# Robust Direct (Hetero)arylation Polymerization in Biphasic Conditions

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S *Supporting Information*

ABSTRACT: The synthesis of conjugated polymers from direct (hetero)arylation polymerization (DHAP) has been achieved for the first time using biphasic water/toluene conditions. This protocol is robust enough to form polymers even when air is introduced in the system. General reactivity is demonstrated for a single set of polymerization conditions with thienyl- or phenyl-based substrates, whether they are electron-rich or electron-poor. Complete characterization from differential scanning calorimetry and ^{1}H NMR and UV−vis−NIR spectroscopies is presented, demonstrating this DHAP protocol offers comparable or better properties than the very best values published thus far. High molecular weights are obtained, showcasing the perfect equilibrium of reactivity and selectivity attained with this method. Moreover, this efficient and versatile methodology, which also uses low-cost, "wet" reagents, is scalable and done at ambient pressure.
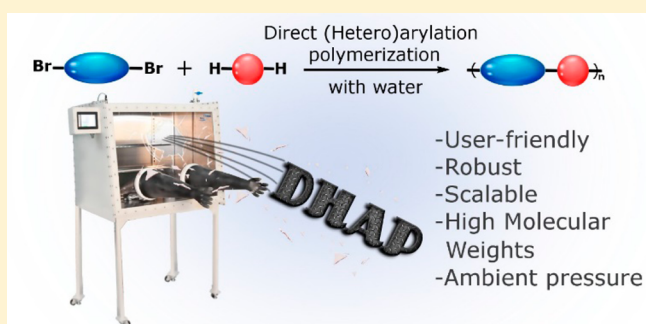
■ INTRODUCTION

Conjugated polymers are innovative materials that combine the mechanical properties of plastics with the conducting or semiconducting properties found in inorganic materials. They can be used as conductors or semiconductors to fabricate flexible, thin, and lightweight devices for applications in transistors,[1] solar cells,[2] and light-emitting diodes,[3] but are also promising for biomedical applications such as photoacoustic imaging[4,5] and as neural interface materials.[6,7] This class of materials is highly attractive from a commercial standpoint since they can be used in simple and high-throughput fabrication techniques based on solutions.[8,9] However, their much-touted low cost has yet to be achieved, and conjugated polymers often account for a large proportion of the total device cost in organic electronics.[10,11]

To lower their overall cost, it is critical to develop and apply new synthetic methods either using cheaper reagents or reducing the total number of synthetic steps. Recently, direct (hetero)arylation polymerization (DHAP) has achieved both objectives by offering a simpler method for C−C bond formation between a (hetero)aryl halide and a nonpreactivated (hetero)aryl, directly activating one of its C−H bonds.[12−15] This eliminates the need to functionalize the monomers with expensive organoboron or organotin derivatives, which are necessary for the commonly used Suzuki and Stille cross-coupling polymerizations.[16] This improvement can lead to an impressive reduction in fabrication cost of up to 35%.[17] For the large-scale production of conjugated polymers, DHAP is very attractive and sustainable as atom economy is high, and little, if any, toxic waste is produced.[18,19] In contrast, Stille polycondensation generates large amounts of trialkyltin derivatives which are toxic and which contaminate the glassware or reactor used.[19]

The development of DHAP is still recent, and new reaction conditions are constantly investigated in the hope of achieving general applicability, high molecular weights, and selectivity even when several C−H bonds are available.[12−15] Studying the formation of defects in DHAP contributed to the identification of the most selective conditions, and many examples demonstrate the high molecular weight, almost defect-free materials obtained using this method.[17,20−27] Branching defects, arising from the β-position of thiophene derivatives, are often mentioned,[28,29] but very few reports demonstrate their presence without a doubt.[21,30,31] In-depth studies of defect formation in DHAP have revealed that common side-reactions are C−Br/C−Br or C−H/C−H homocouplings.[32−34] Similar side-reactions are also observed in Suzuki[35,36] and Stille[37] polycondensations. Materials synthesized using DHAP have now demonstrated performance comparable to those synthesized using traditional methods, demonstrating that this inexpensive synthetic route will play an important role in the production of conjugated polymers.

At the present time, the most selective reaction conditions utilize low-polarity solvents, mainly tetrahydrofuran (THF) or aromatic solvents such as toluene or xylenes. A carbonate base, most commonly cesium carbonate (Cs_2CO_3), is used, and a bulky carboxylic acid additive (for example, pivalic acid, neodecanoic acid, 1-adamantanecarboxylic acid, etc.) is often necessary to achieve high selectivity and reactivity. A

palladium(II) or Pd(0) precatalyst is generally used in combination with tris(*o*-methoxyphenyl)- or tris(*o*-dimethylaminophenyl)phosphine. However, the generality of this reaction can be improved as lengthy optimizations for each monomer couple are often necessary to obtain high-quality materials. Some aspects are also not very user-friendly, which hampers its widespread use, such as utilizing superheated solvents requiring pressurized reaction vessels. Cesium carbonate is expensive, and its replacement should also be sought. Strictly anhydrous conditions and an inert atmosphere are utilized, and some of the best DHAP results are obtained using Schlenk glassware.

To address these issues, we developed the first example of a DHAP protocol using a water/toluene biphasic system, allowing the use of less expensive "wet" reagents and solvents. This methodology can generate polymers even though atmospheric contaminants (i.e., oxygen) are introduced. Furthermore, this reaction is highly selective, reactive, and scalable. Mixing of the liquid phases can be accurately reproduced from batch to batch and could be adapted more easily to continuous flow chemistry, allowing better control of the reaction parameters during scale-up. This improves upon the typical solid/liquid interface of DHAP in apolar media, where grain size of the base and solids sticking to the reaction vessel's sides can affect the effective stoichiometry of some reagents. A variety of monomer couples were found to react readily under these conditions, producing high-molecular-weight, almost defect-free, polymeric materials.

