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Palladium Complexes with Aqueous-Partitioning Dibenzylideneacetone Ligands. A New Strategy for Catalyst Design in Suzuki Polycondensation Reactions

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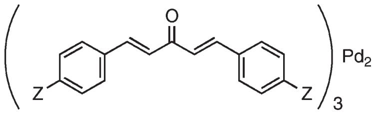
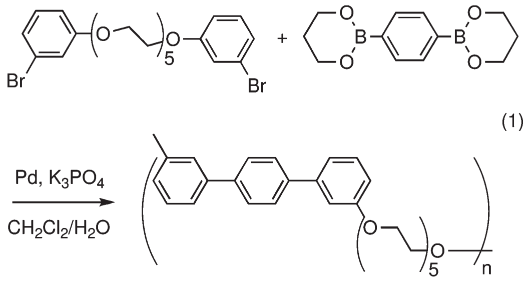
Introduction. Conjugated polyarylenes such as poly(p-phenylene)[1−4] and poly(fluorene)[5−8] derivatives have been the subject of increasing interest in recent years, due primarily to their light-emitting properties, which make them potentially useful candidates for emissive layers in light-emitting diodes[9] and photovoltaic devices.[10] One of the most common means by which these polymers are formed is the Suzuki polycondensation,[11−13] which is based on the small molecule Suzuki coupling reaction between an aryl or alkenyl halide and an aryl or alkenyl boronic acid.[14−16] There have been numerous developments in Suzuki coupling methodology in recent years that have led to remarkable improvements in catalytic efficiency, product yield, and ease of manipulation.[17,18] Despite this fact, most recent Suzuki coupling polycondensations still utilize only slight modifications of the original 1989 protocol,[19] often resulting in molecular weights that are limited to the 10^3-10^4 g/mol regime.[20−23] Unfortunately, the physical properties (toughness, thermal stability, adhesiveness, etc.) of a polymer are extremely sensitive to molecular weight, with samples at the lower end generally producing unacceptable materials.

Recently, our laboratory investigated several of the newly developed Suzuki coupling catalyst systems (which typically involve a palladium source and an electron-rich phosphine or other ligand) to see if they would produce polymers with improved molecular weights in a Suzuki polycondensation.[24] Somewhat disappointingly, none of the new examples that we tested matched the performance of catalyst systems based upon the more traditional tri(o-tolyl)phosphine ligand. One surprising result, however, was that the molecular weights were strongly dependent upon the source of palladium used in the polymerizations. This suggested to us that, in tuning the properties of the ligand (which had been the focus of most of the work in this area), researchers have been attempting to optimize the wrong component of the catalyst system.

One of the most common sources of palladium in Suzuki coupling reactions is tris(dibenzylideneacetone)dipalladium(0), or Pd_2dba_3 (**3**). This compound has the advantageous properties of being soluble and air-stable, and it is known to react rapidly with phosphines and aryl halides for expedient entry into the catalytic cycle.[25,26] However, from extensive electrochemical studies on palladium complexes, Amatore and Jutand have determined that the dibenzylideneacetone (dba) byproducts released from this catalyst induction step remain coordinated to the palladium during the catalytic cycle, rather than serve as uninvolved spectators.[27] Indeed, in recent years, Fairlamb and co-workers have shown that yields and activities in small molecule Suzuki couplings could be improved by varying the substituents on the dba components.[28,29] With this in mind, we have since performed experiments to see whether similar changes to this common palladium source would result in molecular weight improvements in Suzuki polycondensation reactions. This Communication presents the results of this work, in particular the development of versions with water-solubilizing substituents,[30] which we believe could serve as a starting point for the next generation of Suzuki polycondensation catalyst systems.



1: Z = CF_3 **2**: Z = Cl **3**: Z = H
4: Z = CH_3 **5**: Z = OCH_3
7: Z = OH **8**: Z = OAc



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Results and Discussion. In order to screen different catalyst systems, several simultaneous polymerizations (eq 1) were set up utilizing palladium sources **1**−**5** as well as bis[tri(o-tolyl)phosphine]palladium(0) (**6**), which was the optimal catalyst system in our earlier work.[24] As can be seen from the resulting molecular weight data (entries 1−6 in Table 1 and Figure 1), the values obtained from these polymerizations are all very similar, indicating that any electronic effect of the dba component of the catalyst on molecular weights of the polymers appears to be rather negligible. What is clear from the data, however, is the fact that none of the dba precursors match the performance of **6**, which yielded remarkably impressive values for this polymerization (entry 6). Thus, it is apparent that dba ligands, regardless of their electronic substituents, have a deleterious effect on polymer molecular weight.

