

COMMUNICATION

Synthesis of Conjugated Polymers using Aryl-Bromides via Cu-Catalyzed Direct Arylation Polymerization (Cu-DArP)

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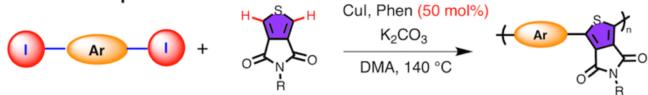
Initial reports on the novel Cu-catalyzed Direct Arylation Polymerization (Cu-DArP) required the use of aryl iodides. Herein, we report the first Cu-DArP methodology using more accessible and practical aryl-bromides with catalytic Cu, leading to a range of conjugated polymers with good molecular weights (up to 17.3 kDa) and undetectable level of defects.

Conjugated polymers are promising materials that attract interest for wide-range of applications such as organic photovoltaics (OPVs), organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), chemical sensors, and bioelectronics.^{1–6} Conventional routes towards the synthesis of these materials often include methodologies such as Stille, or Suzuki polymerizations, which rely on challenging monomer syntheses and generate toxic, stoichiometric by-products.^{7,8} Direct Arylation Polymerization (DArP) has emerged as a simplified and effective synthetic methodology in recent years by directly activating unfunctionalized C-H bonds to achieve efficient aryl-aryl couplings, allowing polymers to be synthesized at low cost with minimized homocoupling or branching defects.^{9–14} Although effort has been made to further improve its sustainability, the vast majority of DArP methodologies rely on low abundance and expensive metal catalysts, such as Pd.^{15–17}

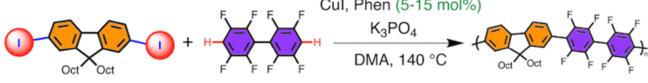
As a more sustainable, low cost metal catalyst, copper has drawn significant interest and has been studied as an alternative catalyst to Pd for conjugated polymer synthesis by oxidative homo-coupling methodology.^{18,19} However, the scope of these polymerizations are limited to homo-polymers, and the use of stoichiometric oxidants has prohibited such conditions from overtaking Pd-catalyzed conjugated polymer synthesis. As an effort to demonstrate copper as an efficient catalyst for the

most prevalent perfectly alternating donor-acceptor type conjugated copolymers, recently, we reported the first copper-catalyzed DArP (Cu-DArP) for the synthesis of various thieno[3,4-c]pyrrole-4,6-dione (TPD) donor-acceptor copolymers.²⁰ In a follow-up study, we reported a Cu-DArP methodology for the synthesis of a fluorinated arylene conjugated copolymer, poly[(9,9-dioctylfluorene-2,7-diyl)-(2,2',3,3',5,5',6,6'-octafluoro-4,4'-diphenylene)] (PDOF-OD) with high molecular weights (M_n up to 24.5 kDa) and low loadings of copper catalyst (only 5 mol%) (Scheme 1).²¹

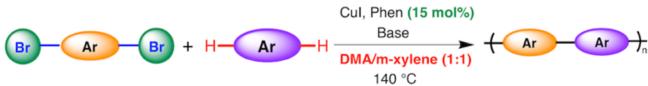
Our First Report:



Our Second Report:



This Work:



Scheme 1. Summary of Cu-DArP development.

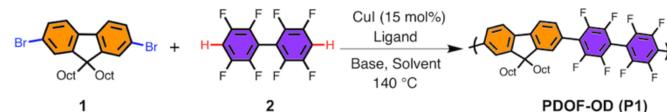
However, the necessity of employing aryl iodides in these studies limited such Cu-DArP strategies to achieve lower cost and greater sustainability, since aryl iodides were found to be much more challenging and expensive to synthesize and purify.²² Specifically, iodination of aromatic C-H bonds often requires unstable, hazardous, and expensive iodination reagents such as N-iodosuccinimide or periodic acid under harsh reaction conditions, and in addition, aryl-iodides generally lack commercial availability compared with their aryl-bromide counterparts.^{20,22} More importantly, aryl-iodides exhibits much higher reactivity and lower stability compared to aryl-bromides. Additionally, C-I bonds can undergo radical-based photolytic-cleavage leading to decomposition of the monomer or potential undesired side reactions.^{23,24} This poses

^a Department of Chemistry and Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, California 90089-1661. Email: barryth@usc.edu

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significant challenges to the practicality of Cu-DArP methodology such as chemical storage and handling, especially when larger scale or industrial settings are envisioned. With the aim of extending Cu-DArP to a significantly more facile, low-cost, and practical synthetic approach, herein, we report the first application of Cu-DArP to the synthesis of conjugated polymers using aryl-bromides.

