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A General and Air-tolerant Strategy to Conjugated Polymers within Seconds under Pd(I) Dimer Catalysis

Guillaume Magnin, Jamie Clifton and Franziska Schoenebeck*

Abstract: While current $M^{(0)}/M^{(II)}$ based polymerization strategies largely focus on fine-tuning the catalyst, reagents and conditions for each and every monomer, this report discloses a single method that allows access to a variety of different conjugated polymers within seconds at room temperature. Key to this privileged reactivity is an air- and moisture stable dinuclear Pd(I) catalyst. The method is operationally simple, robust and tolerant to air.

Although polymers are already omnipresent in nowadays modern society, there is an ever increasing need for innovative materials to meet the next frontier of organic electronics, solar cells or fuel cell developments.^[1] Ultimately, any advance in this arena is intertwined and dependent on the ability to synthesize the desired materials with precision properties. With regard to conjugated polymers, which are largely assembled via $M^{(0)}/M^{(II)}$ -based ($M = Ni$ or Pd) polymerization,^[2] the consensus in the field is that “instead of searching for a universal catalyst, one should tune the catalyst’s electronic and steric properties for each monomer.”^[3] Indeed, for the selection of the various widely employed conjugated polymers in Figure 1^[4] (i.e. polyfluorene, polythiophene, poly-*p*-phenylenes or polycarbazoles that are featured in transistors^[5], photodetectors^[6] and solar cells^[7]), there are also several different, specialized protocols for the best polymerization results reported, featuring Suzuki, Kumada or Negishi type transformations with Ni or Pd catalysts and reaction times anywhere between 30 minutes and 24 hours and temperatures ranging from 0°C to 80°C.^[8]

However, the discovery of innovative materials would be greatly accelerated if there was a single powerful polymerization strategy that allowed access to a library of conjugated polymers via high throughput polymerizations of diverse monomers. Ideally, this strategy is coupled with high practicability, such as a robust catalyst that needs no specialized equipment and is characterized by high speed to maximize throughput.^[9]

In the small molecule world, $Pd^{(0)}/Pd^{(II)}$ based cross coupling strategies are highly dependent on the electronic and steric bias of the substrate and as such frequently require specialized catalysts and conditions.^[10] For example, chemoselective coupling strategies of

polyhalogenated arenes are typically not fully predictable with regard to the favored coupling site and are highly substrate-specific.^[11] By contrast, our group recently established that the use of the air- and moisture stable $Pd^{(I)}$ dimer **1** allows for extremely rapid and highly selective carbon-carbon bond formation of C-Br in the presence of C-Cl and C-OTf.^[12] Most importantly, the coupling was completely independent of the steric or electronic characteristics of the particular substrate.

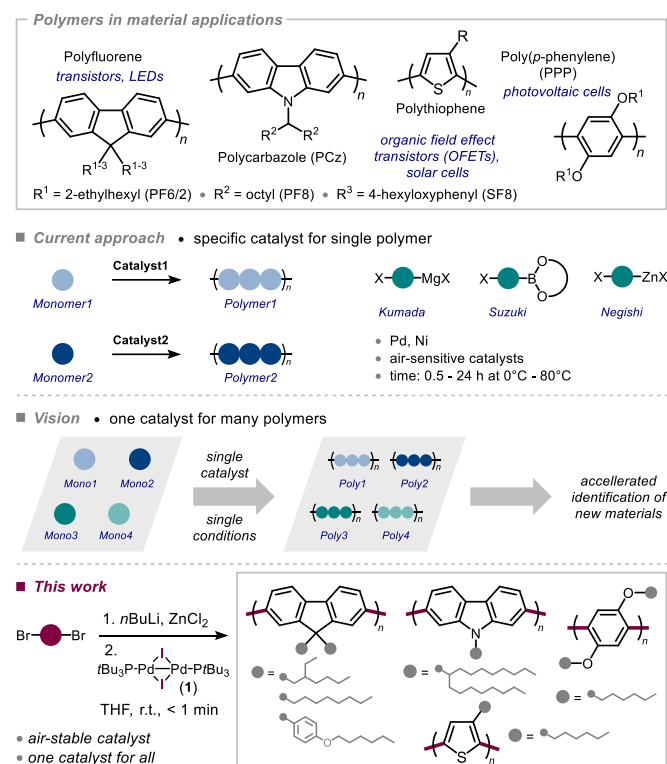


Figure 1. Important polymer classes for materials applications (top), current approaches in transition metal-catalyzed polymerizations, vision and outline of this work (bottom).