Unfortunately, **6** does not provide for the most convenient catalyst system, as it is sensitive to heat, light, and oxygen. Furthermore, it is not presently commercially available, and its purification can require a weeks-long recrystallization for full recovery.[31] Ideally, we would like to find a catalyst system that combines the convenience of the dba precursors with the performance of complex **6**.

Toward this end, we synthesized the hydroxylated dba complex **7** (from the known[32] dibenzylideneacetone

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Table 1. Effect of Catalyst Precursor and Loading on Polymer Molecular Weight[a]

entry	catalyst system	Pd/Br (%)	M_n[b] (g/mol)	M_w[b] (g/mol)	yield (%)[c]
1	**1** + 2P(*o*-Tol)$_3$	1	65 700	118 000	88
2	**2** + 2P(*o*-Tol)$_3$	1	69 800	126 000	93
3	**3** + 2P(*o*-Tol)$_3$	1	60 600	112 400	93
4	**4** + 2P(*o*-Tol)$_3$	1	75 200	148 000	83
5	**5** + 2P(*o*-Tol)$_3$	1	81 500	144 000	74
6	**6**	1	188 000	464 000	89
7	**7** + 2P(*o*-Tol)$_3$	1	131 000	290 000	94
8	**8** + 2P(o-Tol)$_3$	1	104 000	244 000	96
9	**7** + 2P(*o*-Tol)$_3$	2	81 200	134 000	90
10	**7** + 2P(*o*-Tol)$_3$	0.5	75 600	159 000	95
11	**7** + 2P(*o*-Tol)$_3$	0.2	88 900	169 000	92
12	**7** + 2P(*o*-Tol)$_3$	0.1	110 000	264 000	96
13	**7** + 2P(*o*-Tol)$_3$	0.03	51 600	94 800	82

[a] Polymerizations (eq 1) set up with 0.150 mL of organic solvent and 0.300 mL of 3 M K_3PO_4. [b] Values were determined by tandem GPC light scattering and reflect the average of at least two trials. [c] Listed yields (average of at least two trials) are after further purification and include some mechanical loss.

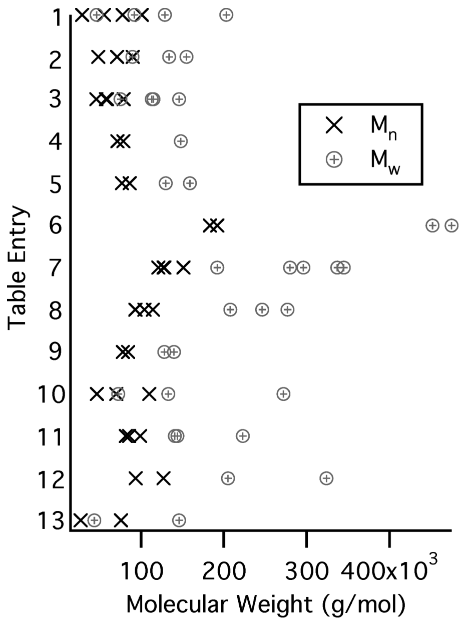


Figure 1. Molecular weights for polymerizations (each point an individual trial) run with different catalyst systems (Table 1).

derivative), with the idea that the phenolic hydrogens would become deprotonated under the basic conditions of the polymerization. The resulting negative charges would then cause the free dba anions to partition into the aqueous phase, where they would be unable to interfere with the desired catalysis occurring in the organic solvent. Complex **7** proved to be air stable in both the solid state and solution. Furthermore, it exhibited excellent solubility in THF, methanol, and dioxane, a fact that allowed us to obtain structure-quality crystals from THF/ether, and thus unambiguous characterization of the compound via X-ray crystallography (Figure 2).

Our first attempts with this precursor, however, did not yield successful polymerizations. Unfortunately, the large crystals of **7** were not significantly soluble in the CH_2Cl_2 solvent found[24] to be optimal for this polymerization, and in the time required for the complex to react and enter the catalytic cycle, molecular weight limiting side reactions such as protodeboronation[33] were able to gain a foothold. Fortunately, freeze-drying **7** from dioxane produced a fine powder that provided polymerization results much more in line with what we had anticipated (entry 7, Figure 3).[34] Indeed, molecular weights with this powdered precursor far surpassed those obtained with the other dba complexes and even approached those produced by **6**.[35] Alternatively, protecting the hydroxyl group as the base-labile acetate resulted in the acetylated complex **8**, which was more soluble in CH_2Cl_2. This precursor produced values (entry 8) that, while not quite as high as those from **7**, were again significantly better than the other standard dba complexes (**1**−**5**).

