

# Conjugated Polymers à la Carte from Time-Controlled Direct (Hetero)Arylation Polymerization

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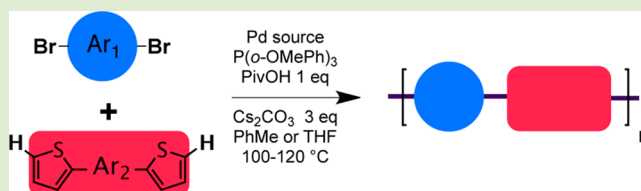
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## Supporting Information

**ABSTRACT:** Direct (hetero)arylation polymerization (DHAP) shows great promise for simple, cheap, and environmentally benign preparation of conjugated polymers, but seems to involve a lack of selectivity when different aromatic C–H bonds are present. We report that some time-controlled DHAP reactions can yield well-defined and processable semiconducting polymers. Following these procedures, various aromatic compounds have been efficiently polymerized, including 2,7-dibromofluorene, 2,7-dibromocarbazole, 1,4-dibromobenzene, bithiophene, dithienyl-benzothiadiazole, and diketopyrrolopyrrole derivatives. All resulting polymers have shown comparable, if not slightly better, properties than their Stille- and Suzuki-synthesized analogs. These findings (re)open the door for the low-cost production of many conjugated polymers for plastic electronics.



The development of plastic electronics was, and still is, strongly linked to the availability of simple, versatile, and reliable coupling procedures (e.g., Stille,<sup>1</sup> Suzuki,<sup>2</sup> Kumada,<sup>3</sup> Negishi,<sup>4</sup> etc.) to afford well-defined and reproducible polymeric semiconductors. However, these state-of-the-art methods generally involve numerous synthetic steps and costly organometallic reagents that give rise to stoichiometric amount of metallic byproducts. Cheaper and more efficient synthetic procedures would clearly be a great asset for the preparation of semiconducting organic polymers and their large-scale applications.<sup>5</sup> To solve these problems, the utilization of the latest synthetic developments in organic chemistry, termed direct (hetero)arylation reactions, seems appealing.<sup>6,7</sup> These new reactions allow the formation of carbon–carbon bonds between (hetero)arenes and (hetero)aryl halides, which do not require organometallic intermediates, thereby significantly reducing both synthetic steps and cost.<sup>8,9</sup> They also contribute to minimizing the presence of difficult-to-remove byproducts that can have a negative impact on the devices.<sup>10</sup>

Although some successful results were recently obtained with carefully chosen monomers,<sup>11–14</sup> direct (hetero)arylation polymerization (DHAP) reactions seem to suffer from a lack of selectivity when different aromatic C–H bonds are present.<sup>15–20</sup> This is a severe limitation since, with polymeric materials, structural defects cannot be removed by further purification processes; they are chemically embedded within the macromolecules. For those reasons, many important conjugated polymers were not investigated by DHAP. Clearly, the demonstration that DHAP can be efficient and selective for a large number of aromatic monomers would bring a highly valuable synthetic tool; in particular, for the low-cost, large-

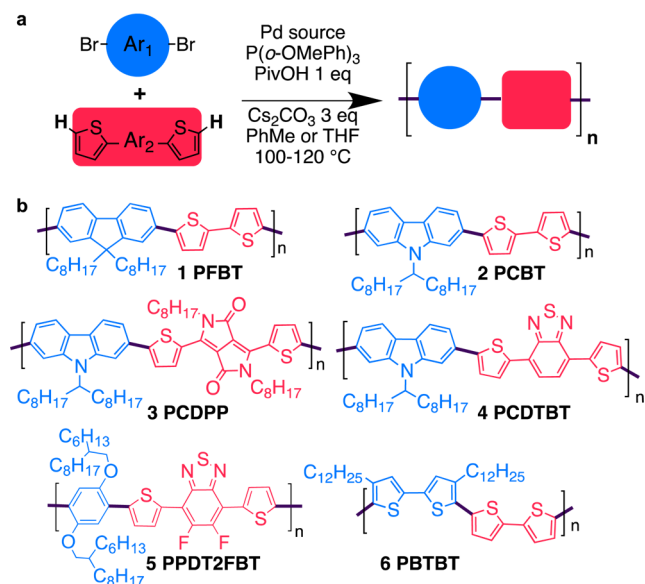
scale, and commercially viable preparation of active components in organic light-emitting diodes, field-effect transistors, solar cells, sensors, and so on.

