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# Synthesis of Linear, High Molecular Weight Aromatic Polyamides by the Palladium-Catalyzed Carbonylation and Condensation of Aromatic Diiodides, Diamines, and Carbon Monoxide

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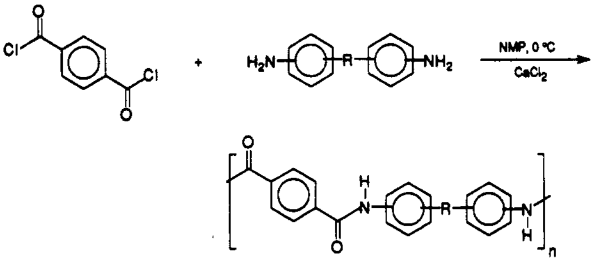
ABSTRACT: High molecular weight aromatic polyamides can be synthesized by the palladium-catalyzed carbonylation and condensation of diiodoaromatics and aromatic diamines. This process is tolerant of a variety of functionality and, in one optimized system, was found to work best with a slight excess of the diamine monomer. At elevated CO pressures, a dramatic difference in reactivity between the *m*-diiodobenzene monomer and the corresponding bromo analogue was observed. In the former case, high molecular weight aromatic polyamide was formed in 1 h, and in the latter, only oligomers were isolated after 24 h. Even at 1 atm of CO, the ultimate molecular weight of the diiodo-derived material was higher than that from the brominated monomer.

## Introduction

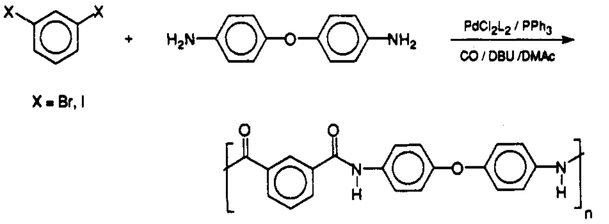
Aromatic polyamides (aramids) have become the mainstays of the high-performance fibers industry because of their unique strength and stiffness properties. The demand for these materials is increasing as new applications are found, especially in the composites area in which high-use temperatures, light weight, chemical resistance, and dimensional stability are crucial.

The conventional route for the preparation of these polymers was developed by Du Pont in the 1960s.[1] It consists of the low-temperature reaction of aromatic diacid chlorides and aromatic diamines in amide solvents like *N*-methylpyrrolidinone (NMP) or *N,N*-dimethylacetamide (DMAc) (eq 1).



(1)

Given the high interest in these materials, exploration into alternate synthetic routes has been the focus of a number of groups. These routes have included the reaction between diisocyanates and diacids at elevated temperatures,[2] the direct condensation of diamines and diacids promoted by phosphates[3] and phosphites,[4] and reactions of diamines with active acyl derivatives.[5] The reaction of silylated diamines and diacid chlorides has also been shown to be an effective method for producing aromatic polyamides, especially where the diamines are relatively unreactive.[6] More recently, Imai reported the first example of aromatic polyamide formation by the palladium-catalyzed carbonylation and condensation of aromatic dibromides and aromatic diamines.[7] This reaction produced modest molecular weight polymers (eq 2; X = Br). Although the carbonylation and coupling reaction offers potential advantages such as the elimination of corrosive, hydrolytically sensitive acid chlorides and the availability of a variety of bishalogenated monomers, the relatively low degree of polymerization is a serious drawback.



(2)

Model studies conducted in our laboratories between iodobenzene, aniline, and carbon monoxide indicated that, under appropriate conditions, *N*-phenylbenzamide formation was fast, clean, and quantitative.[8] The reaction sequence to form this compound is outlined in Scheme I. Oxidative addition of a coordinatively unsaturated Pd(0) complex to iodobenzene gives the Pd(II) aryl intermediate **1**, which is followed by CO insertion into the aryl–palladium bond to form acyl complex **2**. Subsequent attack of aniline leads to the formation of *N*-phenylbenzamide **3** and the regeneration of the active Pd(0) catalyst.

