

**Copper Catalyzed Synthesis of Conjugated Copolymers
using Direct Arylation Polymerization**

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Copper Catalyzed Synthesis of Conjugated Copolymers using Direct Arylation Polymerization

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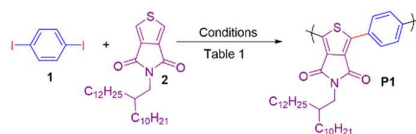
Direct Arylation Polymerization (DARp) has almost exclusively relied on noble metal catalysts, such as Pd. We report the first Cu-catalyzed synthesis of conjugated polymers using DARp. The polymers synthesized show an undetectable level of homocoupling or branching defects, good molecular weights (up 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, including: 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 thieno[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 copolymer.

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Table 1. Synthesis and optimization of P1 using Cu-catalyzed DARP. All reactions listed used K₂CO₃ (4 equiv.) unless otherwise noted

Entry	Ligand ^a	Cat. Mol ^b %	Solvent ^c	Temperature (°C)	Time (h)	Mn (kDa) ^d , Đ ^d	Yield ^e (%)
1	phen	50	DMA	140	72	5.6, 2.20	23
2	phen	50	DMF	140	72	2.4, 1.53	46
3	phen	50	DMA	166	72	4.2, 2.85	29
4	phen	50	DEA	140	72	5.4, 1.56	37
5	dmbpy	50	DMA	140	72	2.6, 1.68	24
6	phen	5	DMA	140	88	2.9, 1.62	15
7	phen	25	DMA	140	88	3.7, 2.13	49
8 ^e	phen	50	DMA	140	48	8.2, 1.64	14 ^f

^aPhenanthroline (phen), 4,4'-dimethyl-2,2'-bipyridine (dmbpy). ^bLoading based on equivalents to each monomer. 99.999%-Puratrem Cu(I) iodide was used as the copper source with a 1:1 ratio to the ligand. ^cN,N-dimethylacetamide (DMA), N,N-diethylacetamide (DEA); concentration for monomers was 0.1 M for all polymerizations. ^dDetermined for polymer products after purification and collection in hexanes. ^e40 equiv. of K₂CO₃ were used. ^fIsolated from the filter directly after the wash.

mer synthesis. Specifically, the original conditions used high concentrations, unfavorable solvents for conjugated polymer synthesis, and bases not commonly found in DARP, e.g. lithium alkoxides. These conditions could be problematic due to solubility issues of the growing polymer chain and chemoselectivity when applied to electrophilic substrates commonly used for conjugated polymer synthesis.

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, Na₂CO₃, 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-dimethylacetamide (DMA) were found to be essential for polymer synthesis (entries 1 and 2), with DMA providing a satisfactory M_n of 5.6 kDa and yield of 23% (entry 1). Raising the temperature from 140 °C to 166 °C (entry 3) did not provide an improvement in M_n (4.2 kDa), although the yield slightly increased (29%). Replacing DMA with N,N-diethylacetamide (DEA) (entry 4) did provide a similar value for M_n (5.4 kDa) and improved yield (37%), relative to entry 1. However, DEA is cost prohibitive compared to DMA 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

based on other studies regarding solvent basicity and C-H activation (Figure S1 in ESI).^{21,22} Solvent

Table 2. Results of the copolymerizations for the monomers depicted in Scheme 2, including: molecular weights (M_n), \bar{D} , and yield.

Polymer ^{a,b}	Equiv. of K_2CO_3	Fraction 1	M_n (kDa) ^a ; \bar{D}	Yield (%) ^a	Fraction 2	M_n (kDa) ^a ; \bar{D}	Yield (%) ^a	Overall Yield (%) ^a
P2a	4	-	-	-	hexanes insoluble	8.8; 2.36	30	30
P2b	40	-	-	-	hexanes insoluble	5.5; 2.9	4	4
P3a	4	acetone	3.2; 1.36	22	hexanes	5.0; 1.37	21	43
P4a	4	-	-	-	hexanes insoluble	10.1; 1.86	55	55
P4b	40	hexanes	2.3; 1.31	10	hexanes insoluble	3.9; 1.30	6	16
P5a	4	hexanes	5.6; 3.17	71	hexanes insoluble	5.9; 3.11	22	93
P5b	40	hexanes	3.55; 1.82	34	-	-	-	34
P6a	4	hexanes	4.8; 1.83	3	-	-	-	3
P6b	40	hexanes	4.4; 1.74	40	hexanes insoluble	9.7; 1.44	7	47
P7b	40	hexanes	5.4; 2.49	97	-	-	-	97