■ RESULTS AND DISCUSSION

Synthesis of PiIEDOT. To develop more robust DHAP conditions able to withstand atmospheric contaminants, we first investigated conditions in the presence of water. As water often needs to be removed from reagents such as bases, acid additives, and solvents prior to polymerization, this would render DHAP more user-friendly, akin to Suzuki polycondensation. Thus, biphasic DHAP conditions were investigated using an equal amount of water and toluene. The first polymerization attempts utilized monomers **1** and **2** to obtain PiIEDOT (see Figure 1). This polymer shows moderate solar cell efficiency[38] and can be used in air-stable organic nonvolatile memories,[39] but it is mostly attractive due to its combination of inexpensive monomers easily obtainable in a large quantity. Monomer **2** (3,4-ethylenedioxythiophene, or EDOT) is also substituted at the 3- and 4-positions with electron-donating
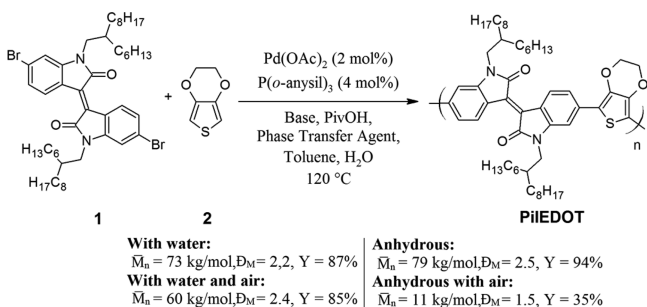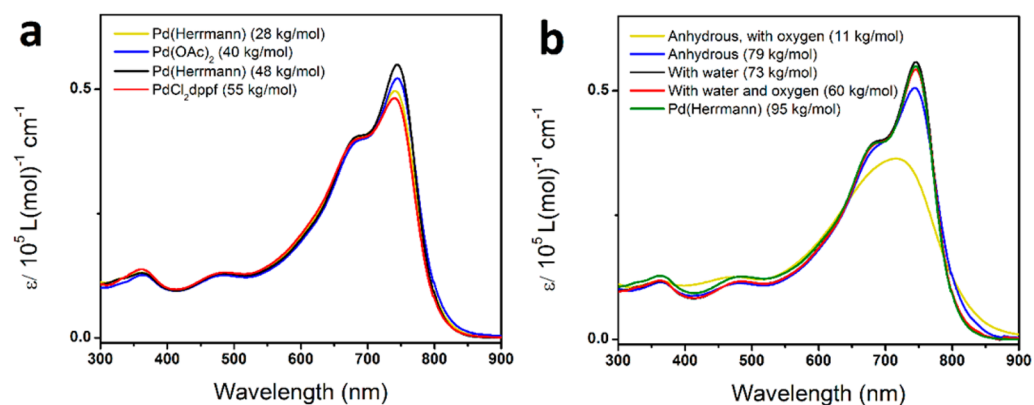
groups, which lowers the polymer bandgap and prevents β-branching reactions.

DHAP using water is new, but direct (hetero)arylation reactions on molecules have been already reported, though with more polar solvents (ethyl acetate) or performed "on water".[40−42] Such conditions would likely result in premature precipitation of the conjugated polymers, limiting their molecular weight. Instead, we adapted a protocol in toluene from our previous work,[38] with added water and with a phase transfer agent (tetrabutylammonium bromide, or TBAB), as described in the experimental procedure in the Supporting Information (SI). The optimization of the polymerization of PiIEDOT is summarized in Tables S1−4 in the SI. A key parameter for this reaction was the choice of the precatalyst. The Herrmann−Beller catalyst, used in our original work, gave very poor results and slow kinetics. On the other hand, $PdCl_2(dppf)$ quickly led to an insoluble (probably high-molecular weight) material. This high reactivity could be controlled by lowering the temperature to 80 °C, yielding a polymer with $\overline{M}_n$ of 55 kg/mol in high yield (82%). Unfortunately, the absorption coefficient of the 0−0 vibronic band (A_{0-0}) was noticeably lower than comparable samples synthesized from our previous method (see Figure 2a), with correspondingly lower absorption ratio between the 0−0 vibronic band and the 0−1 band (A_{0-0}/A_{0-1}). In contrast, the UV−vis spectrum of a polymer synthesized in a pressurized vessel at 120 °C using $Pd(OAc)_2$ as the precatalyst ($\overline{M}_n$ of 40 kg/mol) displayed a higher A_{0-0}/A_{0-1} ratio, similar to the anhydrous conditions. Polymers featuring higher A_{0-0}/A_{0-1} ratios have previously been linked with better device performance in organic electronics,[21,36,43,44] and this ratio is dependent, among other things, upon the molecular weight, polydispersity, and polymer defects.[36,45−47] Thus, using $PdCl_2(dppf)$ as the precatalyst yields a lower-quality PiIEDOT than $Pd(OAc)_2$. Further investigation of the defects was not possible due to the amorphous nature of the polymer and its aggregation in solution, which results in broad peaks in ¹H NMR spectroscopy.[38]