We envisioned that this substrate-independence paired with a *a priori* predictable reactivity of $Pd^{(I)}$ for small molecules might be an ideal feature also for the next dimension of control to assemble macromolecules, therefore potentially allowing the polymerization of a wide range of monomers of diverse steric and electronic characteristics. To this end, we embarked on exploring the potential of the air- and moisture stable $Pd^{(I)}$ dimer **1**^[13] in polymerizations of di-brominated monomers. More specifically, building on our previous findings of extremely rapid C-C couplings with organozinc reagents,^[14] we investigated the $Pd^{(I)}$ enabled polymerization of ‘Br-

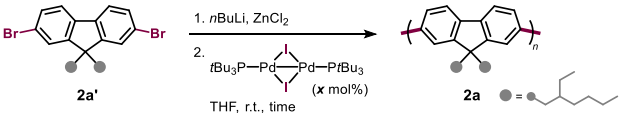
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aryl-ZnX' units and targeted the widely employed polymers shown in Figure 1.

We started our investigations with the all-carbon fluorene system (see Table 1). Owing to their blue-light emitting optical and electronic (hole-transport) properties, polyfluorene polymers find widespread applications ranging from organic devices to nanoscience.^[15] To attempt polymerization, we metalated one C-Br site in dibromofluorene to the corresponding organozinc species in THF at room temperature and subsequently added a solution of Pd^(I) dimer **1** (0.5 mol%) in THF to the mixture in one portion. To our delight, within 30 seconds at room temperature polymerization had already taken place to yield polyfluorene **2a** with a molecular (M_n = 24.5 kg/mol) as well as average molecular weight (M_w of 53.4 kg/mol) and polydispersity (PDI) of 2.18 (see Table 1). When we repeated the reaction and left it stirring for a total of 2 minutes at room temperature, a polymer with greater molecular weight was generated and isolated in 87% yield (entry 2). Considering the rapid speed and operational simplicity of the method, the polymerization capability seemed remarkable. As such, we challenged the method further and systematically lowered the catalyst loading. We found that using as little as 0.005 mol% of Pd^(I) dimer still gave excellent polymerization within 10 min reaction time (entry 4). These results were fully competitive with previous polymerization methods to make polyfluorenes, which range from Pd-catalyzed Suzuki or Ni(dppp)Cl₂ catalyzed Kumada couplings to oxidative strategies (e.g. Ni(cod)₂-based Yamamoto catalysis at 80°C).^[8c] A Negishi-type polymerization was previously realized by Kiriy's laboratory, having prepared **2a** with M_n = 53.1 kg/mol, M_w = 123.1 kg/mol and PDI = 2.32 after 20 h reaction time and using a combination of 1:1 mixture of Pd^(II) source with the air-sensitive, free phosphine, tri-*tert*-butylphosphine.^[16] Since precise metal-to-ligand-ratios are crucial for reproducibility and performance in metal catalyzed coupling reactions,^[17] the use of the bench-stable Pd^(I) dimer **1** presents a convenient advantage, as it circumvents potential reproducibility issues due to inconsistent weighing and metal/ligand ratios. Moreover, as opposed to alternative *Pr*Bu₃-derived Pd⁽⁰⁾ or Pd^(II) catalysts, dimer **1** is completely stable to oxygen. Thus, we were intrigued whether polymerization would also be possible in the presence of oxygen. To this end, we added a solution of dimer **1** in THF to the prepared zincated monomer under open flask conditions.^[18] Entry 6 presents the results (Table 1). There was no impact of external oxygen; the same polymer was obtained as under inert conditions, showing the practicability and robustness of our polymerization method.

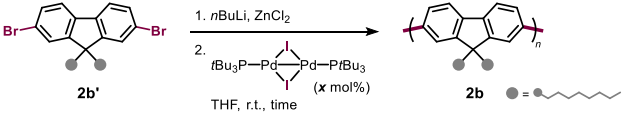
Table 1: Comparison of catalyst performance in the polymerization to afford **2a**^a

					
Entry	Catalyst [mol%]	Time [min]	M_n [kg/mol]	M_w [kg/mol]	PDI
1	0.5	0.5	24.5	53.4	2.18
2	0.5	2	59.7	120.9	2.02
3	0.05	0.5	16.9	34.2	2.03
4	0.005	10	43.3	89.1	2.06
5	0.005	30	51.0	98.9	1.94
6 (in O ₂)	0.5	0.5	24.3*	52.3*	2.15*

^aConditions: [Pd(μ-I)(P*t*Bu₃)₂] (**1**), *n*BuLi (0.98 equiv.), monomer (0.5 mmol, 1.0 equiv.), ZnCl₂ (1.1 equiv.). *open-flask.^[18b]

