]</sup>
1 <sup>[b]</sup>	THF	NDA	78	15 (2.1)
2	2-MeTHF	NDA	81	17 (2.84)
3	GVL	NDA	-	-
4 <sup>[c]</sup>	CPME	NDA	94	31 (4.00)
5	DEC	NDA	-	-
6	THF	BiNDA	87	30 (3.47)
7	2-MeTHF	BiNDA	78	12 (1.78)
8 <sup>[c]</sup>	CPME	BiNDA	98	29 (4.80)
9	THF	NPA	95	22 (3.63)
10	2-MeTHF	NPA	78	12 (2.0)
11 <sup>[c]</sup>	CPME	NPA	82	27 (4.10)
12 <sup>[c,d]</sup>	CPME	NDA	78	41 (4.10)

<sup>a</sup>Measured after polymer purification. <sup>b</sup>Reference 30. <sup>c</sup>Used Schlenk-Tube. <sup>d</sup>Modified conditions of 1 mol % Pd<sub>2</sub>dba<sub>3</sub>, 4 mol% P(o-anisyl)<sub>3</sub>, and 0.8 M concentration.

From these results we then decided to study the effect of changing the acid additive from NDA to either BiNDA or NPA, which both contain carboxylates/carboxylic acids with bulky substituents like NDA. Interestingly, BiNDA provided an improved yield (87%) and M<sub>n</sub> (30 kDa) for THF (entry 6) in comparison to entry 1, while that for CPME (entry 8) shows a similar yield (98%) and M<sub>n</sub> (29 kDa) to that when NDA is employed (entry 4). 2-MeTHF (entry 7) shows a diminished yield (78%) and M<sub>n</sub> (12 kDa) compared to when NDA is used (entry 2). Relative to entry 1, NPA provided an improved yield (95%) and M<sub>n</sub> (22 kDa) for THF (entry 9). For 2-MeTHF (entry 10), NPA provided similar results to that of BiNDA (entry 7) with an M<sub>n</sub> of 12 kDa and a yield of 78%. For CPME (entry 11), both the yield (82%) and M<sub>n</sub> (27 kDa) diminished relative to that of when BiNDA (entry 8) or NDA (entry 4) are used. It is interesting to note the relationship between the solvent and carboxylate additive to the outcome of the polymerization, specifically in regard to M<sub>n</sub> and yield. This is most notable with THF when comparing entries 1, 6, and 9. However, at this time, it is unclear the exact effect of the acid additive on the yield and M<sub>n</sub>, since the acid additive plays an intricate role in the mechanistic pathway for DArP, such as in the concerted metalation deprotonation (CMD) step.<sup>41</sup>

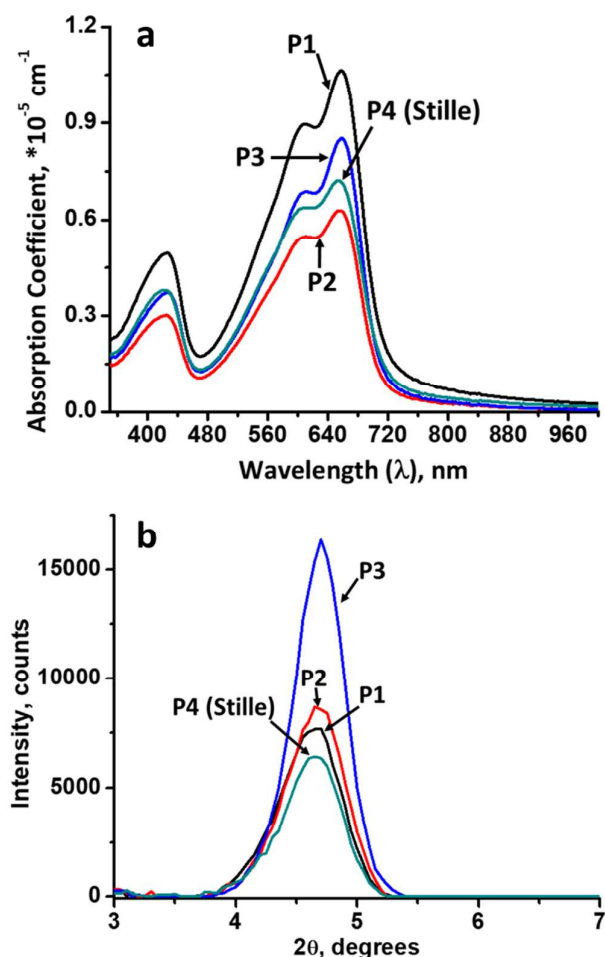


Figure 2. (a) Absorption profiles of PPDTBT polymers P1-P4. (b) GIXRD patterns for PPDTBT polymers P1-P4.

