Room Temperature Synthesis of a Well-Defined Conjugated Polymer using Direct Arylation Polymerization (DArP)

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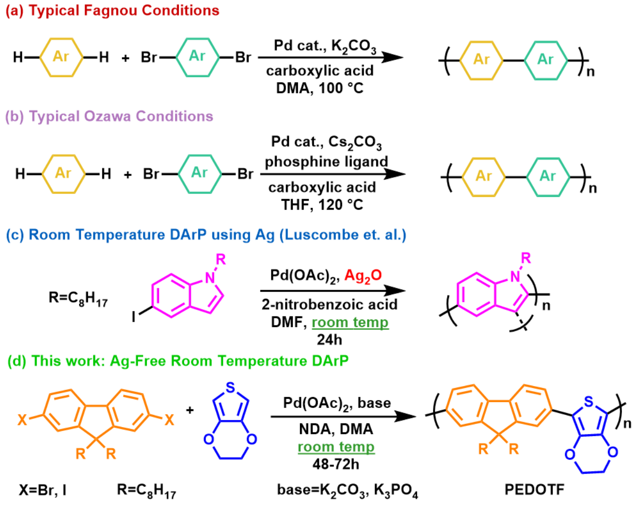
ABSTRACT: While a major improvement to the sustainability of conjugated polymer synthesis, traditional direct arylation polymerization (DArP) still requires high temperatures (typically >100 °C), necessitating a significant energy input requirement. Performing DArP at reduced or ambient temperatures would represent an improvement to the sustainability of the reaction. Here we describe the first report of a well-defined conjugated polymer synthesized by DArP at room temperature. Previous efforts toward room temperature DArP relied on the use of near stoichiometric silver reagents, an expensive coinage metal, which makes the reaction less cost effective and sustainable. Here, room temperature polymerizations of 3,4-ethylenedioxythiophene (EDOT) and 9,9-dioctyl-2,7-diiodofluorene were optimized and provided molar mass (M_n) up to 11 kg/mol of PEDOTF, and performing the reaction at the standard ambient temperature of 25 °C provided M_n up to 15 kg/mol. Model studies using other C-H monomers of varying electron density copolymerized with 9,9-dioctyl-2,7-diiodofluorene provided insight into the scope of the room temperature polymerization, suggesting that performing room temperature DArP is highly dependent on the electron richness of the C-H monomer.

Conjugated polymers are a class of materials with a broad range of applications such as organic light emitting diodes (OLEDs)[1], organic photovoltaics (OPVs)[2], and bioelectronics.[3] Traditionally used cross coupling reactions to synthesize conjugated polymers, especially the Stille-Migita reaction, use stoichiometric amounts of toxic transmetallating reagents, posing an environmental hazard and limiting the scalability of the reaction.[4] Direct arylation polymerization (DArP) eliminates the transmetallating reagent by directly activating the C-H bond, improving the sustainability of the reaction.[5–7] Recently, further improvements to the sustainability of DArP have been made, including using green solvents[8,9] and implementing emulsion or biphasic polymerization methods[10–12] in order to reduce the amount of hazardous organic waste produced, polymerizing under aerobic conditions,[13] as well as replacing Pd catalysts with much cheaper and more abundant Cu based catalysts[14], or by using recyclable heterogeneous catalysts.[15]

Reaction temperature is another factor by which improvements to the sustainability of DArP can be made. Lower temperature reactions or those at room temperature are more energy efficient than reactions that require higher temperatures.[16] Therefore, it is desirable to find conditions for synthesizing conjugated polymers that limit the energy input required for the reaction to proceed.

Traditional DArP conditions use high temperatures (Scheme 1a, 1b), resulting in high energy consumption as well as a less controlled reaction. At lower temperatures, the reaction would be more energy efficient, as well as reducing the amount of side reactions.[17,18] Other methods of synthesizing conjugated polymers at room temperature have been reported, such as Stille polymerization as well as through C-S bond activation, however, organotin functionalization is still required in both cases.[19,20] Reports of room temperature polymerizations of conjugated polymers also exist using extreme pressure (24.4 GPa) or highly acidic conditions (pH 0.45), but such harsh conditions detract from the sustainability of the reaction.[21,22]

Scheme 1. Conditions for Direct Arylation Polymerization



Scheme 1. (a) General scheme of typical Fagnou DArP conditions, where a polar coordinating solvent such as DMA is employed along with a non-nucleophilic base and a carboxylic acid additive. (b) General scheme of typical Ozawa DArP conditions, where the solvent is non-coordinating and a phosphine ligand instead coordinates to the catalyst. (c) Report of room temperature DArP using a Pd/Ag system from Luscombe et. al. where crosslinked polyindole oligomers were formed. (d) This work, a silver-free room temperature synthesis of well-defined conjugated polymer PEDOTF.