With these promising Pd^(I)-triggered polymerization results in hand, we subsequently explored the generality of the method. The alkyl substituents of the polymer units strongly influence the physical properties of the resulting polymers, such as solubility, but also the overall self-assembly and consequently impact the ultimate device performance.^[19] Variability in the latter side chain will hence be advantageous and we next tested whether alkyl chains other than branched ethyl butyl chains are also tolerated. To this end, we subjected the dioctylfluorene derivative **3** to the same polymerization conditions with Pd^(I) (0.5 mol%) at room temperature (Table 2). After just 30 seconds reaction time, we obtained a polymer with M_n = 14.3 kg/mol, M_w = 20.8 kg/mol and PDI = 1.45. Again, performing the polymerization open to the laboratory atmosphere had no impact (see entry 6).^[18b] Previously, the same polymer was synthesized under Suzuki-type polymerization by Yokozawa and co-workers, requiring 30 min reaction time and 5 mol% of sensitive Pd to obtain a similar polymer (M_n = 19.2 kg/mol and PDI = 1.34),^[20] and under Ni(cod)₂-catalyzed Yamamoto conditions over 3 days (to give M_n = 99.5 kg/mol and PDI of 2.36).^[15d] The need for relatively high palladium loading in the former case might stem from the fact that an oxidative addition complex, *i.e.* [(*Pr*Bu₃)Pd(Ph)Br], was utilized as catalyst. Although this pre-formed species circumvents potential weighing inaccuracies in achieving the correct Pd-to-ligand ratios, these complexes were previously found to suffer from inconsistent initiation^[21] and instabilities.^[22]

Table 2: Comparison of catalyst performance in the polymerization to afford **2b**^a

					
Entry	Catalyst [mol%]	Time [s]	M_n [kg/mol]	M_w [kg/mol]	PDI
1	1.0	30	21.8	54.6	2.50
2	0.5	30	14.3	20.8	1.45
3	0.05	30	13.2	18.5	1.40
4	0.005	30	15.4	25.8	1.66
5	0.005	120	15.3	26.1	1.71
6 (in O ₂)	0.5	30	13.1*	23.8*	1.82*

^aConditions: [Pd(μ-I)(P*t*Bu₃)₂] (**1**), *n*BuLi (0.98 equiv.), monomer (0.5 mmol, 1.0 equiv.), ZnCl₂ (1.1 equiv.). *open-flask.^[18b]

As such, the Pd^(I) protocol offers much faster polymerization (30 seconds *vs.* 30 min) using a robust and air-stable catalyst and requiring lower loadings in Pd. To gain greater insight on the Pd-loading, we studied various different catalyst loadings ranging from 1.0 mol % to 0.005 mol % (Entries 1 to 4). In all cases, good M_n and PDIs were obtained after only 30 seconds reaction time, and the polymerization was found to be largely independent of the actual catalyst loading. Similarly, the reaction time had no marked impact on the polymerization; there was no significant change in M_n whether the reaction time was 30 seconds or 2 minutes. These data suggest that the polymerization is completed within 30 seconds at 0.005 mol% Pd^(I) dimer loading, giving the polymeric material in 82% yield upon isolation.^[23]

With independence from the nature of the side chain demonstrated, we next explored the compatibility of the Pd^(I)-based polymerization with electronically varied motifs, more specifically heteroatoms. In this context, a representative materials class is polycarbazole (**3**). Owing to their greater chemical stability compared to polyfluorenes, polycarbazoles are of interest for applications in solar cells.^[24] Once again, we utilized the dibrominated monomer, converted it to the mono-zincated derivative *via* convenient metal-halogen exchange and subjected it to the analogous polymerization conditions for 1 min (0.5 mol% Pd^(I) dimer in THF at room temperature). Pleasingly, this resulted in polycarbazole **3** in 74% isolated yield (with M_n and PDI of 21.3 kg/mol and 2.14, respectively), which is in the realm of previous polymer data with different methods: under Kumada cross coupling using Ni(dppp)Cl₂ (0.9 mol%) a polymer with M_n = 17.4 kg/mol and a PDI of 1.27 was obtained after 24 h reaction time.^[25] Pd-based Suzuki coupling [with a catalyst system of Pd₂(dba)₃ and P(o-tol)₃] and Stille-based polymerization were also previously used.^[24b] While organotin reagents are known for their toxicity,^[24b] Pd₂(dba)₃ is associated with inconsistent quality and stability.^[26] Consequently, there is the danger of imprecise Pd-to-ligand-ratios (and hence inconsistent polymerization performance), as the amount of homogeneous Pd (relative to nanoparticles) in commercial sources tends to vary.^[26] An organozinc-based polymerization has not previously been demonstrated for **3**.