On this basis, further experiments utilized $Pd(OAc)_2$ as the precatalyst. After testing different bases, phase transfer agents, reaction times, and concentrations, we found that an important factor to obtain higher molecular weights was reducing the catalyst load ($\overline{M}_n$ = 57 kg/mol). This improved catalytic system, when used without water, yields a polymer with $\overline{M}_n$ of 79 kg/mol. The reaction outcome is further improved by using tetrabutylammonium chloride (TBAC) instead of TBAB and by using K_2CO_3 as the base ($\overline{M}_n$ = 73 kg/mol, see Figure 1). Surprisingly, when air is introduced in the reaction vessel, a high-molecular-weight polymer is still obtained when water is present, whereas anhydrous conditions with air did not ($\overline{M}_n$ = 60 and 11 kg/mol, respectively). This suggests that the addition of water renders the catalytic system more robust.[48] The materials synthesized with water also had superior optical properties (Figure 2b), with higher A_{0-0}/A_{0-1} ratios, which were even comparable to a higher molecular weight sample synthesized using our previous method ($\overline{M}_n$ = 95 kg/mol).[38]

A final investigation was performed using mesoporous silica-supported palladium catalysts obtained from Silicycle, Silia*Cat* DPP-Pd (a palladium(II) precatalyst) and Silia*Cat* Pd0 (a Pd(0) precatalyst). Solid-supported catalysts can be more easily separated and recovered compared to homogeneous catalysts, reducing the palladium contamination in the polymers.[49,50] Silia*Cat* DPP-Pd offered slightly superior performances

Figure 1. Synthesis of PiIEDOT (see Table S3, entries 6 and 11−13). The phase transfer agent and base used are TBAC and K_2CO_3, except for the anhydrous condition ($\overline{M}_n$ = 79 kg/mol), which used TBAB and Cs_2CO_3. The reactions are performed in pressurized vessels.

Figure 2. UV−vis absorption coefficients in solution in chloroform of PiIEDOT synthesized using the reaction conditions (a) described in Table S1 (entries 2 and 8) and samples synthesized using previously published, anhydrous conditions (Pd(Herrmann))[38] and (b) synthesized using the reaction conditions described in Table S3, from entries 12 (anhydrous, with oxygen), 6 (anhydrous), 13 (with water), and 11 (with water, with oxygen), and a high-molecular-weight sample obtained using previously published conditions (Pd(Herrmann)).[38]
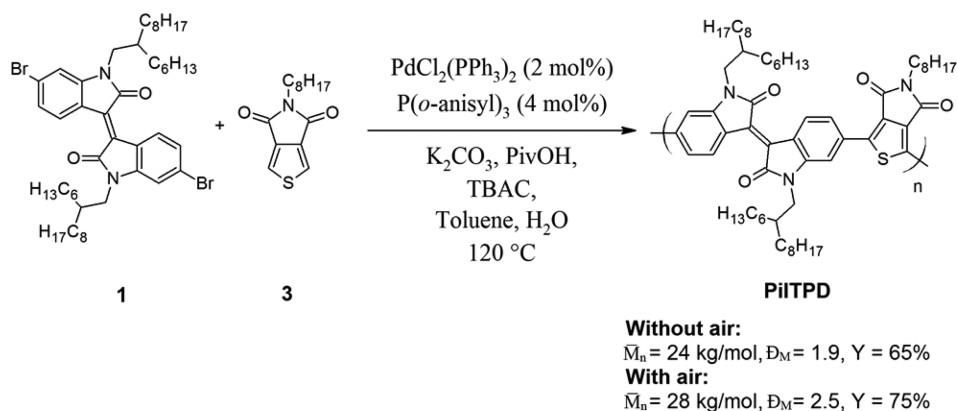
Figure 3. Synthesis of PiITPD with or without the presence of air in the reaction (see Table S5, entries 11 and 12).
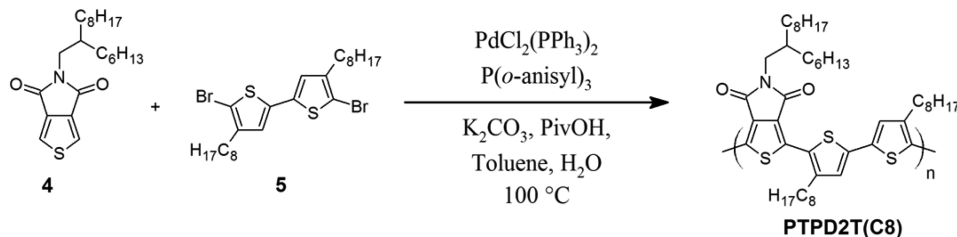
Figure 4. Synthesis of PTPD2T(C8).

compared to that of $Pd(OAc)_2$, providing a material with $\bar{M}_n$ of 84 kg/mol, whereas Silia*Cat* Pd0 resulted in low-molecular-weight materials.

Synthesis of PiITPD. Biphasic DHAP was also attempted using isoindigo and an electron-poor comonomer, namely, 5-octylthieno[3,4-*c*]pyrrole-4,6-dione (monomer **3**). Initial tests were performed using 2 mol % of $Pd(OAc)_2$, Cs_2CO_3, PivOH, TBAB, toluene (concentration of 0.2 M), and water (Table S5, entry 1). This led to a material with a $\bar{M}_n$ of 18 kg/mol, albeit in low yield (45%). Further optimization was performed and is summarized in Table S5 in the SI. Better results were obtained with $PdCl_2(PPh_3)_2$ as the precatalyst, by switching the base to K_2CO_3, and by changing the counteranion of the phase transfer agent, using TBAC instead of TBAB ($\bar{M}_n$ = 24 kg/mol, see Figure 3). This result is similar to what was previously published for PiITPD synthesized by DHAP.[51] In this case, introducing air in the reaction yielded slightly higher $\bar{M}_n$ (28

kg/mol) and yield (75%). UV−vis spectra of the optimized samples (Table S5, entries 11 and 12) are similar to one another and to those previously published (see Figure S19).[51,52] This example demonstrates that robust DHAP reactions in water are also possible with electron-poor thiophene derivatives.