Pioneering studies in Cu-catalyzed small molecule bi-aryl cross-coupling led by Daugulis et al. and Miura et al. reveal that aryl-bromides often lead to no arylation product or much lower yields compared to aryl-iodides, especially when less reactive coupling partners are utilized.^{25–28} You et al. and Gao & Zhou et al. reported Cu-catalyzed direct arylations with low copper catalyst loadings and high yields using aryl-bromides, however, substrates investigated in these studies are limited to azole compounds such as caffeine and benzoxazoles, and reactions are often conducted in highly concentrated solutions (such as 1.2 M) and with a stoichiometric excess of aryl-bromide, which are not consistent with conjugated polymer synthesis.^{29,30} However, studies on ligands and solvents in these reports provided insight and inspiration for us on how to achieve polymeric products using aryl bromides with copper catalysts. The synthesis of PDOF-OD (P1) was first selected as our model system (Scheme 2), since our previous report demonstrated that it could be readily synthesized with high M_n and yields using catalytic copper without directing-group assistance an aryl iodide.²¹ Monomer 2 (2,2',3,3',5,5',6,6'-octafluorobiphenyl) was selected over 1,2,4,5-tetrafluorobenzene because of its ease of handling (much higher boiling point and low volatility), and better comparison can be made to our previous report synthesizing PDOF-OD using the same monomer.²¹ Additionally, Daugulis et al. demonstrated that fluoroarenes can be arylated with high yields using aryl-bromides and catalytic amount (10



Scheme 2. Synthesis of PDOF-OD (P1) using 2,7-dibromo-9,9-diptylfluorene 1 (Conditions listed in Table 1).

mol%) of CuI, albeit with a stoichiometric excess of fluoroarene.²⁶

As shown in Scheme 2 and Table 1, our initial efforts focused on extending our previous work by directly replacing 2,7-diiodo-9,9-diptylfluorene (which gave $M_n = 20.4$ kDa, yield = 71% using 15% Cu-catalyst loading) with 2,7-dibromo-9,9-diptylfluorene as aryl-donor (Table 1, Entry 1). This led to no polymeric precipitation in MeOH, although formation of oligomeric product might have occurred as suggested by the color change that occurred during the reaction. This result supports a much lower reactivity of aryl-bromides compared to aryl-iodides in catalytic direct arylation, which is consistent to reports by Fagnou et al.³¹ Buchwald et al. demonstrated that more electron-rich phenanthroline derived ligands could stabilize Cu(III) intermediates in the N-arylation catalytic cycle, thus accelerating the rate limiting aryl halide activation step.³² However, dimethyl-substituted phenanthroline derived ligands such as Dmbpy and Neocuproine did not yield polymer product (Table 1, Entry 2, 3). Gao & Zhou et al. reported a highly efficient Cu-catalyst system, CuI/PPh₃ (1:3), forming metal complex Cu(PPh₃)₃ *in situ* for direct arylation of benzoxazoles and benzimidazoles with high yields (up to 95%) using a catalyst loading of 5 mol%.³⁰ However, this catalytic system did not yield polymeric product for PDOF-OD using either K₂CO₃ or K₃PO₄ (Table 1, Entry 4, 5), and we postulate that the Cu(PPh₃)₃I

Table 1. Cu-DArP conditions for the synthesis of PDOF-OD and polymerization results.

Entry	Polymer ^a	Ligand ^b	Base ^c	Solvent (Conc.) ^d	Time (hr.)	M_n (kDa) ^e , \bar{D}^e	Yield ^e (%)
1	P1	1, 10-Phenanthroline	K ₃ PO ₄	DMA (0.5 M)	72	-	0
2	P1	Dmbpy	K ₃ PO ₄	DMA (0.5 M)	72	-	0
3	P1	Neocuproine	K ₃ PO ₄	DMA (0.5 M)	72	-	0
4	P1	PPh ₃	K ₂ CO ₃	DMA (0.5 M)	72	-	0
5	P1	PPh ₃	K ₃ PO ₄	DMA (0.5 M)	72	-	0
6	P1	1, 10-Phenanthroline	K ₃ PO ₄	DMA/m-xylene (1:1) (0.5 M)	16	17.3, 2.4	55
7	P1	1, 10-Phenanthroline	K ₃ PO ₄	DMA/o-xylene (1:1) (0.5 M)	72	-	0
8	P4	1, 10-Phenanthroline	K ₂ CO ₃	DMA/m-xylene (1:1) (0.4 M)	72	9.0, 1.7	65
9	P5	1, 10-Phenanthroline	K ₂ CO ₃	DMA/m-xylene (1:1) (0.4 M)	72	5.1, 1.4	26
10	P6	1, 10-Phenanthroline	K ₂ CO ₃	DMA/m-xylene (1:1) (0.4 M)	72	6.4, 1.8	35

