Copper Catalyzed Synthesis of Conjugated Copolymers using Direct Arylation Polymerization
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Robert M. Pankow, Liwei Ye, Barry C. Thompson*

Direct Arylation Polymerization (DArP) has almost exclusively relied on noble metal catalysts, such as Pd. We report the first Cu-catalyzed synthesis of conjugated polymers using DArP. The polymers synthesized show an undetectable level of homocoupling or branching defects, good molecular weights (up to 10 kDa), and good yields (up to 97%).

Conjugated polymers are transformative materials finding a seemingly unlimited number of potential applications, including: organic light emitting diodes (OLED), organic photovoltaics (OPV), electrochromics, transistors (OFET), chemical sensors and biomedical roles.1–4 Direct arylation polymerization (DArP) has allowed for the preparation of conjugated polymers through C-H activation.5,6 This methodology greatly streamlines synthetic routes and eliminates the use of toxic, pyrophoric reagents often employed to prepare monomers for other methods of polymerization, e.g. Stille, Suzuki, Negishi, and Kumada. Through careful investigation and modification of the polymerization conditions, DArP can prepare polymers with undetectable levels of homo-coupling or branching (β) defects, allowing for the defect free synthesis of a variety of conjugated polymer architectures, in-cluding: homopolymers, donor-acceptor copolymers, semi-random copolymers, random copolymers, and porous polymers.7–11 This broad range of scope has placed DArP on-par with the conventional aryl-aryl cross-coupling polymerization methodologies listed above.

The vast majority of DArP methodologies are reliant on precious metals, such as palladium. While Pd provides access to very robust catalysts, allowing for a broad substrate scope, relatively mild conditions, and low catalyst loading, the high cost, low abundance, and relative toxicity make this metal unsustainable.12,13 Finding a suitable replacement for Pd, using a first-row transition metal, such as Cu or Ni, would allow DArP to further its quest as a sustainable, low-cost alternative to other aryl-aryl cross-coupling polycondensations. While there are reports of oxidative direct arylation polymerizations (Oxi-DArP) using catalytic quantities (10-20 mol%) of Cu(OAc)$_2$ affording high molecular weight ($M_n$) polymer products (20-45 kDa) with good yields (85-98%), these methods require a stoichiometric oxidant and they are specific to the synthesis of homopolymers.14,15 This limits the scope for these conditions to overtake current Pd-catalyzed methods that allow for copolymer synthesis with well-defined polymeric structures. Thus, a method employing a copper catalyst that allows for aryl-aryl cross coupling to ultimately yield conjugated copolymers, such as perfectly alternating donor-acceptor or semi-random architectures, has eluded discovery.

Daugulis et al., Miura et al., and others have reported the Cu-catalyzed aryl-aryl cross-coupling for various iodinated arenes and electron-deficient heterocycles, yielding bi-aryl small molecules.16–20 Methods developed by Daugulis et al. were able to achieve cross-coupled products in high yields with mild bases and a low-cost Cu-phenanthroline catalyst using catalytic amounts of the copper catalyst (10 mol %). We were therefore interested in expanding these conditions towards the synthesis of perfectly alternating donor-acceptor conjugated copolymers, and we chose thiено[3,4-c]pyrrole-4,6-dione (TPD) because of its prevalence in conjugated polymers (Scheme 1).

Scheme 1. Optimization of the synthesis of P1 using Cu-catalyzed DArP.

While seemingly straightforward, this undertaking is not necessarily a direct transition from small molecule to conjugated...
Table 1. Synthesis and optimization of P1 using Cu-catalyzed DArP. All reactions listed used K₂CO₃ (4 equiv.) unless otherwise noted.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Cat. Mol%</th>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Mn [kDa]</th>
<th>Ð</th>
<th>Yield (%)</th>
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<tr>
<td>1</td>
<td>phen</td>
<td>50</td>
<td>DMA</td>
<td>140</td>
<td>72</td>
<td>5.6</td>
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<tr>
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<td>50</td>
<td>DMA</td>
<td>140</td>
<td>72</td>
<td>2.4</td>
<td>1.53</td>
<td>46</td>
</tr>
<tr>
<td>3</td>
<td>phen</td>
<td>50</td>
<td>DMA</td>
<td>166</td>
<td>72</td>
<td>4.2</td>
<td>2.85</td>
<td>29</td>
</tr>
<tr>
<td>4</td>
<td>phen</td>
<td>50</td>
<td>DMA</td>
<td>140</td>
<td>72</td>
<td>5.4</td>
<td>1.56</td>
<td>37</td>
</tr>
<tr>
<td>5</td>
<td>dmby</td>
<td>50</td>
<td>DMA</td>
<td>140</td>
<td>72</td>
<td>2.6</td>
<td>1.68</td>
<td>24</td>
</tr>
<tr>
<td>6</td>
<td>phen</td>
<td>5</td>
<td>DMA</td>
<td>140</td>
<td>88</td>
<td>2.9</td>
<td>1.62</td>
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<td>88</td>
<td>3.7</td>
<td>2.13</td>
<td>49</td>
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<tr>
<td>8</td>
<td>phen</td>
<td>50</td>
<td>DMA</td>
<td>140</td>
<td>48</td>
<td>8.2</td>
<td>1.64</td>
<td>14</td>
</tr>
</tbody>
</table>