Synthesis of PTPD2T(C8). To further develop the scope of these biphasic reaction conditions, an example of thiophene on thiophene coupling was investigated. We attempted to synthesize PTPD2T(C8) (see Figure 4), the first push−pull copolymer obtained via DHAP.[53] The complete optimization results are summarized in the SI (Tables S8−S10), while selected reaction conditions are presented in Table 1. The first attempt utilized the same reaction conditions that we developed for the synthesis of PiIEDOT, but molecular weights and yields were unsatisfactory ($\bar{M}_n$ = 4 kg/mol, $Đ_M$ = 1.8, yield = 6%). Testing other precatalysts revealed that $PdCl_2(PPh_3)_2$

Table 1. Selected Optimization Conditions of the DHAP of PTPD2T(C8)[a]

no.	catalyst (mol %)	ligand (mol %)	equiv of K_2CO_3	temp (°C)	$\bar{M}_n$ (kg/mol)	$\bar{M}_w$ (kg/mol)	$Đ_M$	$\bar{M}_n^{NMR}$ (kg/mol)	Y (%)
1[b]	2	4	3.1	120	14	23	1.6		28
2[b]	4	8	3.1	120	12	22	1.8		32
3	4	8	3.1	120	13	20	1.5		81
4	4	16	3.1	100	17	27	1.6		92
5[c]	4	16	3.1	100	25	44	1.8	23	100
6	4	16	10	100	37	68	1.8		95
7	4	16	40	100	52	88	1.7	57	94
8	2	8	40	100	69	132	1.9		98
9	1	4	40	100	72	136	1.9	68	97
10	0.5	2	40	100	66	120	1.8		99
11[d]	1	4	40	100	35	65	1.9		98
12[d]	2	8	40	100	43	80	1.9		95
13[e]	1	4	40	100	62	113	1.8	71	99
14[d,e]	1	4	40	100	39	68	1.7	-	96
15[e]	1	4	3.1	100	N/A[f]				N/A[f]

[a]The catalyst used is $PdCl_2(PPh_3)_2$, and the ligand is $P(o\text{-anisyl})_3$. The other reaction conditions are displayed in Figure 4 and in the experimental procedure details (in the SI). [b]Reaction performed with a phase transfer agent: TBAC. [c]Reaction performed using 1.05 equiv of **5**. [d]Reaction performed without inert atmosphere and nondegassed solvents. [e]Reaction performed in anhydrous conditions. [f]Oligomers were formed and were not isolated.

was a better source of palladium for this polymerization (Table 1, entry 1, $\bar{M}_n$ = 14 kg/mol, $Đ_M$ = 1.6), but the yield was still low at 28%, and the majority of the material was removed during Soxhlet extraction with hexanes. Unlike with PiIEDOT and PiITPD, polymerizations of PTPD2T(C8) with water were slow. Color change of the reaction mixture, which indicates the formation of oligomers and polymers, only occurred after several hours.

To improve reactivity, we investigated several other reaction conditions. Using other ligands did not result in higher molecular weight polymers: tris(2,4,6-trimethoxyphenyl)-phosphine, tri-*tert*-butylphosphonium tetrafluoroborate, triphenylphosphine, tricyclohexylphosphonium tetrafluoroborate, di-*tert*-butyl(methyl)phosphonium tetrafluoroborate, and tris(o-tolyl)phosphine only yielded low-molecular-weight oligomers. Reactions without a phosphine ligand did not yield polymerization products. Using other solvents, such as THF, 1,2,4-trichlorobenzene, 1,2-dichlorobenzene, 1,2-dichloroethane, benzene, *p*-xylene, *o*-xylene, or chlorobenzene inhibited the reaction. Increasing the catalyst load to 4 mol % instead of 2 mol % yielded similar molecular weights, albeit in a slightly higher yield of 32% (Table 1, entry 2). Further increasing it to 7 or 10 mol % had marginal effect. TBAC was detrimental in this case, as a reaction without it increased the yield to 81% (Table 1, entry 3, $\bar{M}_n$ = 13 kg/mol, $Đ_M$ = 1.5).[54] Using 1-adamantanecarboxylic acid instead of PivOH did not increase molecular weights; neither did using K_3PO_4 as the base. Increasing the ligand-to-catalyst ratio from 2:1 to 4:1 increased the yield slightly ($\bar{M}_n$ = 12 kg/mol, $Đ_M$ = 1.5, yield of 88%).

As obtained molecular weights still fell short of those already published,[53,55] ^{1}H NMR spectroscopy of one of the low-molecular-weight materials (conditions from Table 1, entry 3) was used to investigate the structure of this PTPD2T(C8) sample (see Figure 5). The polymer has a well-defined structure with the same main peaks as published examples.[53,55] By analyzing the smaller peaks, we identified the thienopyrrole-dione (TPD) end group at 7.75 ppm. However, there were no signals at 6.97 and 6.92 ppm corresponding to the brominated end group (**2T-Br**). Instead, only the debrominated end group (**2T-H**) was observed (signals at 7.10 and 7.06 and 6.86 ppm).
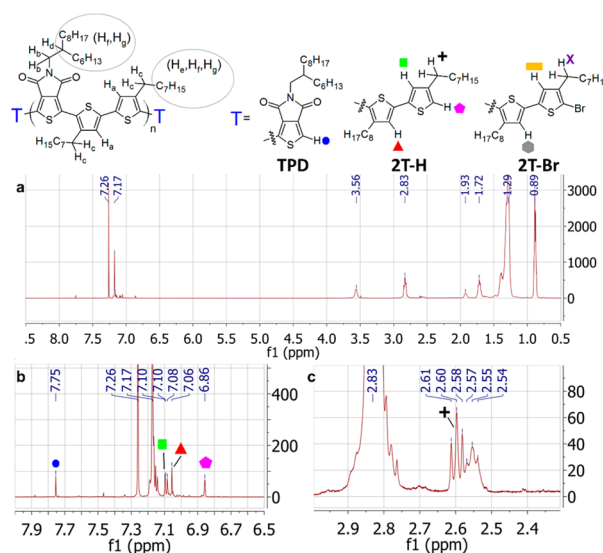

Figure 5. (a) ^{1}H NMR spectrum and (b and c) regions of interests of a low-molecular-weight PTPD2T(C8) sample (Table 1, entry 3) obtained using biphasic DHAP.