Previously, only two methods for room temperature DArP have been reported, the first being P3HT synthesized at good molar mass (14 kg/mol) but in only trace yields.[18] In the other report, Luscombe et al. synthesized polyindole (Scheme 1c) at room temperature using near stoichiometric equivalents of a silver reagent, an expensive coinage metal.[23] Additionally, this polymerization did not produce a well-defined polymer. While this report marked an important step forward in understanding how to improve energy

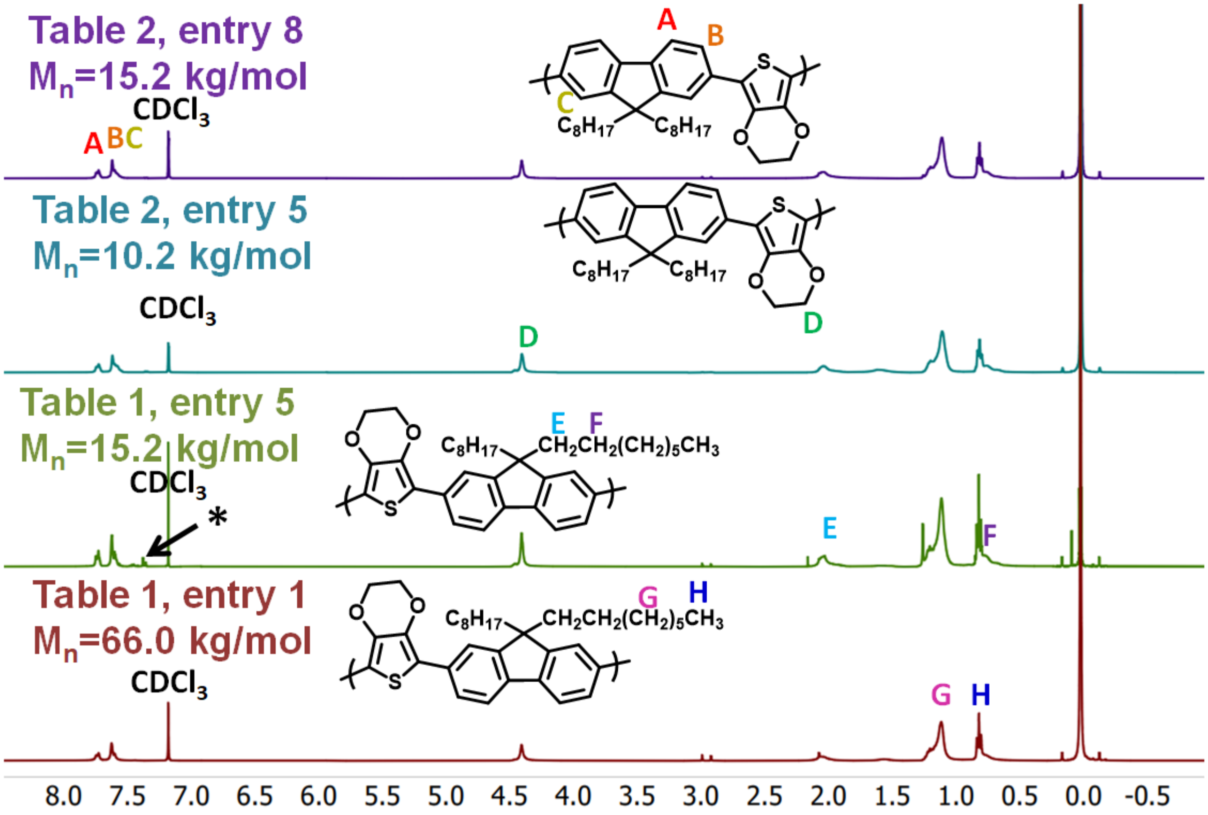


Figure 1. ^{1}H NMR of four of the polymers synthesized. Major resonances are denoted A-H. The * denotes peaks associated with homocoupling. Collected in CDCl3 at 25 °C and 400 MHz.

efficiency in DArP, the addition of near stoichiometric coinage metal adds a significant expense to the reaction, and makes it less sustainable than a reaction without silver.