Table 2. (a) Absorbance spectra for PPDTBT polymers P1-P4. (b) GIXRD patterns for PPDTBT polymers P1-P4.

Entry	Conditions Used (Table 1)	$\lambda_{\max}$ (nm) <sup>a</sup> ; $\alpha$ (cm <sup>-1</sup> ) <sup>a</sup>	$d_{100}$ (Å) <sup>a</sup>	Crystallite Size (nm) <sup>a</sup>
P1	Entry 12	658; $107 \times 10^3$	18.8	14.7
P2	Entry 2	658; $63 \times 10^3$	19.0	15.3
P3	Entry 6	654; $85 \times 10^3$	18.8	17.5
P4 <sup>b</sup>	Stille	656; $72 \times 10^3$	19.0	15.5

<sup>a</sup>Measured on polymer films prepared from a 7 mg/mL DCB solution and annealed at 150 °C for 30 minutes. <sup>b</sup> $M_n$  = 65.0 kDa,  $\bar{D}$  = 1.96.

Since CPME consistently provided the best  $M_n$  and a good yield, we aimed to further improve upon the conditions of this solvent. We found that by increasing the concentration from 0.4 M to 0.8 M we were able to achieve a much higher  $M_n$  of 41 kDa, although the yield decreased to 78%.

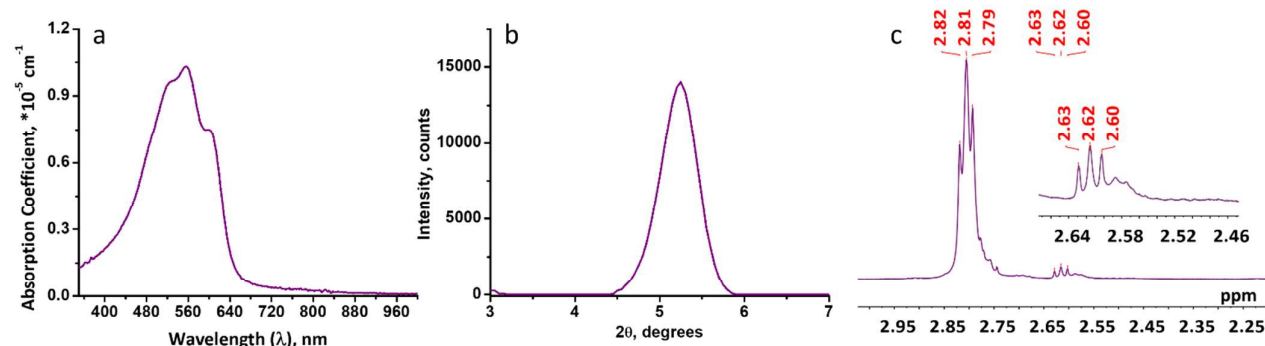
In regards to structural analysis, <sup>1</sup>H NMR spectroscopy, UV-vis absorbance spectroscopy, and GIXRD were used to

compare the synthesized PPDTBT polymers with those previously reported using DArP and Stille. The analysis was performed for the most satisfactory polymer products, which provided the highest  $M_n$  for the different solvents studied. Specifically, entries 12, 2, and 6 from Table 1 were analysed and are labelled as P1, P2, and P3, respectively. The <sup>1</sup>H NMR spectra (see ESI) for these materials matched that of the previously reported PPDTBT prepared using DArP, with no observable deviation.<sup>30</sup>