The calculation of the molecular weight using the end group integrations (H_a:TPD:**2T-Br**:**2T-H** = 92.7:2.4:0:4.9, $\bar{M}_n^{NMR}$ = 11 kg/mol) was in good agreement with the molecular weight obtained by SEC. Several very faint signals are observed in the 8.0−7.5 and the 7.1−6.7 ppm regions of the spectrum, which could indicate small amounts of unidentified defects are present.

To try to reduce undesirable side-reactions, a lower reaction temperature of 100 °C was used. This slightly increased molecular weights and yields (Table 1, entry 4, $\bar{M}_n$ = 17 kg/mol, $Đ_M$ = 1.6, yield of 92%) and suppressed the formation of palladium black, which was usually observed at the end of the polymerization, demonstrating a better stability of the catalyst. However, molecular weights remained low, indicating that debromination side-reactions may limit the chain growth. To confirm this hypothesis, polymerization attempts using an increased stoichiometry of the brominated monomer **5** were

performed (see Table S8, entries 9–14). Molecular weight increased when a 5 mol % excess of **5** was used ($\bar{M}_n$ of 25 kg/mol, $Đ_M$ = 1.8), and the yield was quantitative, demonstrating the incorporation of the excess of monomer into the polymer chain. Homocoupling of the bithiophene monomer **5** is thus very likely, though there is no major change in the NMR spectrum (see Figure S43). Similar results are obtained when using K$_3$PO$_4$ as the base (2.5 mol % excess of **5**, $\bar{M}_n$ = 26 kg/mol, $Đ_M$ = 1.7, yield of 96%). Debromination thus limits molecular weights in this biphasic DHAP method and is not occurring only after the polymerization ends.[56] This is not surprising as this is a common side-reaction in Suzuki reactions, which typically also use biphasic conditions.[57−59]

The slow polymerization speed might allow more time for a side-reaction to occur,[60] which in our case seems enough to limit the molecular weights. To circumvent this problem, the rate of formation of the desired C−C bond must be increased. In our preliminary testing, we observed that agitation impacted the reaction outcome of biphasic DHAP, hinting that the availability of the water-soluble reagents, namely, the base and the acid additive, could be a rate-determining factor. Thus, we increased the amount of the K$_2$CO$_3$ base to 10 equiv, which resulted in a significant increase in the molecular weights (Table 1, entry 6, $\bar{M}_n$ = 37 kg/mol, $Đ_M$ = 1.8) and yield (95%). Increasing again the amount of base to 40 equiv (near-saturated K$_2$CO$_3$ solution) further increased molecular weights (Table 1, entry 7, $\bar{M}_n$ = 52 kg/mol, $Đ_M$ = 1.7, yield of 94%). Reaction rate was noticeably faster, with color change from yellow (color of the catalyst in solution) to bright orange-red in less than 10 min. The influence of the amount of the PivOH additive was also investigated. Using 13 equiv to obtain a PivOH to K$_2$CO$_3$ ratio of approximately 1:3 led to lower molecular weights (Table S10, entry 3, $\bar{M}_n$ = 25 kg/mol, $Đ_M$ = 1.7, yield of 96%), whereas reducing its amount to 0.5 equiv had little influence on the reaction outcome (Table S10, entry 4, $\bar{M}_n$ = 52 kg/mol, $Đ_M$ = 1.8, yield of 96%). A polymerization done without PivOH is much slower, which limits molecular weights (Table S10, entry 5, $\bar{M}_n$ = 36 kg/mol, $Đ_M$ = 1.6, yield of 83%). Pivalic acid is thus not the rate-limiting reagent for this reaction. Base availability, on the other hand, seems to be the key to increasing the reactivity of DHAP in biphasic conditions.

To complete our optimization, we reduced the catalyst load, in line with our optimization of the synthesis of PiIEDOT. At 2 and 1 mol % of Pd, molecular weights and yields were increased to $\bar{M}_n$ = 69 and 72 kg/mol, respectively, and were isolated in nearly quantitative yields (see Table 1, entries 8 and 9). At 0.5 mol %, a small decline in molecular weight is observed (Table 1, entry 10, $\bar{M}_n$ = 66 kg/mol, $Đ_M$ = 1.8, yield of 99%). It is notable this is the highest reported molecular weight for PTPD2T(C8). Scale-up of the reaction to 0.3 mmol (from 0.1 mmol) yielded significantly lower molecular weights (Table S10, entry 17, $\bar{M}_n$ = 12 kg/mol, $Đ_M$ = 1.6, yield of 58%) when using the same vessel size (Biotage microwave vial, size 2−5 mL) and magnetic stirrer. Mixing of the two phases was noticeably poor, which was corrected by using a larger reaction vessel (Biotage microwave vial, size 10−20 mL) with a larger magnetic stirrer. This restored the higher molecular weights (Table S10, entry 17, $\bar{M}_n$ = 68 kg/mol, $Đ_M$ = 1.9, yield of 97%), showcasing the critical importance of providing a high contact surface area between the two liquid phases, and goes along the lines that base availability is a limiting factor in this reaction system. Using the same optimized catalytic system in anhydrous conditions provided a similarly high-molecular-weight material (Table 1, entry 13, $\bar{M}_n$ = 62 kg/mol, $Đ_M$ = 1.8, yield of 99%). Performing the anhydrous reaction using a lower amount (3.1 equiv) of base only produced oligomers. This is an interesting observation as base availability is demonstrated to be of vital importance for DHAP, regardless of the use of a biphasic system.