It was anticipated that this reaction scheme could be utilized in a polymerization process that would give good yields of linear, high molecular weight aromatic polyamides. Recent reports have disclosed the facile regioselective preparation of diiodoaromatic compounds.[9] The potential availability of numerous diiodo compounds prompted the study of their behavior in the palladium-catalyzed carbonylation and coupling reactions with diamines to give poly(aromatic amides). We have previously reported the initial results of the direct comparison of the model coupling of *m*-diiodobenzene and 4,4′-diaminodiphenyl ether and *m*-dibromobenzene and 4,4′-diaminodiphenyl ether.[10] This paper details the results of the model polymer system and the extension to a wide variety of diiodoaromatics and diamine monomers.

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**Scheme I**
**Mechanism of *N*-Phenylbenzamide Formation**

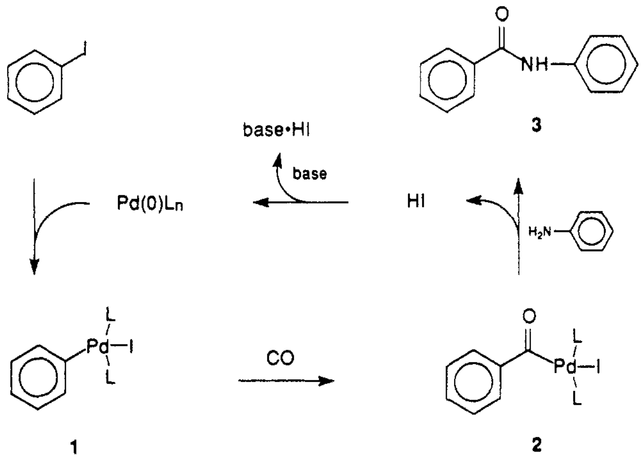


**Table I**
**Preparation of Aromatic Polyamide[a]**

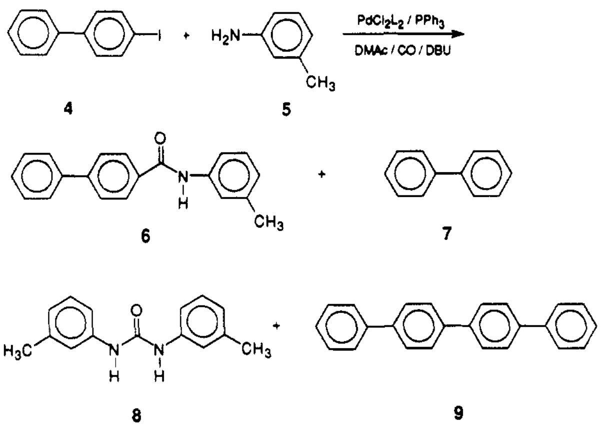
| entry | time (h) | $\eta_{inh}$ (dL/g)[b] | CO pressure | $M_w$[c] | $M_n$[c] |
|---|---|---|---|---|---|
| 1 | 2.5 | 0.34 | 1 atm | 35 300 | 18 700 |
| 2 | 2.0 | 0.37 | 1 atm | 32 900 | 18 200 |
| 3 | 24.0 |  | 1 atm | 34 600 | 14 600 |
| 4 | 22.5 |  | 1 atm | 34 100 | 14 500 |
| 5 | 3.2 | 0.43 | 40 psig | 59 900 | 20 700 |
| 6 | 29.0 | 0.55 | 90 psig | 68 000 | 22 400 |

[a] Reactions run in DMAc (0.33 M) with 2.4 equiv of DBU at 115 °C. Entries 1–4 employed 1.00 equiv of dihalobenzene, 1.02 equiv of 4,4′-ODA, and 6% $PdL_4$ (L = $PPh_3$) as the catalyst. Entries 5 and 6 used 1 equiv of dihalobenzene and 4,4′-ODA and 6% $PdCl_2L_2$ and 12.4% L as the catalyst system. [b] 0.25 wt % in DMAc at 25.0 °C. [c] PMMA equivalent molecular weights.