*Phenanthroline (phen), 4,4′-dimethyl-2,2′-bipyridine (dmby). Loading based on equivalents to each monomer. 99.999%-Puratren Cu(I) iodide was used as the copper source with a 1:1 ratio to the ligand. N,N-dimethylacetamide (DMA), N,N-diethylacetamide (DEA); concentration for monomers was 0.1 M for all polymerizations. Determined for polymer products after purification and collection in hexanes. 40 equiv. of K₂CO₃ were used. Isolated from the filter directly after the wash.

Through optimization of the conditions on a model system, shown in Scheme 1 with polymer P1, we were able to find a satisfactory condition set to apply to a broader substrate scope, allowing for the synthesis of conjugated copolymers with good Mn (4-10 kDa) and yields (30-97%) using low-cost, commercially available reagents. The intention of this study is to illustrate the first step toward the broad scope synthesis of conjugated polymers via C-H activation without noble metals, such as Pd. Listed in Table 1, a variety of conditions were applied towards the synthesis of P1 (Scheme 1) to optimize the molecular weight (Mn) and yield, with the polymers characterized using 1H NMR spectroscopy and SEC. Complete details of the monomer synthesis, polymer synthesis, and characterization are available in the supporting information (SI). Also, a complete listing of the conditions explored is provided in Table S1 of the ESI. The polymerizations were conducted in a sealed high-pressure vessel under a N₂ atmosphere. After the allotted reaction time, the mixtures were precipitated into a cold 10% NH₄OH solution in MeOH, filtered, and washed with water, methanol, acetone, and hexanes. No insoluble material was obtained, which would indicate high levels of branching or structural defects embedded in the polymer chain, and the 1H NMR (see ESI) shows agreement with the proposed structure via integration of the aromatic (8.27-7.76 ppm) and the methylene protons alpha- to the imide nitrogen (3.71-3.58 ppm).¹¹

We fixed the catalyst loading at 50 mol % for the conditions studied in Table 1 because the concentration for our polymerizations (0.1 M) were much more dilute relative to those for Cu-catalyzed small-molecule synthesis (1 M), although lower loadings (5, 25%) did generate polymer product (entries 6, 7). We found that the selection of base, solvent, and the catalyst ligands were critical in the synthesis of P1. Of the bases studied (Cs₂CO₃, NaN₂CO₃, and t-BuOLi in Table S1), only K₂CO₃ was found to provide polymer product. This is likely due to a balance between basicity, solubility, and chemoselectivity with K₂CO₃, given that no reaction was observed aside from t-BuOLi, which lead only to visible decomposition of the substrates and no polymer product (Table S1).

Highly-polar amide solvents, which possess a strong basicity and coordinating ability, such as N,N-dimethylformamide (DMF) and N,N-diethylacetamide (DEA) were found to be essential for polymer synthesis (entries 1 and 2), with DMF providing a satisfactory Mn of 4.4 kDa and yield of 32% (entry 1). Raising the temperature from 140 °C to 166 °C (entry 3) did not provide an improvement in Mn (5.4 kDa), although the yield slightly increased (29%). Replacing DMF with N,N-diethylacetamide (DEA) (entry 4) did provide a similar value for Mn (5.4 kDa) and improved yield (37%), relative to entry 1. However, DEA is cost prohibitive compared to DMF making its general application for conjugated polymer synthesis less appealing. Highly-polar, coordinating amide solvents are required likely due to the limited solubility of the copper catalyst and the base in other organic solvents, and it is also possible that the solvent assists in the deprotonation step.
molecules, such as DMF and chlorobenzene (CB), were found to hinder the polymerization leading to no isolable polymer product, owing to the importance of high-solvent polarity and basicity for these conditions (Table S1).

While various ligands have been explored for copper catalyzed direct arylations in previous studies, we were interested to see how the ligand influenced the outcome of the polymerization. We found that phenanthroline provided the best results in comparison to 1,1'-amide solvents, as evidenced by its precipitation from the reaction mixture at low molecular weights, inhibited this. Since polymerization is amenable to conjugated polymer synthesis due to solubility with varying alkyl substituents (Scheme 2). The partitioning of the reaction mixture reached a qualitatively higher level than the other entries after only 48 hours. Given the result of 8.2 kDa for entry 8, we felt that near optimal conditions were in hand for broadening the scope to other substrates.