^aAll polymerizations were conducted using 15 mol% copper catalyst loading. All polymerizations were conducted at 140 °C. 99.999%-Purarem Cu(I) iodide was used as the copper source. ^bLigand loadings were 1:1 ratio to Cu(I) iodide except for PPh₃ (3:1 ratio to CuI was used). Dmbpy = 4,4'-Dimethyl-2,2'-bipyridine. ^cAll polymerizations were conducted using 4 equivalents of base. ^dN,N-dimethylacetamide = DMA. ^eDetermined for polymer products after purification.

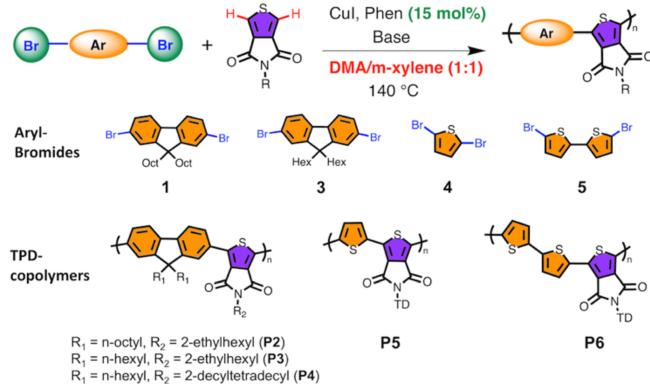
complex might only be efficient for C-2 arylation of azole type substrates.

While our previous work utilized DMA for Cu-DArP reactions, Daugulis et al. reported the best arylation results for fluoroarenes with aryl-bromides when a DMF/m-xylene (1:1) co-solvent system was used, and lower conversions were obtained in DMF.²⁶ Similar trends can be observed throughout these studies that reactions with aryl iodides achieve high yields when DMF is used as the only solvent, however, for aryl bromides, DMF/m-xylene (1:1) appears to be a required reaction parameter.^{25,27} You et al. further confirmed this observation by studying the ratio of DMF/m-xylene co-solvent systems and finds that a 1:1 ratio provides the best yield for arylations of aryl-bromides with caffeine.²⁹ Since our first Cu-DArP report found DMA gives higher M_n and yields compared to DMF, our attention turned to a DMA/m-xylene (1:1) co-solvent system, while keeping CuI/1,10-Phenanthroline (15 mol%) and K_3PO_4 (4 equiv.) as the base constant (Table 1, Entry 6), which gave PDOF-OD of good M_n (17.3 kDa) and good yield (55%) in only 16 hours (due to precipitation of polymerization observed). Interestingly, replacement of m-xylene with o-xylene completely inhibited the polymerization (Table 1, Entry 7), indicating a specific requirement for m-xylene as a co-solvent partner with polar amide solvents (DMF, DMA) for Cu-DArP. These observations are consistent with reports by Daugulis and You et al.^{26,27,29} Density functional theory (DFT) studies on small molecule Cu-catalysed direct arylation reveals a possible neutral catalytic cycle that aryl-bromides undergo, which favours non-polar solvents and may explains the role of m-xylene.³³ This result (Table 1, Entry 6) marks the first catalytic Cu-DArP synthesized conjugated polymer with good M_n and yield using aryl-bromides. To gain a further comparison with our previous report, we increased the Cu-catalyst loading to 50 mol%, which improved M_n to 22.0 kDa with 67% yield (Table S1, Entry 1), however, decreasing the loading to 5 mol% did not give polymer product (Table S1, Entry 2), in contrast to our previous work with aryl iodides in DMA.

With an optimized condition in hand, we were interested to explore the scope of Cu-DArP using other aryl-bromides. We selected thieno[3,4-c]pyrrole-4,6-dione (TPD) co-polymers based on their extensive use in conjugated polymers and the lower acidity of TPD monomer (compared to 2).³⁴ In addition, our first report of Cu-DArP focused on TPD monomers co-polymerized with a variety of aryl-iodides (see Scheme 1), and we proposed that the carbonyl groups on TPD units can act as directing groups to facilitate C-H activation.²⁰ Therefore, it is of great interest to extend this work toward the more sustainable and facile synthetic route via aryl-bromides (Scheme 3).