## Results and Discussion

The system chosen for optimization was the reaction of *m*-diiodobenzene and 4,4′-diaminodiphenyl ether (4,4′-ODA) in DMAc at 115 °C (eq 2; X = I). This gave a soluble polymer that could be directly compared to the one obtained by Imai.[7a] Under 1 atm of CO and with 6% $PdL_4$ as the catalyst, a polymer with $\eta_{inh}$ = 0.37 dL/g and PMMA equivalent $M_w$ = 32 900 was formed (Table I, entry 2). This polymer was indistinguishable from that made using *m*-dibromobenzene (entry 1) in side-by-side reactions and as previously reported.[7a] Allowing both reactions to proceed for 24 h had no deleterious effect on the polymers (entries 3 and 4, respectively). On the basis of the model studies, raising the CO pressure should increase the rate of polymerization.[8] The reaction of *m*-diiodobenzene and 4,4′-ODA run at 40 psig CO with 6% $PdCl_2L_2$ and 12% $PPh_3$ gave an aromatic polyamide with a higher viscosity, $\eta_{inh}$ = 0.43 dL/g, and molecular weight, PMMA equivalent $M_w$ = 59 900. At 90 psig, a further increase was seen with $M_w$ = 68 000; however, higher molecular weights were desired. Various combinations of pressure, catalyst and ligand loading, and temperature failed to provide improved molecular weights.

Side reactions known to occur during palladium-catalyzed coupling and carbonylation reactions are direct coupling, aryl halide reduction, and urea formation, all of which disturb the stoichiometry of the reaction and could lead to decreased molecular weights. To address these concerns, another model system was examined for these side products. We focused on the reaction of 4-iodobiphenyl and *m*-toluidine (eq 3) because the amide that formed would be soluble in DMAc, and any biphenyl that formed from reduction of the halide would be easier to detect by GC than benzene formed from iodobenzene. Anticipated reaction products included the amide **6**, biphenyl **7**, urea **8**, and the direct coupled quaterphenyl **9**.



(3)

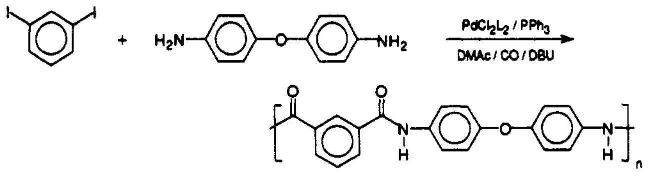
In a reaction with 50% excess of iodobiphenyl, the reduced product **7** was formed in observable amounts. This likely occurred because the activated palladium aryl or acyl iodide intermediate (similar to **1** or **2** in Scheme I) reacted with other species after all the nucleophilic amine was consumed. Adventitious water could generate a palladium hydride intermediate,[11] which would reduce the halide **4** to the free arene **7**. A 50% excess of amine diminished the formation of biphenyl, which was also consistent with this hypothesis. As soon as a palladium acyl species was formed there was enough amine present with which it could react. Neither urea nor quaterphenyl was detected under any conditions employed.

Transferring these observations to polymerization reactions suggested that a short residence time for the diiodo monomers would decrease side reactions. This could be achieved by having an excess of diamine present during most of the reaction and adding the last increment of diiodo compound at the end. A polymerization was performed in which 95% of the theoretical amount of *m*-diiodobenzene was added initially. The other 5% was to be added in three later portions. After 0.5 h of reaction time, 1.7% *m*-diiodobenzene was added followed by an equal amount another 0.5 later. It was then observed that the reaction mixture had become viscous enough to stop the stirbar from spinning. The reaction was terminated and the polymer precipitated into methanol. Subsequent reprecipitation and drying gave an aromatic polyamide with an $\eta_{inh}$ = 1.28 dL/g. This is *3 times better* than previously reported viscosity values[7a] for this polymer made by a carbonylation procedure and puts it into a range for useful polymer properties (Table II, entry 1).

A 5-fold scale-up (entry 2) with an initial loading of 95% *m*-diiodobenzene and only one subsequent addition of 3.7% diiodo monomer gave a polymer with $\eta_{inh}$ = 1.22 dL/g. An aliquot removed just prior to the 3.7% addition showed a polymer with $\eta_{inh}$ = 1.01 dL/g. It was unclear if the higher viscosity of the final polymer was the result of the longer reaction time or of the addition of more diiodo monomer.