To compare our materials produced in biphasic conditions, we synthesized PTPD2T(C8) using the DHAP methodologies previously reported. The first synthesis, published by our group, uses Pd(Herrmann) as the precatalyst with P(*o*-anisyl)$_3$ as the ligand, Cs$_2$CO$_3$ as the base, and superheated THF at 120 °C as the solvent (Berrouard's method).[53] Stirring was found to critically affect reactivity, and after several attempts a material with $\bar{M}_n$ of 47 kg/mol ($Đ_M$ = 2.9) was isolated in 93% yield. Using these reaction conditions with added water did not produce a polymer. We also reproduced the synthesis presented by Ozawa et al.,[55] which produces low-defect materials, though in more limited molecular weights. The reaction conditions are PdCl$_2$(MeCN)$_2$ (1 mol %), P(*o*-anisyl)$_3$, Cs$_2$CO$_3$, PivOH, and superheated THF at 100 °C. In our case, $\bar{M}_n$ was limited to only 18 kg/mol, but only one test reaction was performed. We did not use a glovebox and Schlenk glassware, as used in the original publication, and it is likely water contamination is introduced when the hygroscopic base and acid additive are weighed in air. Water seems detrimental with these reaction conditions, as an attempt with added water did not yield any polymer. These difficulties demonstrate the reproducibility issues which can be encountered in DHAP and highlight the advantages of more robust reaction conditions able to withstand atmospheric contaminants.

The ^{1}H NMR spectra of materials synthesized from Ozawa's and Berrouard's methods are compared with those obtained using our biphasic system (From Table 1, entries 7, 9, and 13) in Figure 6. The polymer synthesized using Ozawa's method features all three types of end groups (ratios of H$_a$:TPD:**2T-Br**:**2T-H** = 94.2:1.1:3.2:1.5), with a calculated molecular weight of $\bar{M}_n^{NMR}$ = 13 kg/mol. This polymer's spectrum only has a very small number of minor peaks which might be caused by unidentified defects, demonstrating the excellent selectivity of this catalytic system. However, the fact that the molecular weight is lower and that brominated functions remain after over 24 h of reaction time means this catalytic system is not active or stable enough to achieve high degrees of polymerization. In contrast to this sample, all the other polymers analyzed, including the one made using Berrouard's method, only have debrominated **2T-H** end groups. It was not investigated whether debromination occurs during polymerization and acts as an end-capping reaction, or if it happens after the polymer is formed. The absence of TPD end groups, however, could be indicative of possible C−H/C−H homocoupling defects. This cannot be confirmed since there is no observable minor peak shifted downfield, which would be linked to TPD−TPD repeat units.[61] The polymer sample synthesized using Berrouard's method features several minor (<1%) unidentified peaks (maybe bithiophene−bithiophene homocouplings), as does the polymer synthesized using anhydrous conditions (from Table 1, entry 13). The polymers synthesized using water appear to have many fewer defects, closer to Ozawa's method. This newly developed reaction system, apart from being very robust, is a good compromise between reactivity and selectivity for the synthesis of PTPD2T(C8).
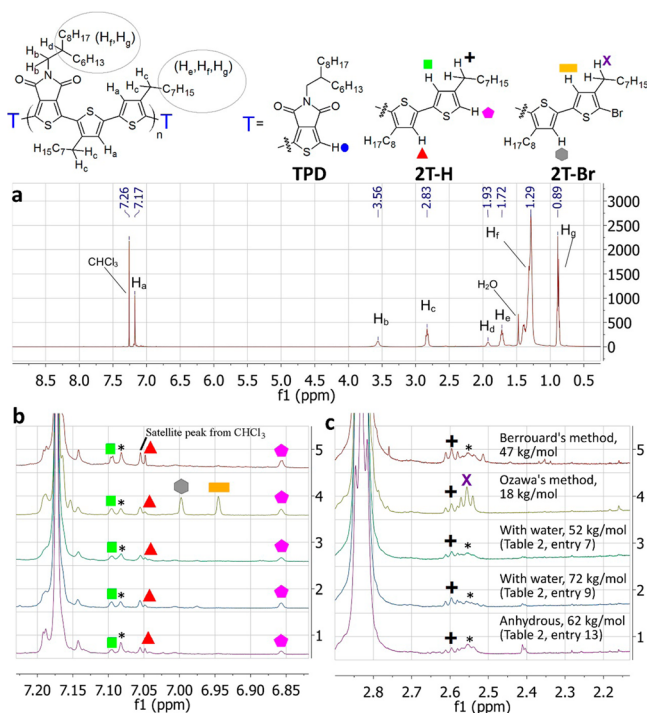
Figure 6. (a) ^{1}H NMR spectrum of PTPD2T(C8) (from Table 1, entry 9) and (b and c) zoomed parts of the ^{1}H NMR spectra of samples synthesized using previously published DHAP conditions (Berrouard et al.[53] and Ozawa et al.[55] methods) and from methods presented in this work (from Table 1, entries 7, 9, and 13). End groups are analyzed, and peaks marked with * are unidentified peaks also observed by Ozawa et al.