Herein we report the first instance of a well-defined conjugated polymer synthesized in good yield by DArP at room temperature and further, without the use of coinage metal additives. The conditions chosen for this study were Fagnou-derived conditions[5,24] (Scheme 1a), where a polar solvent, typically N,N-Dimethylacetamide (DMA) coordinates to the palladium catalyst, since these conditions typically require lower temperatures than for Ozawa conditions. In Ozawa conditions, where the solvent is non-coordinating (typically THF or toluene) and a phosphine ligand is instead used to coordinate to the catalyst, heating is typically required at or above 120°C[5,25] (Scheme 1b). The polymer investigated in this study is PEDOTF (Scheme 1d) due to the high reactivity of the monomers under Fangou conditions as shown in a previous study using a heterogeneous palladium catalyst, where high molar mass PEDOTF was synthesized through DArP even after only 30 minutes with heating at 100 °C.[15] PEDOTF also has potential applications in electrochromics and OLEDs, due to its electroluminescent properties.[26]

Using 3,4-ethylenedioxythiophene and either 9,9-dioctyl-2,7-dibromofluorene or 9,9-dioctyl-2,7-diiodofluorene, a variety of polymerization conditions were investigated, including the nature of the halogen, choice of base, reaction concentration and reaction time, in order to optimize the polymerization at lower temperatures.

Table 1. Investigating temperature dependence using conditions from Scheme 1d with dibromofluorene[a]

Entry[b]	base	Temp (°C)	M$_n$ (kg/mol)[c]	Đ[c]	Yield (%)
1	K_2CO_3	100	66.0	4.40	98
2	K_2CO_3	70	30.5	2.30	82
3	K_2CO_3	50	5.6	2.98	50
4	K_3PO_4	50	28.9	2.35	60
5	K_3PO_4	40	15.2	1.76	56
6	K_3PO_4	30	8.9	1.97	53

[a]All polymerizations conducted using conditions shown in Scheme 1d. [b]All entries used 9,9-dioctyl-2,7-dibromofluorene (X=Br), a 5% catalyst loading for Pd(OAc)$_2$, a 48 hr reaction time, and run at 0.3M in DMA, see SI for experimental details. [c]Estimated by GPC (140 °C, 1,2,4-trichlorobenzene) calibrated with polystyrene standards.

Standard Fagnou-derived conditions were initially tested, using potassium carbonate and neodecanoic acid as the base and carboxylic acid additive respectively, and heating the reaction at 100 °C for 48 hrs. The polymerization was run in DMA at a concentration of 0.3M as is typical for DArP. This condition yielded a high molar mass polymer of 66.0 kg/mol (Table 1, entry 1). Reducing the temperature to 70 °C resulted in a reduced M$_n$ of 30.5 kg/mol (Table 1, entry 2). Further reducing the temperature to 50 °C produced a polymer of M$_n$ 5.6 kg/mol (Table 1, entry 3), which is an insufficient molar mass, based on the benchmark of properties saturating in the classic conjugated polymer poly(3-hexylthiophene) (P3HT) at around 10 kg/mol.[27] This shows that at temperatures below 70 °C under these conditions the monomers are not reactive enough to produce a polymer of sufficient molar mass during the given reaction time.

In order to overcome the decreased reactivity due to lowered temperature, the base was changed from potassium carbonate to the stronger base potassium phosphate, which resulted in a significant increase in M_n to 28.9 kg/mol(Table 1, entry 4) at 50 °C, however dropping the temperature further to 40°C under the same conditions reduced the M_n to 15.2 kg/mol (Table 1, entry 5), and while an acceptable molar mass, further decreasing the temperature to 30°C caused the molar mass to fall below the threshold of 10 kg/mol, providing a polymer of only 8.9 kg/mol (Table 1, entry 6). Although the polymer in Table 1 entry 5 was not synthesized at room temperature, it is still significant that such good molecular weight and yield was achieved at 40°C even when using the less reactive brominated monomer. In fact, all polymers synthesized in Table 1 showed yields of greater than 50%.