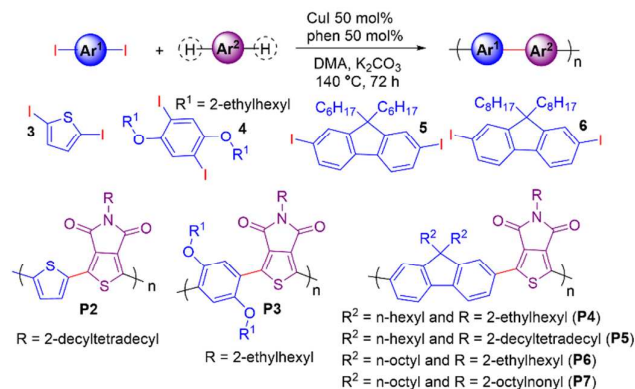
^aMeasured after polymer purification. ^bPolymerizations with 4 equivalents of K_2CO_3 are denoted with "a", while 40 equivalents is denoted with "b".

mixtures, 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'-bis(diphenylphosphino)ferrocene (dppf) (Table S1), 4,4'-dimethyl-2,2'-bipyridine (dmbpy) (entry 5), and neocuproine (Table S1), where aside from phenanthroline only dmbpy provided polymer product albeit with lower M_n (5.6 versus 2.6 kDa, respectively). Phenanthroline's optimal performance as a ligand is likely attributable to its strong binding to copper and low-level of steric hindrance near the metal center. This confirms the findings of others, and provides an easily obtained catalyst from relatively bench-stable, low-cost constituents^{16,23} Lowering the catalyst loading to 25 and 5 mol % provided satisfactory results after optimizing the solvent, ligand, temperature, and base (entries 6 and 7, respectively), although the values for M_n decreased relative to entry 1 (2.9 and 3.7 kDa versus 5.6 kDa, respectively). However, these results do show that this methodology is compatible with lower catalyst loadings, although longer polymerization times are likely required to achieve comparable M_n to higher loadings. While Daugulis et al. were able to achieve lower catalyst loadings (10 mol %) for the synthesis of small-molecule biaryls, the concentration was significantly higher (1 M) and the bases more reactive (t-BuOLi), which are not amenable to conjugated polymer synthesis due to solubility and chemoselectivity issues.¹⁶ Although many DARp protocols use higher concentrations (>0.1 M) more favorable for polycondensation reactions, the low solubility of P1 in polar, amide solvents, as evidenced by its precipitation from the reaction mixture at low molecular weights, inhibited this.^{5,6}

In attempts to further increase the M_n of P1 from 5.6 kDa (entry 1), we increased the equivalents of base. While the other entries of Table 1 used 4 equivalents of K_2CO_3 , based on a report by Leclerc et al. we found that an extreme excess of base (40 equivalents, K_2CO_3) afforded the highest value for M_n

for P1 (8.2 kDa), likely helping to facilitate C-H activation (entry 8).²⁴ Although soluble in $CHCl_3$ and DCB, the collected polymer product for entry 8 was insoluble in hexanes, 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 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.

Scheme 2. Synthesis of polymers P2-P7 using conditions derived from Table 1.

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 fraction 2), either acetone, hexanes, or off the filter directly, where the M_n , \bar{D} , and yield are listed for each respective fraction, along with the overall yield for combined fractions. As with P1, all polymers (P2-P7) were soluble in organic solvents, i.e. indicating an absence of undesired defects embedded in the polymer chain. Replacement of the phenylene donor of P1