Control experiments were run in which exact 1:1 stoichiometry was present initially and were compared to those with a permanent 5% deficiency and those to which 5% was added over time (entries 3–5). In all cases the lowest molecular weights were seen with exact 1:1 stoichiometry. The next highest molecular weights were obtained from those reactions where 1:1 stoichiometry had been achieved by 95 + 5 addition and the best were from

**Table II**
**Aromatic Polyamide Optimization Experiments**[a]



| entry | % diiodobenzene added | $\eta_{inh}$ (dL/g)[c] | $M_w$[d] | $M_n$[d] | comments |
|---|---|---|---|---|---|
| 1 | 95 + 1.7 + 1.7 | 1.28 | 208 000 | 93 000 | |
| 2 | 95 + 3.7 | 1.22 | 163 000 | 79 400 | after 95%, 1.01 dL/g |
| 3 | 100 | 0.37 | 59 400 | 33 300 | |
| 4 | 95 | 1.13 | 202 000 | 100 000 | |
| 5 | 95 + 5 | 0.90 | 140 000 | 42 000 | |
| 6 | 95 + 3.5 | 0.96 | 132 000 | 59 500 | |
| 7 | 95 | 0.06 | 1 900 | 1 600 | dibromo, no $PPh_3$ |
| 8 | 95 | 1.17 | 195 000 | 89 400 | no $PPh_3$ |
| 9 | 95 | 1.10 | 190 000 | 85 300 | LiCl, no $PPh_3$ |
| 10 | 95 | 0.84 | 91 600 | 38 200 | 1000 psig, no $PPh_3$ |
| 11 | 95 | | | | dibromo, 650 psig CO |

[a] Polymerization conditions: DMAc (0.18–0.26 M), 2.4 equiv of DBU, 90 °C, 90 psig, 1.5 h, 3% $PdCl_2L_2$ (L = $PPh_3$), 6% L unless otherwise noted. [b] % DIB added relative to 100% 4,4'-DDA. [c] 0.25 wt % in DMAc at 25.0 °C. [d] PMMA equivalent molecular weights.

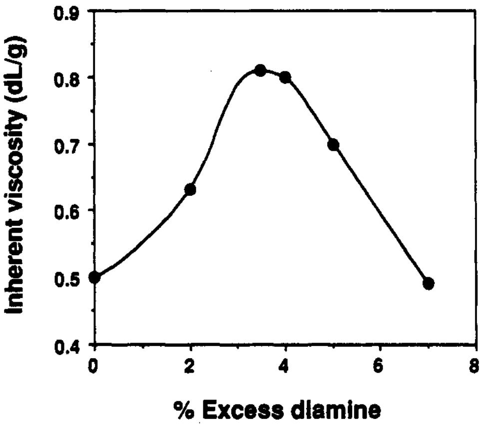


**Figure 1.** Effect of excess diamine on the reaction of *m*-diiodobenzene with 4,4'-diaminodiphenyl ether. Reactions in DMAc (0.33 M), 90 °C 95 psig CO, 6% $PdCl_2L_2$ (L = $PPh_3$), 12% L, 1.5 h, and 2.4 equiv of DBU.

polymerizations with a 5% deficiency of *m*-diiodobenzene (entries 5 and 4).

To determine if a 5% excess of diamine was optimal for this polymerization, a series of reactions varying the stoichiometry were carried out. Figure 1 shows that maximum viscosities were obtained at a 3.5% excess diamine loading. (It is interesting to note that maximum viscosity values in the previous work of Imai also required about a 3% excess of the diamine.[7a]) It is assumed that, with this excess concentration of diamine, the reduction of iodoaromatics is minimized. Further excess amine results in lowering of the molecular weight due to imbalance of the stoichiometry. In other words, a 3.5% excess of diamine, in this polymerization, yields the best overall functional stoichiometry because it will decrease the reduction of the aryl iodide.

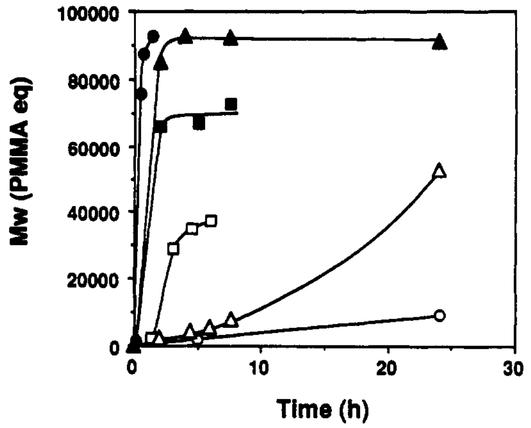


**Figure 2.** Effect of CO pressure on aromatic polyamide formation between diiodoaromatics and dibromoaromatics. Reaction in DMAc (0.33 M), 90 °C, 3% $PdCl_2L_2$, (L = $PPh_3$), 6% L, and 2.4 equiv of DBU. (□) bromo, 1 atm; (■) iodo, 1 atm; (△) bromo, 20 psig CO; (▲) iodo, 20 psig CO; (○) bromo, 90 psig CO; (●) iodo, 90 psig CO.