As shown in Table S2 and Scheme 3, we initially focused on extending the optimized polymerization condition using 50 mol% Cu-catalyst from our first report to this study with aryl-bromides. Through careful optimization of reaction conditions (See ESI), TPD-copolymer P4 was successfully synthesized with good M_n of 10.4 kDa and yield 72% (Table S2, Entry 6), which is the highest M_n reported for TPD co-polymers synthesized via Cu-DArP. The DMA/m-xylene (1:1) co-solvent system was further confirmed to be critical for Cu-DArP of aryl-bromides. Moreover, the introduction of a non-polar solvent, m-xylene, was found to not only increase the reactivity of

aryl-bromides toward Cu-DArP, but improve the solubility of the resulting copolymers, allowing highly concentrated (0.4 M) Cu-DArP



Scheme 3. Synthesis of TPD-copolymers using aryl-bromides as donor units (Conditions listed in Table 1 and Table S1).

reactions to occur without premature precipitation. Surprisingly, decreasing the Cu-catalyst loading from sub-stoichiometric 50 mol% to catalytic 15 mol% gave comparable M_n (9.0 kDa) and yield (65%) of P4 (Table 1, Entry 8). This result indicates the first TPD-copolymer synthesized via catalytic CuI, which is a remarkable step forward for Cu-DArP especially when compared with our first report, in which the more reactive aryl iodides required 50 mol% Cu-catalyst loading for polymerizations to proceed. It is worth-noting that TPD-acceptor monomers are found to be less reactive towards C-H activation, since even Pd-catalyzed DArP requires di-iodide functionalized aryl-donors.³⁵

With optimal conditions in hand, we were emboldened to further broaden the scope of aryl-bromides in Cu-DArP. Thiophene based aryl bromides 4 and 5 (Scheme 3) were chosen because of the prevalence of such TPD-copolymers (P5, P6) in organic electronics.^{34,36} With only 15 mol% Cu-catalyst loading, P5 was synthesized with M_n = 5.1 kDa and yield = 26% (Table 1, Entry 9), which is similar to that obtained from the di-iodide counterpart with 50 mol% Cu-catalyst loading.²⁰ 5,5'-dibromo-2,2'-bithiophene (5) was co-polymerized with the TPD monomer to provide P6 with improved M_n (6.4 kDa) and yield (35%) (Table 1, Entry 10). We attributed the lower M_n and yields of P5 and P6 to lower solubility of these polymers in highly concentrated solutions as reported in previous studies, and it is worth-noting that even with the highly reactive Stille-polycondensation, P6 was synthesized with M_n of 7.08 kDa, which is only slightly higher than our Cu-DArP protocol.^{34,36}

To validate the proposed structures synthesized via Cu-DArP using aryl-bromides, ^1H NMR spectra were collected. Complete ^1H NMR spectra can be found in the Supporting Information (ESI), and all analyses performed were referenced to our previous Cu-DArP studies.^{20,21} Figure 1 shows detailed peak-assignments and end group analyses of two representative polymers from Table 1 (P1, Entry 6 and P4, Entry 8). For P1 (PDOF-OD) synthesized in this study, the major resonances located at δ 7.94 and δ 7.59 match identically to our previous report as well as a literature report.^{21,37} End group assignments were performed based on our previous report, where detailed end group analyses were conducted based on model compounds.²¹ As shown in Figure 1, integral ratios of the end group