Table 2. Investigating temperature dependence using diiodofluorene using conditions from Scheme 1d[a]

Entry[b]	base	Temp (°C)[f]	M_n (kg/mol)[h]	Đ[h]	Yield (%)
1	K_2CO_3	50	48.0	1.71	52
2	K_2CO_3	40	26.8	3.26	33
3	K_3PO_4	40	33.6	3.38	61
4	K_3PO_4	R.T.	6.7	2.14	49
5[c]	K_3PO_4	R.T.	10.2	2.02	51
6[c,d]	K_3PO_4	R.T.	15.4	2.42	68
7[c, e]	K_3PO_4	R.T.	10.1	1.88	68
8[c]	K_3PO_4	25	15.2	2.24	65
9[c, g]	K_3PO_4	R.T.	11.6	2.13	60

[a]All polymerizations conducted using conditions shown in Scheme 1d. [b]All entries used 9,9-dioctyl-2,7-diiodofluorene (X=I), a 5% catalyst loading for Pd(OAc)$_2$, a 48 hr reaction time, and a 0.3M reaction concentration unless otherwise noted, see SI for experimental details. [c]Reaction time was 72 hrs. [d]Catalyst loading was 20%. [e]Catalyst loading was 2%. [f]R.T. denotes that reaction stirred in ambient conditions with no temperature control (21-22°C). [g]Reaction concentration was 0.4M. [h]Estimated by GPC (140 °C, 1,2,4-trichlorobenzene) calibrated with polystyrene standards.

The 9,9-dioctyl-2,7-dibromofluorene monomer was then exchanged for 9,9-dioctyl-2,7-diiodofluorene, given the increased reactivity of oxidative addition for Pd in C-I bonds over C-Br bonds. Returning to potassium carbonate as the base and heating the reaction at 50°C, the reaction yielded a polymer of M_n 48 kg/mol (Table 2, entry 1). This is over an 8-fold increase in molar mass as compared to the reaction under the otherwise same conditions using the 9,9-dioctly-2,7-dibromofluorene, which gave a M_n of 5.6 kg/mol (Table 1, entry 3). Even when this condition is used with the stronger base potassium phosphate (Table 1, entry 4), the molar mass is still much lower than when the 9,9-dioctyl-2,7-diiodofluorene is used. This speaks to the higher reactivity of the C-I bond assisting in forming the C-C bond in place of a surplus of energy in the form of heat to drive the reaction.

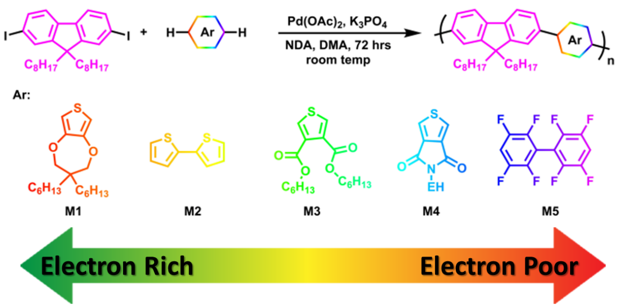
Similarly to the reactions with 9,9-dioctyl-2,7-dibromofluorene, decreasing the temperature to 40 °C gave a lower M_n of 26.8 kg/mol (Table 2, entry 2), as well as a decreased yield of 33%. However, when the base was changed to potassium phosphate at 40 °C, the molar mass increased to 33.6 kg/mol (Table 2, entry 3) and the yield was boosted significantly to 61%. Using these conditions, but running the reaction at ambient room temperature yielded a polymer with a low M_n of 6.7 kg/mol (Table 2, entry 4).

This result, although providing a polymer of insufficient molar mass, gave encouraging evidence that the polymerization still proceeded under ambient temperatures (without temperature control at ambient 21-22 °C). Increasing the reaction time from 48 hrs to 72 hrs boosted the molar mass to 10.2 kg/mol (Table 2, entry 5). This result represents the first instance of a well-defined conjugated polymer synthesized by DArP at room temperature with sufficient molar mass and yield.