To investigate these questions about the lack of selectivity of DHAP, we started our study with 2,2'-bithiophene. Bithiophene is one of the worst case scenarios due to the absence of an orienting group (e.g., electron withdrawing substituent) or steric protection to induce selectivity between  $\alpha$  and  $\beta$  protons. As an example, we revisited the polymerization of 2,7-dibromo-9,9-dioctylfluorene with 2,2'-bithiophene following the conditions described by Kanbara et al.<sup>19</sup> As previously reported by these authors, we obtained an insoluble polymeric material (PFBT) after 3 h of polymerization. Carrying out the reaction in a polar solvent such as dimethylacetamide (DMAc) was found to accelerate the polymerization but can also activate some unwanted positions.<sup>21,22</sup> In order to get a better control of this polymerization reaction, we carried out the reaction in toluene (THF can also be utilized), a more suitable solvent displaying inertness in the catalytic cycle.<sup>23</sup> The kinetics of this polymerization reaction was monitored under different experimental conditions (Pd sources, ligands, bases, additives, and concentrations), and general optimized procedures are shown in Figure 1. As recently reported by Ozawa et al.,<sup>23,24</sup> a carboxylate source (i.e., pivalic acid) is essential to generate a palladium carboxylate that induces C–H bond cleavages of the heteroarenes, whereas a suitable ligand is necessary to gain

Received: October 15, 2014

Accepted: December 8, 2014

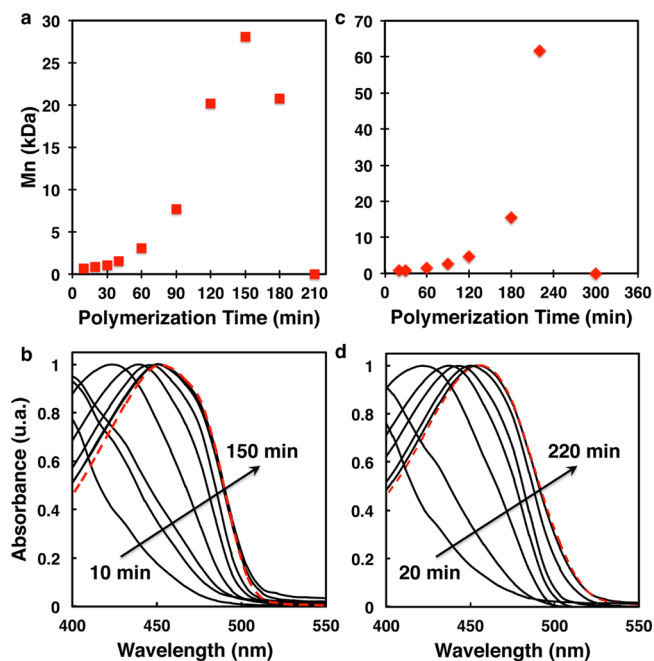
Published: December 11, 2014



**Figure 1.** Direct (hetero)arylation polymerization. (a) General conditions used for DHAP. (b) Poly(9,9-dioctyl-2,7-fluorene-*alt*-2,2'-bithiophene) (**1 PFBT**), poly(*N*-9''-heptadecanyl-2,7-carbazole-*alt*-2,2'-bithiophene) (**2 PCBT**), poly[*N*-9''-heptadecanyl-2,7-carbazole-*alt*-3,6-bis(thiophen-5-yl)-2,5-dioctyl-2,5-dihydropyrrolo[3,4]pyrrole-1,4-dione] (**3 PCDDP**), poly[*N*-9''-heptadecanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (**4 PCDTBT**), poly[(2,5-bis(2-hexyldecyloxy)phenylene)-*alt*-(5,6-difluoro-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]-thiadiazole)] (**5 PPDT2FBT**), and poly[(2,2'-bithiophene-4,4'-didodecyl)-*alt*-2,2'-bithiophene] (**6 PBTBT**).

good catalytic activity in less polar solvents such as toluene and THF.