The thermal transitions of the same PTPD2T(C8) samples were investigated using DSC measurements. The resulting thermograms are presented in Figure 7 and reveal that the polymers synthesized in biphasic conditions have higher melting and crystallization temperatures than the three other samples. The highest molecular weight sample also features the highest melting temperature at 242 °C, which is higher than any recorded for this polymer.[53,55] This indicates that this sample has a more stable crystalline phase, which can be linked not only to molecular weights, but also to the high regioregularity of the polymer. The sample obtained from Berrouard's method has thermal transitions at lower temperatures compared even to the low-molecular-weight sample made using Ozawa's method, confirming that this polymer contains more defects than the others.
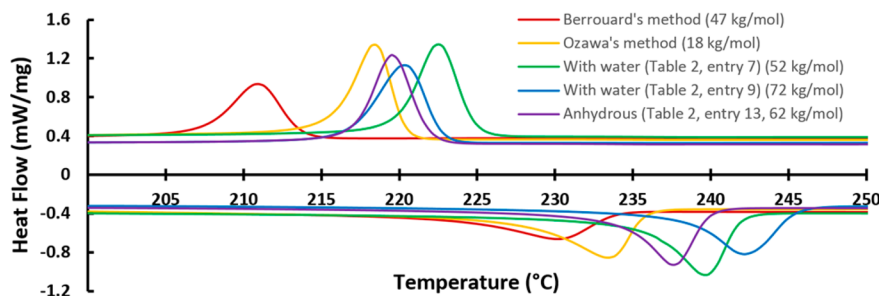
Finally, we investigated the robustness of the reaction in air. With the introduction of air, molecular weights dropped significantly ($\bar{M}_n$ = 35 kg/mol, $Đ_M$ = 1.9, yield of 98%). Increasing the catalyst load to 2 mol % increased the $\bar{M}_n$ to 43 kg/mol. An anhydrous reaction in the presence of air yielded similar results ($\bar{M}_n$ = 39 kg/mol, $Đ_M$ = 1.7, yield of 96%). Polymers of reasonable molecular weight are still isolated even though a large amount of oxygen is present, demonstrating the resilient nature of these DHAP conditions.

Applicability to Other Systems. Following these results, the optimized catalytic system was tested on a variety of other monomer couples, as shown in Table 2 and Figure 8. Using this modified protocol, PiITPD showed higher molecular weights ($\bar{M}_n$ = 34 kg/mol, $Đ_M$ = 3.2) and yield (92%) while retaining similar optical properties (see Figure S19 in the SI). For PiIEDOT, molecular weights were also higher ($\bar{M}_n$ = 93 kg/mol, $Đ_M$ = 2.9), similar to previously published results,[38] though yield was limited to 77% because of the formation of high-molecular-weight material that is insoluble in chloroform. This residual material was not analyzed, but was completely soluble in 1,2-dichlorobenzene at 100 °C. In contrast to our previous attempts, PiITPD and PiIEDOT are readily obtained without using a phase transfer agent.

Scalability of the polymerization of PiIEDOT was investigated, with a reaction on 0.3 mmol of monomer successfully yielding a high-molecular-weight material ($\bar{M}_n$ = 93 kg/mol, $Đ_M$ = 2.4, yield of 95%). Scale-up to 2.0 mmol was performed using an airtight reactor equipped with a mechanical stirrer. An even higher molecular weight ($\bar{M}_n$ = 137 kg/mol, $Đ_M$ = 2.6) material was obtained in nearly quantitative yield (98%). This increase in molecular weight, the highest to date for this polymer, might have been possible due to the higher torque provided by the mechanical stirring, leading to a better mixing of the phases even when the solution became viscous as the polymerization progressed.

Application to other monomer couples was attempted, and two fluorene-based copolymers were successfully synthesized using EDOT or 2,2′-bithiophene (to form PFEDOT and PF2T, respectively) as the comonomers. Previous optimizations of biphasic DHAP were unsuccessful for these materials (Tables S6 and S7 of the SI), but this methodology allowed the formation of PFEDOT (Table 2, entry 5) with a high $\bar{M}_n$ of 63 kg/mol. The ^{1}H NMR spectrum of PFEDOT indicates a well-defined structure (Figure S44 in the SI), and the only minor peaks present can be assigned to end groups. The DSC thermogram (Figure S27 in the SI) reveals a glass transition temperature (T_g) of 153 °C, a much higher value than was previously published for PFEDOT (129 °C),[62] though no crystallization peak is observed. Similarly, PF2T was obtained in

Figure 7. DSC thermograms of PTPD2T(C8) samples synthesized using previously published DHAP conditions (Berrouard et al.[53] and Ozawa et al.[55] methods) and from methods presented in this work (from Table 1, entries 7, 9, and 13).

Table 2. Molecular Weights of the Polymers Obtained Using the Reaction Conditions Described for the Synthesis of PTPD2T(C8) in Table 1, Entry 9