Exploring further optimization, catalyst loading effects were then investigated using the conditions from Table 2, entry 5, and it was found that increasing the loading from 5% to 20% provided a polymer with an increased M_n of 15.4 kg/mol (Table 2, entry 6), and decreasing the catalyst loading to 2% gave a polymer of 10.1 kg/mol(Table 2 entry 7). Clearly, drastically increasing catalyst loading has a small effect on the molar mass of the polymer; however decreasing the catalyst loading does not significantly affect the molar mass, implying that the reactivity of the room temperature reaction is not strongly reliant on the amount of catalyst present in the reaction. The polymerization was also run in a temperature controlled bath at 25 °C using otherwise the same conditions from Table 2 entry 5, which is considered to be standard room temperature. This afforded a polymer of 15.2 kg/mol (Table 2, entry 8), demonstrating the impact of even a few degrees higher reaction temperature.

Finally, increasing the reaction concentration from 0.3M to 0.4M did not appear to have a significant impact on the molar mass of the polymer, providing a M_n of 11.6 kg/mol (Table 2, entry 9). The conditions used in entries 5 and 8 of Table 2 were replicated to investigate repeatability, and were found to give similar molar masses (see Supporting Information for details). Polymerizations using conditions from Scheme 1c, as well as conditions from Table 2 entry 5 with the additions of the Ag-based reagent were also attempted, however neither condition was successful (see Supporting Information for details). Also using conditions from Table 2 entry 5, but with the stronger base lithium *tert*-butoxide, decomposition was observed, and no polymer was recovered (see Supporting Information for details). Additionally, excluding light from the reaction did not have an effect on the molecular weight or yield (see Supporting Information for details), although some room temperature small molecule direct arylation reactions have been shown to be light sensitive.[28,29] There is also precedent for hexafluoroispropanol (HFIP) to facilitate room temperature small molecule C-H activation reactions.[30] However, when HFIP was tested as a solvent in this system no polymer was recovered (see Supporting Information for details). Analysis using ^{1}H NMR shown in Figure 1 does not show any significant differences in the polymers synthesized using four different conditions from Table 1 and Table 2. There may be some amount of homocoupling present, accounting for the small peaks seen at 7.5 ppm, which is known to happen when using a Pd^{II} catalyst.[31] However, these polymers are still well-defined linear polymers since no beta-branching occurs, as fluorene is known to react cleanly without branching side reactions under direct arylation conditions.[32]

Scheme 2. The scope of electron rich vs. electron deficient C-H monomers on reactivity



Scheme 2. (a) General scheme of room temperature polymerizations using monomers M1-M5 (ProDOT-Hx$_2$, 2,2-bithiophene, 3,4-dihexyl-3,4-thiophenedicarboxylate, 5-(2-ethylhexyl)-4H-Thieno[3,4-c]pyrrole-4,6(5H)-dione, 2,2′,3,3′,5,5′,6,6′-Octafluorobiphenyl. All polymerizations were carried out with co-monomer 9,9-dioctyl-2,7-diiodofluorene, using K_3PO_4, NDA, DMA at a concentration of 0.3 M and a reaction time of 72 hrs.

In order to more broadly probe reactivity under ambient temperature, we examined several other C-H monomers (Scheme 2, M1-M5) ranging from highly electron rich to highly electron deficient. The most electron rich C-H monomer of M1-M5, ProDOT-Hx$_2$, is still less electron rich than EDOT[33], and has precedent for use in DArP.[34] The thiophene derivatives M2-M4 have each also been used in high temperature DArP reactions, notably bithiophene has been used in the synthesis of N2200, an important n-type polymer, using DArP.[35] The most electron deficient of the C-H monomers used in this study, octafluorobiphenyl (M5), has also been polymerized using direct arylation.[36] Using the same conditions which yielded a good molar mass of PEDOTF at room temperature (Table 2, entry 5), each monomer M1-M5 was copolymerized with 9,9-dioctyl-2,7-diiodofluorene.

