Convenient Synthesis of Functional Polyfluorenes via a Modified One-Pot Suzuki−Miyaura Condensation Reaction

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As conjugated polymers continue to revolutionize the field of organic optoelectronics, they are evolving from esoteric materials produced on a small synthesis laboratory scale to a wide range of specialty chemicals being produced by commercial manufacturers. As such, typical metal-mediated aryl cross-couplings (Yamamoto, Stille, and Suzuki reactions) are continuously being refined for yield, extent of conversion, and catalyst loading.[1] In particular, the Suzuki and Stille reactions require aryl dihalide and dimetalated (boron and tin, respectively) comonomers (or a monohalo/monometalated monomer) in theoretical perfect stoichiometric balance to achieve high molecular weights. Thus, monomer purity and stability under the polymerization conditions are of the utmost importance.

Polyfluorene derivatives have received significant attention in the past few years due to their facile synthesis and emission of pure blue or cyan light (barring backbone impurities causing energy traps and emission in the green).[2–9] The Suzuki polymerization is the most widely used synthesis of polyfluorene derivatives due to a simple conversion of the aryl dihalide comonomer to the boronic acid or ester (less toxic and more environmentally friendly than the tin reagents used in its analogue, the Stille reaction). The most widely employed synthetic methodology for conversion of the aryl dihalide to the corresponding borylated comonomer uses pyrophoric reagents such as *n*-butyllithium to form the dianion that reacts with the appropriate borylating reagent to give the disubstituted derivative in moderate yields. The subsequent comonomers are difficult to purify in many cases and usually require chromatography to remove unreacted or partially reacted material and byproducts from the reaction. In addition to an undesirable chromatography step, the alkyllithium derivatives are incompatible with pendant functionalities such as esters and halo groups. Recently, the group of Miyaura discovered a novel metal-mediated reaction to generate aryl diboronates in high to quantitative yields.[10] This chemistry, commonly dubbed the “Suzuki−Miyaura reaction” (or just the “Miyaura reaction”) utilizes a hypodiboric ester such as bis(pinacolato)diboron as the borylating reagent in combination with a palladium catalyst and potassium acetate. Miyaura specifically chose potassium acetate in order to minimize aryl−aryl cross-coupling byproducts and noted that use of other bases such as potassium carbonate lead to significant oligomer formation.[10] Some reports have utilized other methodologies to form symmetrical and unsymmetrical biaryls via a one-pot Suzuki−Miyaura reaction.[11,12]

Capitalizing upon the reactivity of these conditions, Masuda’s group used the Suzuki−Miyaura reaction with a stoichiometric equivalent of aryl dihalide:bis(pinacolato)diboron = 1:1, under conditions known to exhibit Suzuki cross-coupling reactions.[13] This work resulted in low to moderate molecular weight polythiophene, poly(phenylene ethynlene), and poly(azobenzene) derivatives, demonstrating proof-of-concept that bis(pinacolato)diboron can be used to simultaneously generate a boronic ester and subsequently form polymer in one pot. However, it was found that the success of polymerization depended greatly upon the structure of the monomer, and the highly basic conditions utilized obviated the use of polymers with pendant functional groups such as esters and (due to the high temperatures) halides.

Recent work published by our group effectively demonstrated that the Suzuki polymerization could be run by the replacement of a Brønstead base with cesium fluoride.[14] This methodology allowed for the polymerization of polyfluorene derivatives with ester functionalities; however, all reported polymers in this work were prepared with fluorenyl diboronates containing only alkyl substiutents and the ester groups attached to the dihalo comonomer.

Work reported here combines the fluoride-promoted Suzuki polymerization with the Suzuki−Miyaura polymerization concept introduced by Masuda to form high molecular weight polyfluorene derivatives, in one pot, to generate polymers with pendant group functionality (specifically haloalkyl, ester, and alcohol) that were previously synthetically inaccessible.

The fluoride-mediated Suzuki polymerization of fluorenes reported by our group suggests that the fluoride ion can effectively coordinate to, and activate, an aryl boronic ester for subsequent transmetalation with palladium. However, because a Suzuki−Miyaura reaction using fluoride ion to activate bis(pinacolato)diboron, to our knowledge, has not been reported, it was important that the conditions of the reaction be optimized to (1) allow the borylation of the aryl dihalide monomer and (2) allow facile polymerization. With regards to the latter, it is evident that not only the choice of catalyst was important for the polymerization but also the choice of solvent because high molecular weight polymers tend to precipitate from poor solvents, especially those solvents loaded with salt. Scheme 1 illustrates the general reaction pathway for the optimization. We chose 2,5-dibromo-9,9-dioctylfluorene to generate poly(9,9-dioctylfluorene) (PFO) as the polymerization reaction for optimization because of PFO’s ubiquity and importance in the