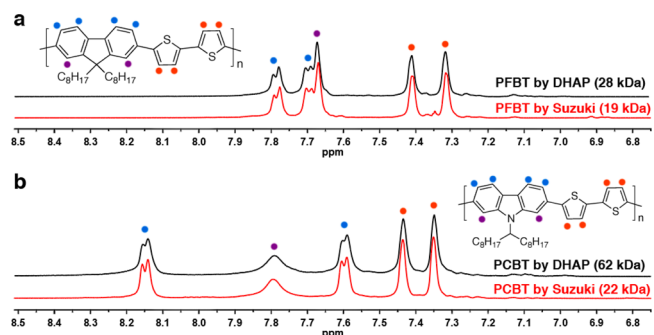
Following these conditions (see Supporting Information (SI), polymerization methods, for details), a Carothers-equation-like behavior was observed during the first 150 min of this step-growth polymerization reaction involving 2,7-dibromo-9,9-dioctylfluorene and 2,2'-bithiophene (Figure 2a). After that period of time, the reaction medium tends to form gels that could be related to a lack of solubility of the growing polymer chains. After 210 min, only insoluble materials were recovered. This insolubility could be related to the formation of too high molecular weight polymers or to the formation of cross-linked materials. Although it is hard to well characterize insoluble materials, we noticed a certain analogy with Yamamoto polymerization reactions where a very rapid and efficient polymerization reaction may limit the solubility of the resulting polymers. To verify these kinetics results, UV–visible absorption spectra of aliquots were recorded (Figure 2b and SI, Figures S1–S4). A bathochromic shift of the absorption maximum was observed as a function of the polymerization time. Interestingly, the UV–visible absorption spectrum of the soluble and high molecular weight PFBT sample obtained after 150 min shows essentially the same features (with a maximum of absorption at 449 nm) as those reported for this polymer prepared from classical Suzuki polymerizations (SI, Figure S4). To corroborate these results, a second polymerization reaction was conducted between 2,7-dibromo-*N*-9''-heptadecanycarbazole and 2,2'-bithiophene. According to Figure 2c, the same trends in terms of molecular weight evolution and lack of solubility after prolonged polymerization times were observed for this polymer (PCBT). Moreover, Figure 2d exhibits similar



**Figure 2.** Evolution of the polymer PFBT and PCBT during polymerization. (a) Number-average molecular weight ( $M_n$ ) of the PFBT chloroform soluble fraction as a function of the polymerization time. (b) Chloroform-solution UV–visible absorption spectrum of PFBT as a function of the polymerization time; UV–visible absorption spectrum of the Suzuki-polymerized PFBT (red dashed). (c) Number-average molecular weight ( $M_n$ ) of the PCBT chloroform soluble fraction as a function of the polymerization time. (d) Chloroform-solution UV–visible absorption spectrum of PCBT as a function of the polymerization time; UV–visible absorption spectrum of the Suzuki-polymerized PFBT (red dashed).

bathochromic shifts as a function of time (and increase of the molecular weight), together with a saturation (and increase of the absorption maximum at 454 nm that fits well with that obtained from standard Suzuki couplings (SI, Figures S5–8).