The absorbance spectra for polymers P1-P3 are shown in Figure 1a with a Stille-PPDTBT (P4) for reference ( $M_n$  = 65 kDa and  $\bar{D}$  = 1.96). The absorption profiles for DArP polymers P1-P3 all match that of P4 (656 nm), with a  $\lambda_{\max}$  ranging from 654-658 nm for the polymers P1-P3. A vibronic shoulder is apparent for all of the polymers, indicating a minimization, if not exclusion, of  $\beta$ -defects. The absorption coefficients ( $\alpha$ ) for polymers P1-P3 all appear to follow a trend based on the  $M_n$  value. P1, with the highest value for  $M_n$  at 41 kDa, possesses the largest value for  $\alpha$  ( $107 \times 10^3$  cm<sup>-1</sup>, Table 2), while P2, with the lowest value for  $M_n$  (between polymers P1-P3) at 17 kDa has the smallest value for  $\alpha$  ( $63 \times 10^3$ ). Interestingly, DArP polymers P1 and P3 have larger values for  $\alpha$  than the Stille-PPDTBT, P4. This may be due to trace metallic residues or structural irregularities from Stille polymerization in P4 causing poor interactions between polymer chains that help facilitate light absorbance.<sup>42-44</sup>

Shown in Figure 2b, the diffraction patterns from GIXRD shows a similar  $d_{100}$  spacing for polymers P1-P4. This similarity in the lamellar spacing for the materials is expected since the alkyl chains on the dialkoxyphenylene donor are the same for all of the PPDTBT polymers studied. Crystallite size for polymers P1-P4 were calculated using the Scherrer equation (see ESI for  $2\theta$  and FWHM values). The crystallite size for polymers P1, P2, and P4 are all relatively similar (14.7-15.5 nm), while that for P3 is slightly larger (17.5 nm). This and the apparent larger degree of crystallinity for P3 may suggest improved morphological purity of the polymer sample allowing for increased crystalline domain sizes and abundance, given that the polymer products were all subjected to identical conditions for purification and film preparation.<sup>45-47</sup> We suspect this improvement in semi-crystallinity could be due to the employment of BiNDA as the additive. However, investigations regarding this are still ongoing, since the specific reason the additive can enhance semi-crystallinity is still uncertain.

Because CPME provided the best results both in yield and  $M_n$  for PPDTBT, we were interested to see its effect toward the synthesis of P3HT. Also, while PPDTBT is a well characterized polymer, especially using different DArP protocols, the complexities associated with its structure and potential defects arising from such do not allow for as thorough of analysis as P3HT, for example.



**Figure 3.** (a) Absorption spectrum of P3HT (P5) synthesized in table 2 (entry 3). (b) GIXRD diffraction pattern for P3HT (P5). (c) Determination of the regio-regularity (RR) of P3HT synthesized using DArP via  $^1\text{H}$  NMR spectroscopy. Collected in  $\text{CDCl}_3$  at 25 °C and 600 MHz.

**Table 3.** Conditions explored for P3HT synthesis. All polymerizations used  $\text{Pd}_2\text{dba}_3$  as the palladium source,  $\text{P}(\text{o-anisyl})_3$  as the phosphine ligand, CPME as the solvent, and  $\text{Cs}_2\text{CO}_3$  as the base.

Entry	Yield (%) <sup>[a]</sup>	$M_n$ (Đ) <sup>[a]</sup>	Concentration (M)	Catalyst mol %	Time (hours)	$\lambda_{\text{max}}$ (nm) <sup>b</sup> ; $\alpha$ ( $\text{cm}^{-1}$ )	$d_{100}$ (Å) <sup>b</sup>	Crystallite Size (nm) <sup>b</sup>
1	0	-	0.8	1	72	-	-	-
2	insoluble	-	0.2	4	72	-	-	-
3	34	12 (1.30)	0.2	4	24	555; $103 \times 10^3$	16.8	17.0

<sup>a</sup>Measured after polymer purification. <sup>b</sup>Measured on polymer films prepared from a 7 mg/mL DCB solution and annealed at 150 °C for 30 minutes.

The defect-analysis regarding P3HT has been well-studied, and offers another handle for evaluating the efficacy of a new DArP synthetic method to provide the minimization or absence of defects.