Table 3. Polymerization outcomes for monomers of varying electron density

Entry[a]	monomer	Temp (°C)	M_n (kg/mol)[b]	Đ[b]	Yield (%)
1	M1	R.T.	3.7	1.93	22
2	M2	R.T.	1.8	1.94	22
3	M3	R.T.	--	--	--
4	M4	R.T.	--	--	--
5	M5	R.T.	--	--	--
6[c]	M1	100	24.5	2.94	98
7[c]	M5	100	24.0	2.42	74

[a]All entries use conditions detailed in Scheme 2. [b]Estimated by GPC (140 °C, 1,2,4-trichlorobenzene) calibrated with polystyrene standards. [c]Reaction heated at 100°C.

The only monomers of those investigated which polymerized to any degree at room temperature were M1 and M2, giving 3.7 and 1.8 kg/mol respectively (Table 3, entry 1 and 2). It is possible that the polymer made using M2 contains some β-defects, however the extremely low M_n of this polymer makes ^{1}H NMR analysis difficult. While these reactions did not produce sufficiently high molar mass polymers and had poor yields of 22% for each, the results give insight into the reactivity that drives the room temperature reaction. Acknowledging that the standard Fagnou conditions used in these reactions are not optimized for more electron deficient C-H monomers,[37] polymerizations heated at 100 °C with otherwise identical conditions using M1 and M5 were investigated. These reactions produced polymers with good molar masses (Table 3, entries 6 and 7), even for the highly electron poor monomer M5, showing that even with a lack of optimized conditions for these particular monomers, the reaction still proceeds efficiently at high temperatures. In contrast, at room temperatures, only C-H monomers with sufficient electron richness were observed to polymerize.

In analyzing these outcomes, we consider the possibility that with a lack of energy from heat needed to overcome the energy barriers associated with the widely accepted CMD (concerted metalation-deprotonation)[38–40] path, the room temperature reactions may be proceeding through an alternate path, such as Heck-type or S_EAr, both of which have been considered as potential mechanistic pathways for direct arylation, though S_EAr has largely been disregarded in this aspect.[5] A Heck-type mechanistic pathway would favor electron rich monomers such as EDOT and ProDOT which are highly electron rich and could efficiently coordinate to the Pd catalyst species so that insertion can occur, and allow for the reaction to proceed.[28,41,42] This is further supported by the lack of reactivity observed for electron poor monomers M3-M5 at room temperature, which would have less affinity to coordinate to the catalyst. Overall, from these limited results it appears that more electron rich C-H monomers are better suited for room temperature DArP using the explored conditions.

In conclusion, conditions for synthesizing the conjugated polymer PEDOTF through DArP at room temperature have been developed. Molar masses up to 10.2 kg/mol at ambient temperature and 15.2 kg/mol at 25°C were achieved through optimization of the choice of base, halogen coupling partner, reaction time, catalyst loading and concentration. Even when using the less reactive 9,9-dioctly-2,7-dibromofluorene, 15.2 kg/mol was achieved at the significantly reduced temperature of 40°C. We found that only electron rich C-H monomers were able to react at room temperature, and we hypothesize that room temperature DArP may not be proceeding through a traditional CMD pathway, and instead may be proceeding through a Heck-type path. This study is the first instance of a well-defined conjugated polymer synthesized at room temperature and in good yield through DArP without the use of a silver-based reagent. This serves as another improvement to the sustainability of DArP, by making the reaction more energy efficient. Future work will focus on expanding the scope of this condition to produce different polymers through DArP at room temperature, as well as improving our understanding of the DArP reaction mechanism at room temperature.

ASSOCIATED CONTENT

Supporting Information.

Experimental procedures including the synthesis and characterization for all monomers and polymers. This material is available free of charge via the Internet at http://pubs.acs.org

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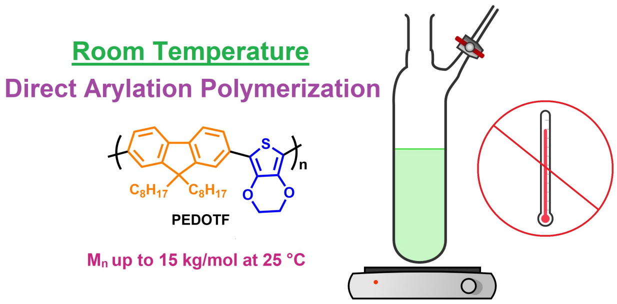
Room Temperature
Direct Arylation Polymerization
S
O
O
C_8H_{17}
C_8H_{17}
n
PEDOTF
M_n up to 15 kg/mol at 25 °C