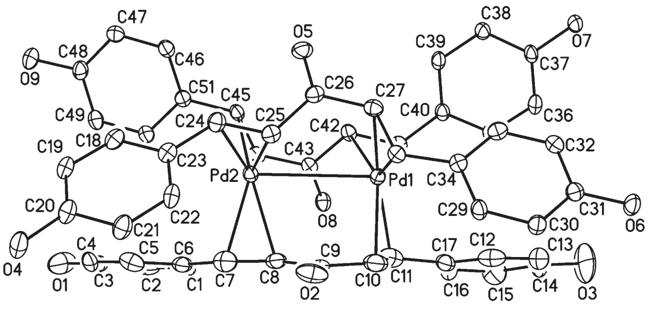
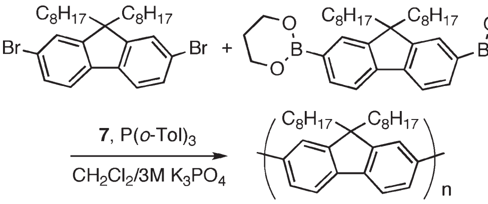


Figure 2. ORTEP crystal structure for complex **7**.

Next we set up polymerizations to investigate the optimal catalyst loading. From the resulting data (entries 9−12), it appears that 1% Pd/Br provided the best results and that, somewhat surprisingly, higher loadings actually caused molecular weights to go down. Viable molecular weights could be attained with loadings as low as 0.03%, although scatter in the data did become an issue at the lower catalyst concentrations.

Finally, in order to verify that this catalyst system works for other Suzuki polycondensations, we used it to synthesize a known polyfluorene from the dibromide and diboronic ester monomers (eq 2). In a nonoptimized single trial, we were able to obtain the product polymer in 92% yield with molecular weight values of 81 000 g/mol and 239 000 g/mol for M_n and M_w, respectively, as determined by GPC relative to polystyrene standards,[37] which compares well with literature GPC values for this polymer synthesized via both Suzuki polycondensation[38] and Grignard metathesis[39,40] methodologies. Furthermore, with some optimization, polyfluorenes with even higher molecular weights should be achievable with this catalyst system, perhaps even reaching the impressive values obtained for polyfluorenes via Yamamoto condensation polymerizations.[41,42]



(2)

In conclusion, we have developed new, convenient, palladium dba catalyst precursors which yield molecular weights in a Suzuki Polycondensation (eq 1) that are superior to those obtained with more traditional systems. While their performance still did not match that of bis[tri(*o*-tolyl)-phosphine]palladium(0) (**6**), which remains the best catalyst system we have screened to date, new dba complexes **7** and **8** offer considerable advantages in terms of air stability and convenience. Perhaps more importantly, they provide a starting point for a new direction in catalyst design for Suzuki polycondensation reactions. Indeed, incorporation

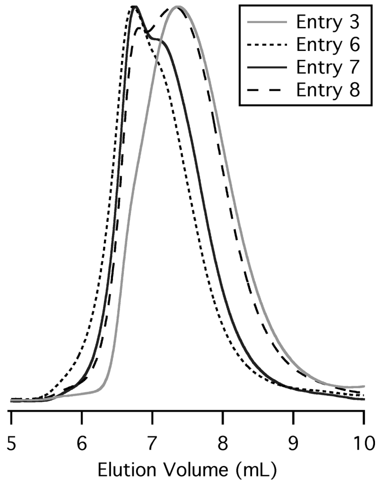


Figure 3. GPC chromatograms[36] for polymerizations with different catalyst systems.

of additional water-solubilizing groups could generate dba ligands that are even more efficient at partitioning into the aqueous phase (thus providing less interference with the desired catalysis in the organic phase), thereby improving the molecular weights of the polymers generated even further. In addition, once we have a system in which the dba ligands act as the truly benign spectators that they have long been thought to be, we can return to studies on the phosphine component and obtain optimization results that are unclouded by unwanted interactions with the dba ligand, which will possibly lead to the development of yet more advanced catalyst systems. Studies toward this end are currently underway.

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Supporting Information Available: Experimental procedures for the synthesis of **7** and **8**, the screening polymerizations (eq 1), and the polyfluorene synthesis (eq 2); X-ray crystallographic characterization data for **7**; ^{1}H NMR spectra for monomers used in screening polymerizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) As was the case with our previous polymerizations (ref 24), the chromatograms exhibit bimodality with the high molecular shoulder gaining in prominence (and becoming the main peak for the higest molecular weight examples) with increased gellation during the polymerization. This may be due to a Trommsdorff-like effect in

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(37) By tandem GPC-light scattering, these values were determined to be M_n = 102 000 g/mol and M_w = 125 000 g/mol. The large discrepancy in the polydispersities between the two techniques suggests that there is some non-size-exclusion adhesion of the polymer chains to the GPC columns. Since light scattering measures M_w values for the fractionated samples, the M_w value is probably accurate, while the M_n value determined by GPC-LS is likely inflated. It is worth noting that most literature values for polyfluorene have been determined by GPC relative to polystyrene.

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