However, because of the physical property differences, e.g. solubility, between P3HT and PPDTBT, the direct translation of the conditions used for PPDTBT synthesis was not successful, shown in Table 2. Specifically, the high-concentration (0.8 M) and low catalyst-loading (1 mol %) found successful for PPDTBT did not afford any polymer product for P3HT (entry 1). Also, it was found that lowering the concentration (0.2 M) and raising the catalyst loading (4 mol %) only afforded insoluble polymeric material that could not be characterized. Either the  $M_n$  was too high to allow for solubility or the polymer had high levels of embedded defects, such as  $\beta$ -defects (entry 2). However, when the reaction time was decreased from 72 hours to 24 hours we were able to obtain isolable polymer product with a yield of 34% and 12 kDa, and no insoluble material was observed (entry 3). It is possible that more extensive optimizations can be carried out for the synthesis of P3HT to improve the yield and  $M_n$ , but we only wished to see if CPME can be successfully employed for the synthesis of P3HT with a minimization of defects.

The value for  $\lambda_{\text{max}}$  (555 nm) and  $\alpha$  ( $103 \times 10^3 \text{ cm}^{-1}$ ) show agreement with previous reports of P3HT synthesized using DArP and Stille, depicted in Figure 3a and 3b, respectively as

well as the values for  $d_{100}$  (16.8 Å).<sup>31</sup> Shown in Figure 3c, the regio-regularity of the synthesized P3HT (P5) was determined using  $^1\text{H}$  NMR spectroscopy ( $\text{CDCl}_3$ , 25 °C). The RR was determined using previously described methods, calculated by determining the ratio of the integrals spanning from  $\delta$  (ppm) 2.90-2.65 and 2.90-2.40. Based on this ratio, the RR was found to be 93%, and the presence of  $\beta$ -defects (62.35) were not observed.<sup>31,32</sup> Also, the presence of a vibronic shoulder (Figure 3a) and the value for  $d_{100}$  (16.8 Å) indirectly show the absence or an undetectable level of  $\beta$ -defects for the synthesized P3HT.<sup>31</sup> This value for RR is similar to that obtained with other ethereal solvents, such as THF and 2-MeTHF, at 120 °C, which were 93.8% and 96.2% RR, respectively.<sup>31</sup> It is possible that more extensive optimization may allow for improved RR, such as lowering the catalyst loading or changing the catalyst. These results, however, provide support for CPME to produce polymer products with a very low to undetectable level of defects. Furthering the scope of CPME towards the synthesis of other conjugated polymers using DArP will likely take some optimization, in regard to temperature and time, but this solvent successfully presents itself as a greener, more benign alternative to solvents commonly employed.<sup>48</sup>



## Conclusions

In summary, we report the application of green, sustainable solvents towards the synthesis of PPDTBT and P3HT via DARp. Solvents studied include 2-MeTHF, CPME, GVL, and DEC. The additives BiNDA and NPA were also evaluated for their ability to produce quality polymer products, e.g. high  $M_n$  and yield. Of the solvents studied we found that CPME provided the best results towards the synthesis of PPDTBT, affording polymer product with  $M_n$  of 41 kDa and a yield of 78%, significantly higher than the value of 15 kDa when THF is employed under the more hazardous high-pressure conditions. In regards to the additives studied, NPA and BiNDA, a solvent dependence was observed and the effect of this is still under investigation. However, BiNDA provided a major improvement in comparison to NDA for the synthesis of PPDTBT when THF is the solvent, increasing the  $M_n$  and yield from 15 kDa and 70% to 30 kDa and 87%. Application of CPME towards P3HT synthesis provided a polymer product with 93% RR and no detected  $\beta$ -defects with an  $M_n$  of 12 kDa. We believe the results here provide an initial step towards the inclusion of green solvents in DARp and further its environmental compatibility, low-cost, and reduction of chemical hazards relative to other conjugated polymer synthetic methods. Future work will seek to expand upon the scope presented here with the inclusion of other reagents and monomers that align with the principles of green and sustainable chemistry.

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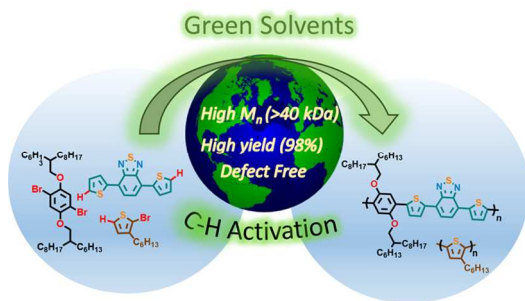


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## Graphical Abstract



Green solvents, notably cyclopentyl methylether (CPME), are found to be highly effective in Direct Arylation Polymerization (DAP).