Scheme 1

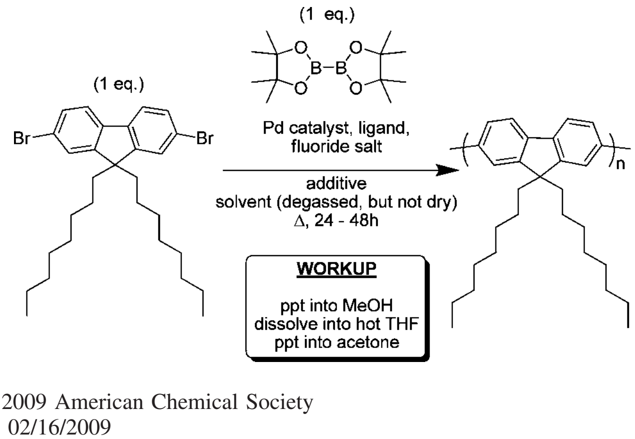

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Table 1. Optimization of the Polymerization of Poly(9,9-dioctylfluorene) (All Reactions Were Performed at 80 °C Unless Otherwise Indicated)

no.	catalyst	ligand	ligand (mol %)	salt	TBAB (mol %)	solvent	yield (%)	M_n (kDa)	M_w (kDa)	PDI
1	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	CsF		dioxane	84	12.1	23.2	1.92
2	$Pd_2(dba)_3$	DPPF	3	CsF		dioxane	80	9.7	16.6	1.70
3	$Pd(OAc)_2$			CsF		dioxane	0			
4	$Pd(PPh_3)_2Cl_2$			CsF		dioxane	34	9.8	16.7	1.71
5	$Pd_2(dba)_3$	DPPF	1.5	CsF		THF	31	2.4	3.0	1.26
6	$Pd_2(dba)_3$	$HP(^tBu)_3BF_4$	6	CsF		dioxane	7	8.2	13.7	1.66
7	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	Bu_4NF		dioxane	4	6.4	9.8	1.54
8	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	CsF		25% $PhCH_3$ in dioxane	70	9.4	16.7	1.77
9	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	CsF		50% $PhCH_3$ in dioxane	56	7.2	11.0	1.53
10[a]	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	CsF	20	$PhCH_3$	94	24.2	50.9	2.10
11	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	CsF	5	$PhCH_3$	70	9.4	15.3	1.63
12[a,b]	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	CsF	20	$PhCH_3$	23	6.8	8.2	1.21
13[c]	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	CsF	20	$PhCH_3$	88	18.4	35.9	1.96
14[a,d]	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	CsF	20	$PhCH_3$	98	26.9	58.3	2.17

[a] TBAB was added after 22 h of reaction. [b] The reaction was heated at reflux (ca. 112 °C). [c] TBAB was added after 1 h of reaction. [d] Monomer concentration was 0.09 M.

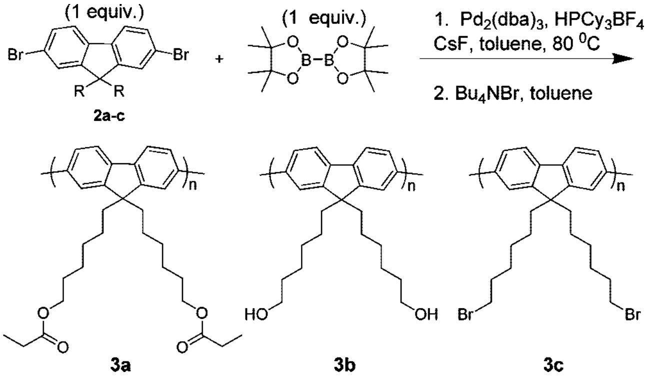
literature and because its inert alkyl side chains would not be expected to coordinate to the catalyst or otherwise interfere with the polymerization chemistry. It can be seen from Scheme 1 that a number of variables could be changed to vary polymerization conditions: feed ratio, catalyst, ligand, salt, solvent, temperature, reaction time, and additives.

Table 1 shows an abbreviated list of the optimization conditions and results. The full set of reactions, including those found in Table 1, can be found in the Supporting Information. The first variable tested was the catalyst and ligand system, shown by entries 1−4 in Table 1; dioxane as the solvent and other reagent conditions were chosen from previously reported fluoride-mediated polymerization work. It can be seen that the $Pd_2(dba)_3/PCy_3$ system was the best of the four and provided an M_n of 12.1 kDa with a PDI of 1.92 after precipitation. Other fluoride sources were explored: Bu_4NF, shown in entry 7 (to increase fluoride solubility), and KF (to decrease fluoride solubility), and it was found that CsF provided the best results. It was observed that the polymer precipitated during the reaction and all subsequent reactions in dioxane produced similar or lower molecular weights; these results indicate that the solvent may have produced a polymer molecular weight leveling effect due to the insolubility of higher molecular weight species. Switching the solvent to THF yielded lower molecular weight polymers, possibly due to THF coordination to the active catalyst, the best of which is shown in entry 5 in Table 1.