Given the rapid polymerization rates under Pd^(I) conditions, we set out to have a closer look at the consumption of monomer over time and set up 13 parallel polymerization runs to make **3** with 0.5 mol% Pd^(I) dimer **1**, which were quenched with methanol at different time intervals and subjected to GC-MS analyses (Figure 2). Our data indicate that within 15–20 seconds, roughly 90% of the monomer had already been consumed. Moreover, a GPC analysis of an aliquot taken at 20 seconds showed that a polymer with a molecular weight of M_n = 15.3 kg/mol and PDI of 2.14 had formed. Additional GPC analyses after 1 and 2 min reaction times (when also no more consumption of monomer was seen), gave analogous polymers with M_n of 21.9 and PDI of 2.14, indicating that polymerization appears to be completed within 1 min reaction time at room temperature under Pd^(I) dimer conditions.

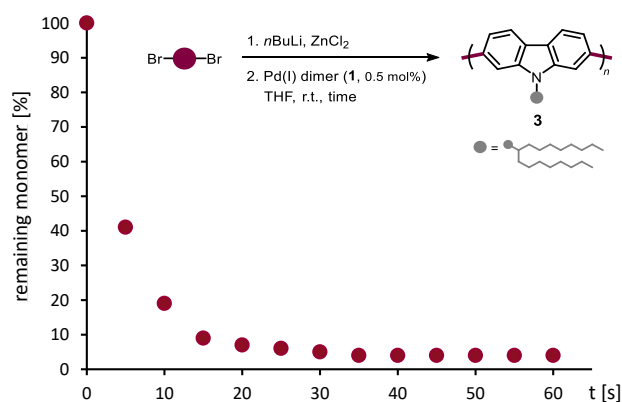


Figure 2. Monomer consumption versus time in the polymerization to form polycarbazole **3**. Conditions: [Pd(μ-I)(P^tBu₃)₂] (**1**), *n*BuLi (0.98 equiv.), monomer (0.5 mmol, 1.0 equiv.), ZnCl₂ (1.1 equiv.).

Clearly, the polymerizations under Pd^(I) dimer conditions proceed similarly rapidly and efficiently regardless of the alkyl side chain in

the monomer or the presence of nitrogen heteroatoms, suggesting that this method could indeed have potential for syntheses of a range of polymers. A frequent motif in materials for electronic applications are also arenes or heterocycles. We therefore next assessed the compatibility of the polymerization protocol to make π -rich materials. We succeeded in the generation of poly(3-hexylthiophene)^[27] **5** within 1 min at r.t. under Pd^(I) dimer catalysis (0.5 mol%). In addition, we assessed having an arene in the side chain as spacer (**2c**) or as actual monomer to generate polyarene **4**. In both cases, ether bonds are present as linkers which could potentially sterically and electronically impact the catalyst performance. Once again, we saw very rapid and efficient polymerizations (table 3) in less than 1 min in these cases (using 0.5 mol% of Pd^(I) dimer **1**). This gave rise to **4** (with M_n of 9.9 kg/mol and PDI of 1.45) and poly(2,7-[9,9-bis(4-hexyloxyphenyl)fluorene] polymer **2c** with a molecular weight of M_n of 44.3 kg/mol and a PDI of 1.80 (in 74% isolated yield). For comparison, while **2c** was not previously made under Negishi-type coupling, under Pd(PPh₃)₄ (0.5 mol%) catalyzed Suzuki-type polymerization over 48 h at reflux, polymer **2c** was previously made with M_n of 12 kg/mol and PDI of 2.40 (in 71%).^[28]

Table 3: Performance of Pd(I) iodo dimer **1** in the polymerization of different polymer classes.^a

Entry	Polymer	Catalyst [mol%]	Time [s]	M_n [kg/mol]	M_w [kg/mol]	PDI
1	3	0.5	20	15.3	32.9	2.14
2	3	0.5	60	21.3	45.7	2.14
3	3	0.5	120	23.1	43.2	1.86
4	4	0.5	35	9.9	15.6	1.45
5 (in O ₂)	4	0.5	30	9.3*	18.0*	1.94*
6	2c	0.5	60	44.3	80.1	1.80
7	5	0.5	60	5.9	7.2	1.20

^aConditions: [Pd(μ-I)(P^tBu₃)₂] (**1**, 0.5 mol%), *n*BuLi (0.98 equiv.), monomer (0.5 mmol, 1.0 equiv.), ZnCl₂ (1.1 equiv.). *open-flask.^[18b]

In summary, using a single air- and moisture stable Pd^(I) dimer catalyst, we achieved extremely rapid polymerization to a variety of widely employed conjugated polymer classes, *i.e.* polyfluorenes, polycarbazoles, polyphenylenes and polythiophene. The method is operationally simple, highly robust, tolerates air as well as catalyst loadings as low as 0.005 mol%. We anticipate that these findings will result in widespread applications in academic and industrial materials research.

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Additional Notes

A patent application has been filed by RWTH Aachen University on this research.

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Polymerization Methods

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