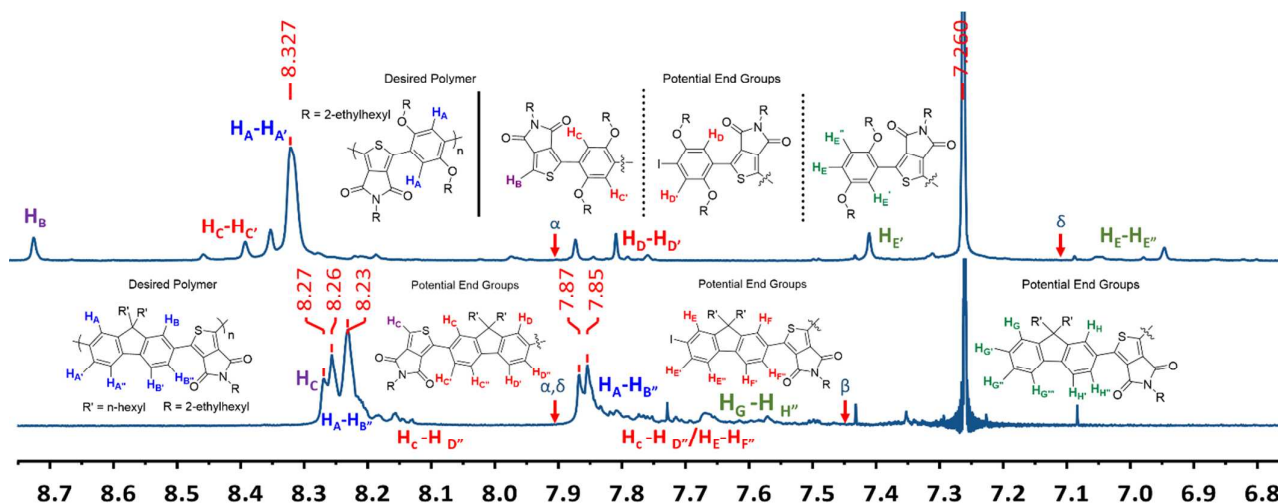


Figure 1. ^1H NMR of P3 (top) and P4 (bottom) with sites for end-groups, acceptor-acceptor (α), donor-donor (δ), and branching defects (β) based on homocoupled products denoted. Conducted in CDCl_3 at 25 $^\circ\text{C}$

with thiophene (P2a) provided a polymer product with similar M_n (8.8 kDa) and yield (30%) when 4 equivalents of K_2CO_3 were used (versus 5.6 kDa and 23% yield for P1). However, when 40 equivalents of K_2CO_3 were used (P2b) the M_n 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 M_n (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.)²⁵ and that P3 possesses a polymer structure more amenable to non-polar media (as evidenced by Ozawa et al.)²⁶ 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 M_n 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 M_n and yield (P4-P7) compared to P1-P3. P4, which has hexyl substituents on the fluorene, provided the highest M_n (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 M_n (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 M_n (9.7 kDa) for fraction 2 with 40 equivalents of base (P6b). These conditions were then replicated for P7, which incorporates 2-octylnonyl TPD. This gave a lower M_n 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 sterics

and solubility observed for the fluorene-TPD copolymers P4-P5, the 2-octylnonyl 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 biaryls 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.²⁶⁻³³ For P3, the major resonance found corresponds to that of the desired polymer structure based on literature precedent (δ 8.32).²⁶ The spectrum also indicates that potential defects, including α -defects (δ 7.89) and δ -defects (δ 7.10), are not an observable feature as the corresponding resonances are not apparent.^{34,35} For P4, the major resonances correspond to that of the desired copolymer (δ 8.27-8.23 and δ 7.86).²⁷ Resonances which would indicate high levels of homocoupling defects, such as α -defects (δ 7.89), δ -defects (δ 7.88), and β -defects (δ 7.45), were not observed.^{33,35,36}

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 M_n (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.

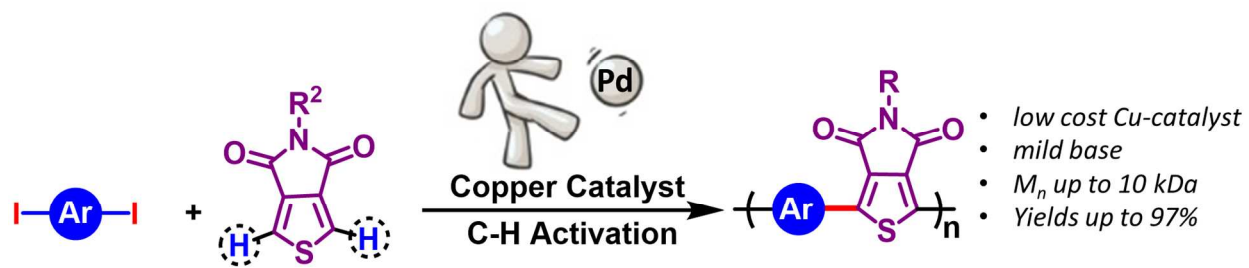
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Notes and references