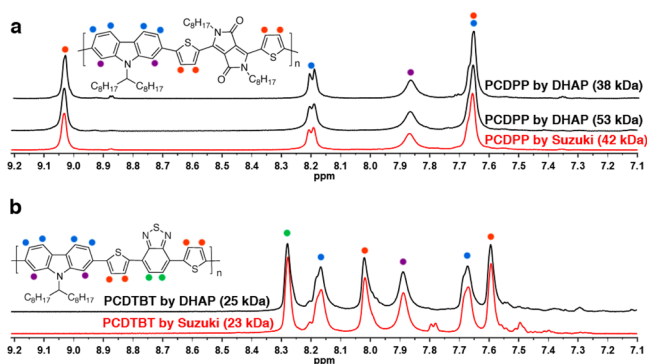
To further characterize both polymers,  $^1\text{H}$  NMR analyses were undertaken and compared with the  $^1\text{H}$  NMR spectra of the same polymers obtained from Suzuki polymerization. Figure 3 clearly shows that both polymerization reactions (DHAP and Suzuki) lead essentially to the same polymeric structures (PFBT and PCBT). No evidence of branching can be observed, and the extra little peaks found in the  $^1\text{H}$  NMR



**Figure 3.**  $^1\text{H}$  NMR spectra of PFBT and PCBT. (a)  $^1\text{H}$  NMR spectra of the aromatic region of PFBT in TCE at 80 °C made by DHAP in black and Suzuki in red. (b)  $^1\text{H}$  NMR spectra of the aromatic region of PCBT in TCE at 80 °C made by DHAP in black and Suzuki in red.

spectra can be related to different end groups (see SI). As recently highlighted by Sommer<sup>25</sup> and Janssen,<sup>26</sup> homocouplings could also be a source of defects. However, in our study, no evidence of carbazole homocoupling was observed (no peaks at 8.25, 7.90, or 7.65 ppm for P[Cbz]).<sup>25</sup>

Some concerns about ill-defined couplings were also recently reported for the synthesis of some diketopyrrolopyrrole-based (DPP) copolymers by DHAP.<sup>20</sup> Therefore, the polymerization of 2,7-dibromo-*N*-9''-heptadecanycarbazole with 2,5-di-*n*-octyl-3,6-dithiophen-2-yl-pyrrolo(3,4-*c*)pyrrole-1,4-dione was investigated. This polymer (PCDPP) has already been prepared from Suzuki couplings and has revealed interesting physical properties.<sup>27</sup> Once again, a careful analysis of the kinetics of the DHAP reaction has allowed the preparation of soluble and high-molecular weight polymeric materials ( $M_n$  up to 53 kDa). Characterization by <sup>1</sup>H NMR measurements has also revealed a well-defined structure similar to that obtained from Suzuki couplings (Figure 4a). The extra peaks near 8.9 ppm are related



**Figure 4.** <sup>1</sup>H NMR spectra of PCDPP and PCDTBT. (a) <sup>1</sup>H NMR spectra of the aromatic region of PCDPP in TCE at 90 °C made by DHAP in black and Suzuki in red. (b) <sup>1</sup>H NMR spectra of the aromatic region of PCDTBT in TCE at 90 °C made by DHAP in black and Suzuki in red.

to the presence of end groups since their intensity decreases as the molecular weight increases. Once again, no evidence of carbazole homocoupling was observed. Moreover, both polymers exhibit similar UV–visible absorption spectra with a maximum around 655 nm (Figure S10). To further evaluate the quality of the polymer obtained from DHAP, field-effect transistors were fabricated and tested using PCDPP as a channel semiconductor. As described in the SI, hole mobility up to 0.54 cm<sup>2</sup>/(V·s) was achieved in bottom-gate bottom-contact field effect transistors, whereas the mobility of the polymer prepared by Suzuki coupling polymerization was of 0.27 cm<sup>2</sup>/(V·s).

We have also performed the synthesis of another well-known polycarbazole derivative,<sup>28,29</sup> namely, poly[*N*-9''-heptadecanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT), using the optimized DHAP procedures (see SI). Fully soluble PCDTBT was obtained with a  $M_n$  of 37 kDa. We measured an UV–visible absorption maximum at 561 nm. Hole mobility up to 0.017 cm<sup>2</sup>/(V·s) was obtained in OFETs, which is higher than the values measured for its Suzuki-synthesized analog, tested in the same conditions (hole-mobility of 0.0053 cm<sup>2</sup>/(V·s)). Once again, <sup>1</sup>H NMR spectra revealed a structure similar to that obtained from Suzuki couplings (Figure 4b).