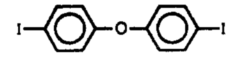
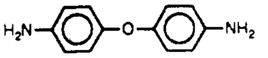
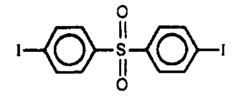
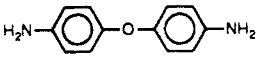
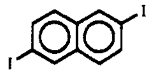
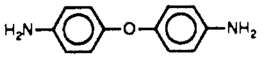
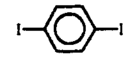
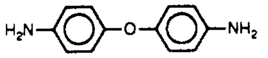
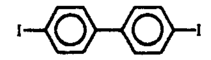
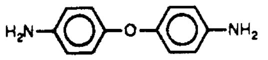
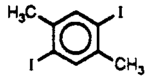
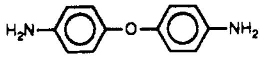
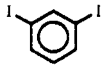
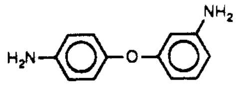
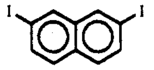
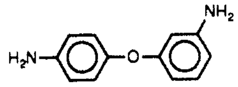
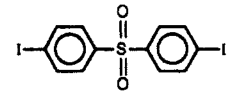
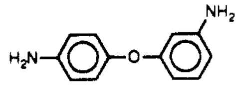
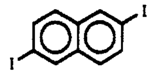
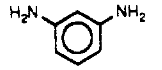
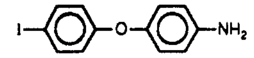
Up to this point, polymerization reactions were run 90 min under 90 psig CO, at 90 °C with 3% $PdCl_2L_2$ and 6% $PPh_3$ as the catalyst system. As noted in the literature,[12] Pd(0) complexes can undergo oxidative addition to aryl iodides without the presence of added phosphine ligands. When free triphenylphosphine was left out of the polymerization reaction, high molecular weight polymer was still formed (entry 8). The presence of the two added phosphine ligands was crucial for the polymerization with the dibromo derivatives (entry 7). When the extra phosphine was removed, only oligomers of $M_w$ = 1900 were obtained. In contrast, the diiodo monomer gave an aromatic polyamide of $M_w$ = 195 000. The presence of LiCl also had no deleterious effect on the raction (entry 9). While not necessary with this polymer system, it does permit less soluble aromatic polyamides to remain in solution and thus achieve high molecular weight.

The polymer formed at 1000 psig CO attained a respectable molecular weight (entry 10) with $M_w$ = 92 000. The higher CO pressure did have a small adverse effect on the polymerization reaction when using *m*-diiodobenzene. However, a profound effect was seen with *m*-dibromobenzene, which failed to produce any polymer under CO pressures of 650 psig (entry 11).

In order to more clearly demonstrate the difference in reactivity between the diiodo- and dibromobenzenes, three head-to-head experiments were performed.[10] In these cases, aliquots of stock solutions of solvent, base, diamine, catalyst, and ligand were made and added to the appropriate halogenated monomer (eq 2). A 3% excess of the diamine, relative to the dihalide, was used in all cases. Figure 2 shows that, after 6 h at 1 atm of CO, the bromo reaction had formed an aromatic polyamide of $M_w$ = 37 000. Even at these low CO pressures, the iodo analogue produced a polymer with $M_w$ = 72 500 after only 2 h. A slight increase in CO pressure to 20 psig had a dramatic effect. The dibromo reaction had only produced a polymer with $M_w$ = 53 000 after 24 h while the diiodobenzene gave a polymer with $M_w$ = 92 000 after 4 h. A final comparison was at 90 psig CO where no polymer formation was observed, even after 24 h, with dibromobenzene. In contrast, the diiodo reaction gave high polymer, $M_w$ = 92 000, within 1 h.