- 1 A. Facchetti, *Chem. Mater.*, 2010, **23**, 733–758.
- 2 B. C. Thompson and J. M. J. Frechet, *Angew. Chem., Int. Ed.*, 2008, **47**, 58–77.
- 3 D. T. McQuade, A. E. Pullen and T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537–2574.
- 4 E. Smela, *Adv. Mater.*, 2003, **15**, 481–494.
- 5 J.-R. Pouliot, F. Grenier, J. T. Blaskovits, S. Beaupré and M. Leclerc, *Chem. Rev.*, 2016, **116**, 14225–14274.
- 6 N. S. Gobalasingham and B. C. Thompson, *Progress in Polymer Science*, DOI:10.1016/j.progpolymsci.2018.06.002.
- 7 N. S. Gobalasingham, R. M. Pankow, S. Ekiz and B. C. Thompson, *J. Mater. Chem. A*, 2017, **5**, 14101–14113.
- 8 H. Bohra, S. Yu Tan, J. Shao, C. Yang, A. Efreem, Y. Zhao and M. Wang, *Polymer Chemistry*, 2016, **7**, 6413–6421.
- 9 F. Lombeck, F. Marx, K. Strassel, S. Kunz, C. Lienert, H. Komber, R. Friend and M. Sommer, *Polym. Chem.*, 2017, **8**, 4738–4745.
- 10 H. Aoki, H. Saito, Y. Shimoyama, J. Kuwabara, T. Yasuda and T. Kanbara, *ACS Macro Lett.*, 2017, 90–94.
- 11 E. Iizuka, M. Wakioka and F. Ozawa, *Macromolecules*, 2015, **48**, 2989–2993.
- 12 K. S. Egorova and V. P. Ananikov, *Organometallics*, 2017, **36**, 4071–4090.
- 13 Egorova Ksenia S. and Ananikov Valentine P., *Angew. Chem. Int. Ed.*, 2016, **55**, 12150–12162.
- 14 Q. Huang, X. Qin, B. Li, J. Lan, Q. Guo and J. You, *Chem. Commun.*, 2014, **50**, 13739–13741.
- 15 A. Faradhiyani, Q. Zhang, K. Maruyama, J. Kuwabara, T. Yasuda and T. Kanbara, *Mater. Chem. Front.*, DOI:10.1039/C7QM00584A.
- 16 H.-Q. Do, R. M. K. Khan and O. Daugulis, *J. Am. Chem. Soc.*, 2008, **130**, 15185–15192.
- 17 T. Kawano, T. Yoshizumi, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2009, **11**, 3072–3075.
- 18 H.-Q. Do and O. Daugulis, *J. Am. Chem. Soc.*, 2008, **130**, 1128–1129.
- 19 N.-N. Jia, X.-C. Tian, X.-X. Qu, X.-X. Chen, Y.-N. Cao, Y.-X. Yao, F. Gao and X.-L. Zhou, *Scientific Reports*, 2017, **7**, 43758.
- 20 Y.-T. Song, P.-H. Lin and C.-Y. Liu, *Adv. Synth. Catal.*, 2014, **356**, 3761–3768.
- 21 B. G. Hashiguchi, K. J. H. Young, M. Yousufuddin, W. A. Goddard and R. A. Periana, *J. Am. Chem. Soc.*, 2010, **132**, 12542–12545.
- 22 L. Ackermann, *Chem. Rev.*, 2011, **111**, 1315–1345.
- 23 R. A. Altman, A. Shafir, A. Choi, P. A. Lichtor and S. L. Buchwald, *J. Org. Chem.*, 2008, **73**, 284–286.
- 24 F. Grenier, K. Goudreau and M. Leclerc, *J. Am. Chem. Soc.*, 2017, **139**, 2816–2824.
- 25 X. Guo, R. P. Ortiz, Y. Zheng, M.-G. Kim, S. Zhang, Y. Hu, G. Lu, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc.*, 2011, **133**, 13685–13697.
- 26 M. Wakioka, N. Ichihara, Y. Kitano and F. Ozawa, *Macromolecules*, 2014, **47**, 626–631.
- 27 J. Kuwabara, K. Yamazaki, T. Yamagata, W. Tsuchida and T. Kanbara, *Polym. Chem.*, 2015, **6**, 891–895.
- 28 R. M. Pankow, N. S. Gobalasingham, J. D. Munteanu and B. C. Thompson, *J. Polym. Sci. Part A: Polym. Chem.*, 2017, **55**, 3370–3380.
- 29 S.-Y. Chang, P.-H. Lin and C.-Y. Liu, *RSC Adv.*, 2014, **4**, 35868–35878.
- 30 Y. Zou, D. Gendron, R. Neagu-Plesu and M. Leclerc, *Macromolecules*, 2009, **42**, 6361–6365.
- 31 B. Walker, J. Liu, C. Kim, G. C. Welch, J. K. Park, J. Lin, P. Zalar, C. M. Proctor, J. H. Seo, G. C. Bazan and T.-Q. Nguyen, *Energy Environ. Sci.*, 2013, **6**, 952–962.
- 32 Belton Colin R., Kanibolotsky Alexander L., Kirkpatrick James, Orofino Clara, Elmasly Saadeldin E. T., Stavrinou Paul N., Skabara Peter J. and Bradley Donal D. C., *Advanced Functional Materials*, 2013, **23**, 2792–2804.
- 33 N. Fomina and T. E. Hogen-Esch, *Macromolecules*, 2008, **41**, 3765–3768.
- 34 T. Vahlenkamp and G. Wegner, *Macromol. Chem. Phys.*, 1994, **195**, 1933–1952.
- 35 P. Berrouard, F. Grenier, J.-R. Pouliot, E. Gagnon, C. Tessier and M. Leclerc, *Org. Lett.*, 2011, **13**, 38–41.
- 36 M. Imit and A. Adronov, *Polym. Chem.*, 2015, **6**, 4742–4748.

Table of Contents Entry



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