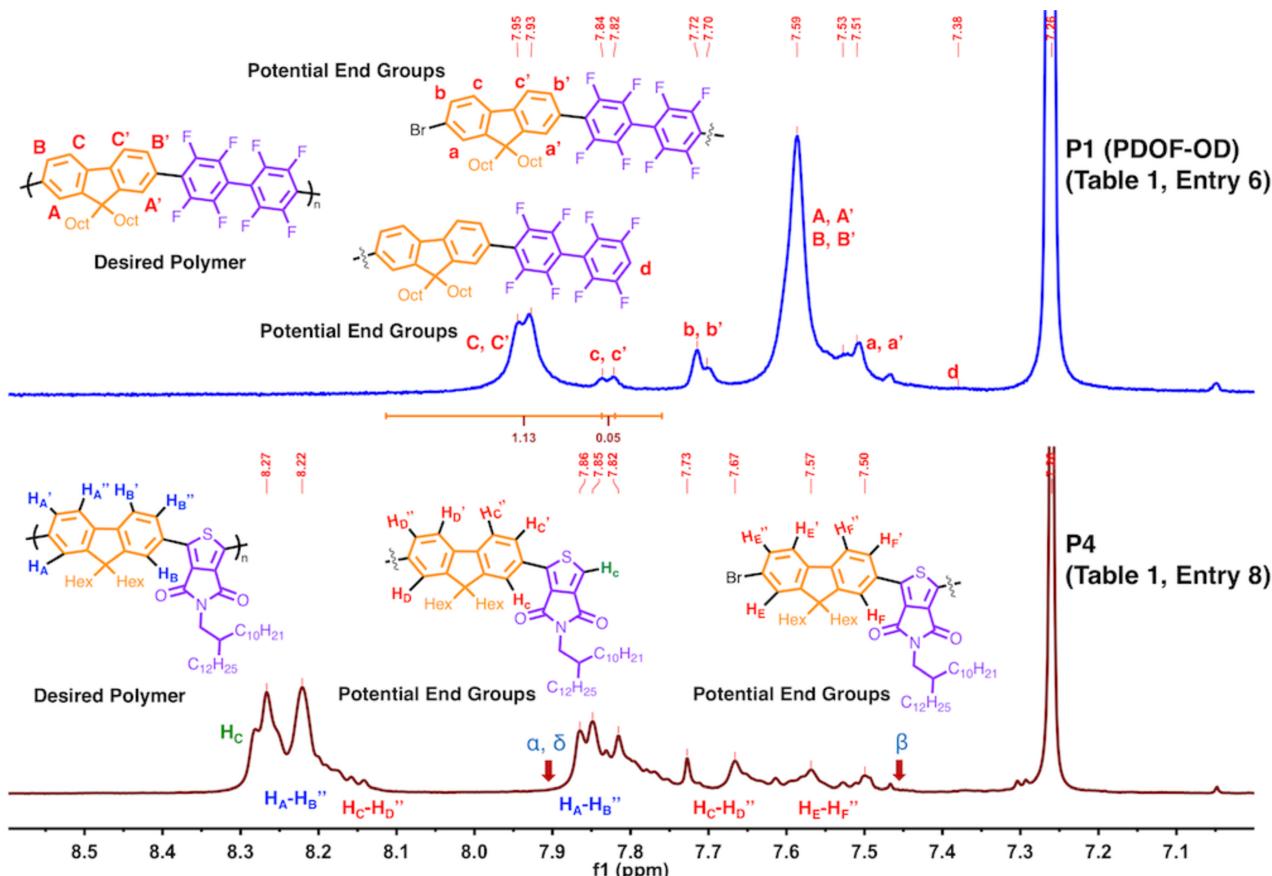


Figure 1. ^1H NMR analyses of representative P1 (PDOF-OD) (Table 1, Entry 6) and P4 (Table 1, Entry 8) polymers. Potential resonances for end groups and defects are denoted. δ = donor-donor homocoupling (δ 7.89), α = acceptor-acceptor homocoupling (δ 7.88), β = branching defects. Collected in CDCl_3 at 25 °C and 500 MHz.

c, c' and the polymeric protons C, C' can be determined as 1:23, which is very similar to repeat units given by GPC M_n value (1:25 for 17.3 kDa). Based on previous reports, this indicates a likely absence of β branching defects.^{21,37} For TPD copolymers, as shown in Figure 1, the representative polymer P4 provides identical major resonance signals (δ 8.22-8.27 and δ 7.86 for $\text{H}_\text{A}-\text{H}_\text{B}''$) compared to our first Cu-DArP report.²⁰ Potential structural defects such as donor-donor (δ (δ 7.89)), acceptor-acceptor (α) (δ 7.88) coupling, or branching defects (β) (δ 7.89) were not observed.²⁰

In conclusion, we report the first Cu-DArP methodology for the synthesis of conjugated polymers using aryl-bromides. Replacing aryl-iodides is of significant importance for Cu-DArP because expensive, synthetically-challenging, and unstable aryl iodides prohibit Cu-DArP from becoming a more general and practical method. To overcome the lower reactivity of aryl-bromides in Cu-DArP, we discovered from the synthesis of PDOF-OD (P1) that the use of a DMA/m-xylene (1:1) co-solvent system is critical for polymerizations to occur, providing P1 with M_n = 17.3 kDa and good yield 55% with a catalytic 15 mol% of Cul. The DMA/m-xylene (1:1) co-solvent system was further confirmed as an efficient solvent of choice for Cu-DArP by providing P4 with satisfactory M_n of 9.0 kDa, and 65% yield using catalytic 15 mol% Cul, which is the first TPD-copolymer synthesized via catalytic copper. ^1H NMR of both P1 and P4 confirm the proposed polymer structures, showing minimization or absence of homo-coupling or branching

defects. This study has significantly advanced Cu-DArP, demonstrating the capacity of this synthetic methodology for a broad scope of conjugated polymers with a variety of aryl-bromides using catalytic copper.

Conflicts of interest

There are no conflicts to declare.

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