All these results clearly show that DHAP can be a very efficient tool to make various well-defined and processable conjugated polymers. Both high efficiency and selectivity can be achieved by optimizing the experimental conditions and, more specifically, the polymerization time. To show the broad scope of the reaction, we synthesized another polymer, PPDT2FBT,<sup>30</sup> based on a dibromoarene (dibromo-2,5-bis[(2-hexyldecyl)oxy]-benzene) and a dithieno-benzothiadiazole (5,6-difluoro-4,7-di-2-thienyl-2,1,3-benzothiadiazole). We obtained, using our optimized conditions,  $M_n$  of 50 kDa with PDI of 2 and comparable UV–vis absorption and <sup>1</sup>H NMR spectra (see SI) to those measured for its Stille analog.

To demonstrate the full versatility of these conditions for DHAP, we have extended this methodology to bithiophene-bithiophene couplings. For this purpose, we investigated the copolymerization of 4,4'-didodecyl-2,2'-bithiophene with 2,2'-bithiophene derivatives with both DHAP and Stille procedures (Figure 1 and SI). Both polymers (PBTBT) exhibit an absorption maximum around 485–488 nm in chloroform solution and comparable <sup>1</sup>H NMR spectra. These results are also in agreement with those previously reported for this class of materials.<sup>31</sup> However, we noticed that well-defined and high molecular weight PBTBT could not be obtained by DHAP when 5,5'-dibromo-2,2'-bithiophene and 4,4'-didodecyl-2,2'-bithiophene were used as comonomers. These results could be related to the activation of aromatic C–H bonds at adjacent  $\beta$ -positions, which is not the case if the polymerization proceeds from 5,5'-dibromo-4,4'-didodecyl-2,2'-bithiophene and 2,2'-bithiophene. Furthermore, this issue does not arise in the case of bromoarene-based (i.e., fluorenes, carbazoles, benzenes, etc.) monomers due to the relative inertness of the protons in our polymerization conditions. To support these assumptions, we have calculated and compared the Gibbs free energies ( $\Delta G_{298\text{ K}}^\ddagger$ ) of C–H cleavage of 5,5'-dibromo-2,2'-bithiophene and 2,2'-bithiophene by density functional theory (DFT) for the concerted metalation-deprotonation (CMD). These calculations estimate a  $\Delta G_{298\text{ K}}^\ddagger = 28.3$  kcal/mol for the adjacent  $\beta$ -protons of the brominated monomer versus 29.7 kcal/mol for the 2,2'-bithiophene, while the  $\alpha$ -positions have values of about 24.5 kcal/mol. The presence of bromine atoms activates the  $\beta$ -protons by lowering the CMD barrier by 1.4 kcal/mol. Dehalogenation of the nonprotected brominated thiophene units could also explain the limited polymerization yields. Similar observations were recently reported for other thiophene-based polymers<sup>32</sup> and oligomers.<sup>33</sup> Hence, these results and calculations could provide guidelines when choosing the monomers.

With all these examples, it is then believed that many known conjugated polymers could be (re)prepared from DHAP instead of using the traditional Suzuki or Stille couplings, including many highly valuable thiophene-containing conjugated polymers that were previously believed to be impossible to synthesize by this new method. DHAP could also make possible the synthesis of conjugated polymers that are difficult or just not possible to prepare by traditional methods. When successfully applied, it will always provide simple, low-cost, and environmentally benign syntheses of conjugated polymers.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedures and polymers characterization data: Figures S1–S41 and Tables S1–S4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by both discovery and strategic grants from NSERC. M.L. thanks the Killam Foundation for a fellowship. We would like to thank Hyosung Choi, Han Young Woo, and Alan J. Heeger for providing a PPDT2FBT sample and Jean-Rémi Pouliot for his help.

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