Provided in Table 2, conditions derived from the optimization of the synthesis of P1 (entries 1 and 8 in Table 1) were applied to a series of aryl donors (3-6) and TPD acceptors with varying alkyl substituents (Scheme 2). The partitioning of Table 2 is based on the solvent fraction that the polymer product was collected for the same reaction (fraction 1 or 2), either acetone, hexanes, or off the filter directly, where entries 1-7 were collected in the hexanes wash. This is likely why the yield for entry 8 is low relative to entries 1-7, since the hexanes soluble fraction of entry 8 was not included in the calculation of overall yield. Also, the reaction time is less for entry 8 (48 versus 72 hours), since the amount of precipitate present in the reaction mixture is low relative to entries 1-7, since the hexanes soluble fraction of entry 8 was not included in the calculation of overall yield. Also, the reaction time is less for entry 8 (48 versus 72 hours), since the amount of precipitate present in the reaction mixture is low relative to entries 1-7, since the hexanes soluble fraction of entry 8 was not included in the calculation of overall yield. Also, the reaction time is less for entry 8 (48 versus 72 hours), since the amount of precipitate present in the reaction mixture is low relative to entries 1-7, since the hexanes soluble fraction of entry 8 was not included in the calculation of overall yield.
with thiophene (P2a) provided a polymer product with similar Mₚ (8.8 kDa) and yield (30%) when 4 equivalents of K₂CO₃ were used (versus 5.6 kDa and 23% yield for P1) However, when 40 equivalents of K₂CO₃ were used (P2b) the Mₚ and yield decreased (5.5 kDa, 4%). This trend was also observed for P3, P4, and P5, where increasing the equivalents of base led to lower yield and Mₚ (P2b-P5b). It should be noted no polymer product was obtained for P3 when 40 equivalents of base were used, which is why this entry is excluded from the table. It is believed sensitivity to the amount of base could be due to lower polymer solubility in a highly polar reaction medium, leading to premature precipitation of the polymer, given that P2 is a polymer possessing low-solubility outside of chlorinated solvents (as evidenced by Marks et al.). Inclusion of a dialkoxy phenylene donor (4), providing P3, gave a satisfactory yield of 43% (P3a). However, it is believed the bulky alkyl chains, caused steric hindrance near the Cu-metal center, and unfavorable solubility of this polymer in polar amide solvents caused the premature precipitation of P3, leading to lower than expected values for Mₚ in the acetone wash (2.9 kDa) and the hexanes wash (5.0 kDa) relative to P1.

Inclusion of alkyl fluorene donors provided the highest values for Mₚ and yield (P4-P7) compared to P1-P3. P4, which has hexyl substituents on the fluorene, provided the highest Mₚ (10.1 kDa) for polymers P1-P7 and a good yield (55%). Incorporation of a bulkier alkyl chain on TPD, 2-decyltetradecyl, gave a lower value for Mₚ (4.1 kDa) in fraction 2 relative to P4, but the overall yield for P5 is much higher (93% versus 55%, respectively). The octyl substituted fluorene (6) afforded satisfactory Mₚ (9.7 kDa) for fraction 2 with 40 equivalents of base (P6b). These conditions were then replicated for P7, which incorporates 2-octynyl TPD. This gave a lower Mₚ than P6b (5.4 kDa versus 9.7 kDa), but the overall yield was significantly improved and the highest reported for this study (97%). Given the sensitivity to steric and solubility observed for the fluorene-TPD copolymers P4-P5, the 2-octynyl TPD was selected over 2-decyltetradecyl for P7. It should be noted that the bromide analog of 6 did not provide any reaction, indicating the potential need for the higher reactivity of an aryl-iodide.

To assess potential structural defects within the polymer, 1H NMR spectroscopy was employed and the spectra for known polymers P2-P7 was referenced to literature spectra, which were collected under the same conditions. Defect analysis was performed by referencing to the known homopolymers or homocoupled biaryl for each of the synthesized polymers in order to determine a major presence of donor-donor (δ), acceptor-acceptor (α), or branching defects (β) present in the aromatic region. End-group assignments are illustrated in Figure 1, and are based on known polymers and model compounds with similar structure to that of the synthesized polymers. For P3, the major resonance found corresponds to that of the desired polymer structure based on literature precedent (δ8.32). The spectrum also indicates that potential defects, including α-defects (δ7.89) and δ-defects (δ7.10), are not an observable feature as the corresponding resonances are not apparent.

For P4, the major resonances correspond to that of the desired copolymer (δ8.27-8.23 and δ7.86). Resonances which would indicate high levels of homocoupling defects, such as α-defects (δ7.89), δ-defects (δ 7.88), and β-defects (δ 7.45), were not observed. In summary, the first report of a methodology for perfectly alternating donor-acceptor conjugated polymer synthesis was developed that uses Cu-catalyzed DArP, offering an initial step towards the replacement of noble metals, such as Pd. Conjugated polymers were prepared in good yields (up to 97%) and Mn (up to 10 kDa). The recovered polymer product was soluble in organic solvents and characterized using NMR spectroscopy, which indicates an absence or minimization of undesired couplings. Future work will seek to explore the substrate scope for the given condition set, decrease catalyst...
loadings, and find more mild conditions by exploring different copper catalysts and polymerization conditions.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**


As an effort to replace Palladium catalysts, we report the first example of a Copper-catalyzed Direct Arylation Polymerization (DArP).