It is well-known that toluene is a good solvent for the Suzuki synthesis of PFO under normal conditions, but the solubility of CsF in toluene is low. Therefore, four reactions were performed with various mixtures of dioxane and toluene. (Dioxane was used to solubilize the CsF, and toluene was used hypothetically to increase the solubility of the polymer in solution; see entries 8 and 9 in Table 1.) None of the dioxane/toluene mixtures were successful in generating high molecular weight PFO. In 100% toluene, the reaction yielded no isolable polymer, evidenced by the failure of a precipitate to form by the addition of a small aliquot of the reaction to methanol; however, when a small amount (20 mol %) of tetrabutylammonium bromide (TBAB) in degassed toluene was added to the reaction after a 22 h reaction time, polymer formed after an additional 24 h of reaction (entries 10, 12, and 14). High yields and molecular weights indicated that a phase transfer catalyst in the toluene system was necessary for the polymerization to proceed at a reasonable rate.

Interestingly, if TBAB was added at the beginning of the reaction (entry 12), the polymer had lower molecular weight, indicating that the Suzuki−Miyaura reaction was inhibited by the presence of a significant concentration of fluoride in solution.

Scheme 2



The effect of TBAB concentration and time of addition was explored. It was found in concentration studies that (1) 5 mol % (entry 11) or 100 mol % added after 22 h of reaction and (2) 20 mol % TBAB added after 1 or 5 h failed to reproduce the high molecular weight and yield of the 20 mol % reaction. To explore the consumption of bis(pinacolatodiboron) more quantitatively, a further polymerization reaction was carried out in toluene using the high yield/M_n conditions described in Table 1, entry 10. Periodically, aliquots of the reaction were removed from solution and diluted with toluene, and the hypodiboric ester quantity was monitored via GC relative to pyrene as an internal standard. It was seen that after 6 h ~25% of the bis(pinacolatodiboron) remained, and after about 16 h, the reagent was fully consumed (Figure S-1 in the Supporting Information). These results, combined with the aforementioned time studies of the addition of TBAB, indicate that the borylation reaction is sensitive to the concentration of fluoride and that the polymerization reaction is promoted by the subsequent addition of a phase transfer catalyst.

To test the functional group compatibility of the polymerization reaction, several functional fluorene derivatives were synthesized and polymerized as shown in Scheme 2, with characterization results reported in Table 2. It can be seen that polyfluorenes of substantial M_n with ester, alcohol, and halogen functionality can all be synthesized by this methodology.

Table 2. Yield and Molecular Weight Properties for Functionalized Polyfluorenes

compound	functional group description	yield (%)	M_n (kDa)	M_w (kDa)	PDI
3a	ester	90	14.0	32.6	1.44
3b	alcohol	51	34.9	69.2	1.98
3c	halogen	57	13.1	24.3	2.24

Although yields for the latter two were not quantitative, we presume that further optimization of system-specific reactions can produce polymers with higher molecular weight and yields.

In summary, we have utilized the Suzuki–Miyaura reaction in order to develop an effective one-pot polymerization to prepare functionalized polyfluorenes. Critical control of reaction conditions provided high yields and polymers with degrees of polymerization on the order of 60–70.

Experimental Section. *Typical Polymerization Procedure (Details for Table 1, Entry 10).* To a 50 mL round-bottom flask containing a magnetic stir bar was added 2,7-dibromo-9,9-dioctylfluorene (0.500 g, 0.912 mmol), bis(pinacolato)diboron (0.225 g, 0.912 mmol), $Pd_2(dba)_3$ (19.9 mg, 0.018 mmol), tricyclohexylphosphonium tetrafluoroborate (18.9 mg, 0.054 mmol), and cesium fluoride (0.94 g, 6.20 mmol). The round-bottom flask was attached to a reflux condenser containing a septum punctured with a needle for an argon/vacuum inlet. The flask was evacuated and backfilled with argon three times, after which degassed toluene (35 mL) was transferred to the mixture via cannula. The reaction was immediately immersed in an oil bath at 80 °C and stirred for 24 h at that temperature. Tetrabutylammonium bromide (58.8 mg, 0.184 mmol) dissolved in degassed toluene (5 mL) was added to the reaction via a syringe, and the reaction was stirred for an additional 24 h. The reaction was cooled to RT, the solvent was removed in vacuo, and the reaction was reconstituted in a minimal amount of hot THF (~5 mL) and precipitated into methanol (100 mL). The solids were isolated by filtration over a 20 μM Osmonics filter, redissolved in hot THF (~5 mL), and precipitated into acetone. After filtration over a 20 μM Osmonics filter, the product was isolated as 331 mg (94%) of a yellow solid. GPC (vs PS): M_n = 24 200 g/mol, M_w = 50 900 g/mol, PDI = 2.10.

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Supporting Information Available: Materials, instrumentation, methods, a complete table of polymerization reactions, and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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