entry	polymer	reaction scale (mmol of each monomer)	$\bar{M}_n$ (kg/mol)	$\bar{M}_w$ (kg/mol)	$Đ_M$	Y (%)
1	PiIEDOT	0.1	93	271	2.9	77
2	PiIEDOT	0.3	93	224	2.4	95
3	PiIEDOT	2.0	137	354	2.6	98
4	PiITPD	0.1	34	110	3.2	92
5	PFEDOT	0.1	63	192	3.0	97
6	PF2T	0.1	32	148	4.6	90
7	PDPP2T(C8)	0.1	58	104	1.8	97
8	PTPD3T(C12)	0.1	40	94	2.4	93
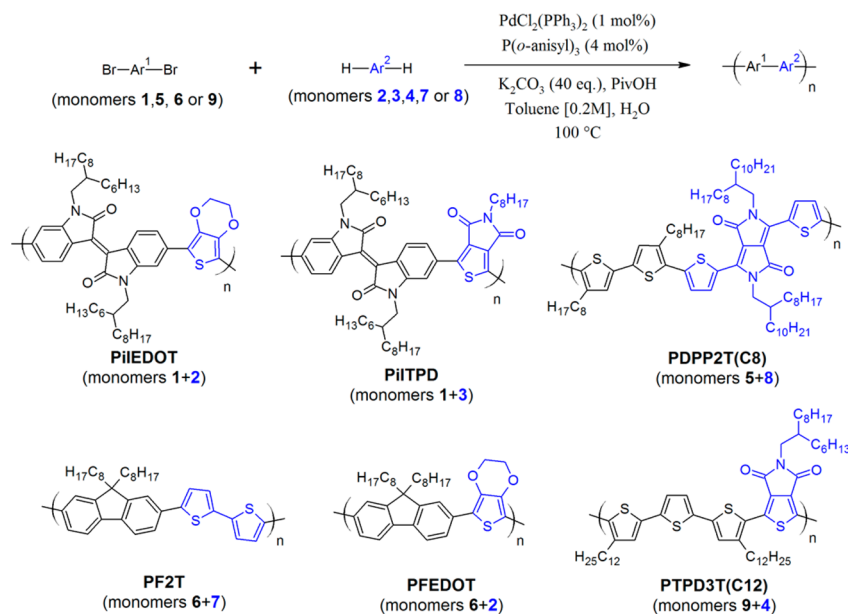
Figure 8. Synthesis of other polymers using the optimized polymerization conditions.

a high $\bar{M}_n$ of 32 kg/mol, which is the highest value reported for this polymer. The ^{1}H NMR is also well-defined (Figure S45 in the SI), with identical minor (end group) peaks as those reported for a defect-free PF2T.[24] The UV–vis absorption spectra are also identical to that for this defect-free material (Figure S20). The DSC analysis reveals a T_g at 100 °C (see Figure S28). Two melting and two crystallization peaks are observed (238/282 °C and 241/282 °C, respectively) and are higher than those previously reported.[62,63] This particular example demonstrates that this new catalytic system can be used to polymerize unsubstituted bithiophene to obtain almost defect-free, high-molecular-weight materials in biphasic conditions.

A diketopyrrolopyrrole (DPP) derivative (monomer 8) was also polymerized with comonomer 5 to form PDPP2T(C8). DPP derivatives are used to synthesize some of the highest-performing organic field effect transistors[64,65] and solar cells[66,67] and are thus valuable targets for application in DHAP. This polymer, which is synthesized for the first time, was formed easily using our method, achieving a high $\bar{M}_n$ of 58 kg/mol and nearly quantitative yield of 97%. This polymer has crystallization and melting temperatures of 208 and 227 °C, respectively. The ^{1}H NMR spectrum (Figure S46 in the SI) shows the polymer is well-defined, though the peaks are too broad to allow end group analysis. This polymer exhibits a low bandgap (1.35 eV), and its UV–vis–NIR absorption profile

(Figure S21) is devoid of any long-wavelength shoulder, which would indicate the presence of DPP homocoupling.[35]

The last polymer synthesized using this method is PTPD3T-(C12), a copolymer of the TPD monomer 4 and a terthiophene derivative (comonomer 9, see Figure 8). This polymer is used in high-performance organic solar cells.[43,68] Again, polymerization was easily achieved with high molecular weight ($\bar{M}_n$ = 40 kg/mol, $Đ_M$ = 2.4, yield of 93%), a result similar to that from the original publication,[68] which used Stille polymerization, and double that reported recently for PTPD3T(C12) synthesized by DHAP.[43] The ^{1}H NMR (Figure S47 in the SI) confirms the alternated structure of the polymer. A minor peak at 7.79 ppm can be associated with TPD end groups, and peaks at 7.10 and 6.90 ppm can be associated with debrominated monomer 9 end groups. No brominated end group is identified, in line with our observations for PTPD2T(C8). Very few minor peaks are present, and they are difficult to distinguish from the background noise, meaning that this polymer is almost defect-free. The calculated NMR molecular weight is $\bar{M}_n^{NMR}$ = 36 kg/mol, in good agreement with the SEC results. Melting and crystallization temperature, 304 and 282 °C, respectively, are higher than those previously published (290 and 259 °C).[68] The UV–vis absorption spectrum is similar to those published, but the vibronic structure is more defined (Figure S21).

CONCLUSION

In summary, we have developed robust toluene/water biphasic direct (hetero)arylation polymerization (DHAP) conditions at ambient pressure using a low-cost base (K_2CO_3) and a catalytic system which is resilient, to a certain extent, to the presence of oxygen. The polymerization conditions presented herein were found to be general and provided several examples using halogenated phenyl or thiophene derivatives copolymerized with other thiophene derivatives, electron-poor or electron-rich. For instance, unsubstituted bithiophene reacted selectively, affording a well-defined, mostly defect-free conjugated polymer in high yield. The precatalyst used and its amount played a critical role in obtaining higher-molecular-weight materials. We also demonstrated that a major limiting factor of DHAP reactions is the availability of the base, and large excess of this critical component provided higher reactivity, which allowed the formation of a higher proportion of the desired C−C bonds relative to end-capping debromination reactions. Increasing the amount of base also augmented the reactivity in anhydrous conditions, giving useful insight for improving these reaction systems. Most of the polymers presented in this work possess either higher molecular weights, red-shifted UV−vis−NIR absorption maxima, and/or higher melting and crystallization temperatures when compared to data for previously published examples made using DHAP or other cross-coupling reactions. It is anticipated that this work will provide a basis for more developments of robust, user-friendly DHAP conditions and convenient alternatives to Stille and Suzuki polymerizations.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b12955.

Experimental and characterization details, monomer and polymer synthesis, spectra, and tables of data (PDF)

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Notes

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ACKNOWLEDGMENTS

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