We believe that the difference in rate of molecular weight buildup and the sensitivity difference to CO pressure between the diiodo- and dibromobenzene is due to a change in the rate-determining step. It is well documented that zero-valent palladium compounds undergo oxidative addition to aryl iodides faster than the corresponding aryl bromides.[13] It is also known that, for the esterification of aryl bromides with CO, palladium, and an alcohol,

Table III
Aromatic Polyamides[a]

| entry | diiodo monomer | diamine monomer | ratio (%)[b] | $M_w$[c] | $M_n$ |
|---|---|---|---|---|---|
| 1 |  |  | 95 | 86 000 | 44 500 |
| 2 |  |  | 95[d] | 30 800 | 19 100 |
| 3 |  |  | 95[e] | 33 500 | 22 300 |
| 4 |  |  | 96[f] | 26 500 | 17 200 |
| 5 |  |  | 97[g] | 44 800 | 27 100 |
| 6 |  |  | 97[g] | 30 700[h] | 8 200[h] |
| 7 |  |  | 97 | 68 300[h] | 26 700[h] |
| 8 |  |  | 97 | 88 400[h] | 36 600[h] |
| 9 |  |  | 97[d] | 54 100 | 31 700 |
| 10 |  |  | 95 | 37 600 | 22 100 |
| 11 |  |  |  | 23 800[i] | 14 200[j] |

[a] Reaction conditions: DMAc (0.18–0.26 M), 115 °C, 90 psig CO, 2.4 equiv of DBU, 6% $PdCl_2L_2$ ($L = PPh_3$), 4–6 h, reprecipitated 2× from MeOH. [b] % of the stoichiometric amount of diiodo compound used relative to 100% diamine. [c] Absolute molecular weights. [d] 2 equiv of LiCl added to reaction. [e] 3 equiv of LiCl added to reaction. [f] Reaction run in NMP. [g] Reaction run in NMP with 4 equiv of LiCl. [h] PMMA equivalent molecular weights, single precipitation of polymer. [i] PMMA equivalent $M_w$ = 45 300. [j] PMMA equivalent $M_n$ = 25 700.

oxidative addition is the rate-limiting step.[14] Higher CO pressures have been shown to promote a greater degree of CO coordination to Pd(0),[15] rendering the palladium less nucleophilic and thus slowing the oxidative addition reaction.[16] Therefore, in the dibromoaromatic polymerization, the rate-determining step is the oxidative addition of palladium, and increasing the CO pressure suppresses this reaction. In the diiodo case, the rate-determining step is CO insertion. Increasing the CO pressure increases the rate of reaction and the rate of molecular weight gain. This behavior mimics that seen in the model compound study. Namely, higher CO pressures accelerate the overall amidation rate for iodoaromatics and suppresses amidation of the bromo analogs.[8]

The reason for the difference in the final molecular weight of the polymers obtained for these reactions is less clear. The rate of polymer formation should not affect the final molecular weight of the polymer if the reaction can be carried to sufficient conversion. We believe that side reactions of the amine or dibromobenzene occur during the slow reaction and limit the conversion. Most likely is reduction of the aryl–bromide bond to the free arene as seen earlier in the iodoaromatics (eq 3). This would disturb the stoichiometry necessary for high molecular weight. At extended reaction times, deactivation of the catalyst is possible which would also limit molecular weight.

To demonstrate that the synthesis of high molecular weight aromatic polyamides was not limited to a single case, a variety of other diamines and diiodo compounds were examined. Table III shows the monomers used and the molecular weights of the polymers obtained. These results represent single, unoptimized reactions in which 95–97% of the stoichiometric amount of the diiodo monomer was used. In some cases the addition of LiCl was necessary to maintain solubility during the polymerization. The variety of diiodo monomers that performed well in this reaction encompassed electron-rich and -poor compounds as well as linked and fused-ring derivatives. The AB monomer (entry 11) also produced polymers with moderately high molecular weight.

## Summary

We have demonstrated that high molecular weight aromatic polyamides can be prepared by the palladium-catalyzed carbonylation and coupling reaction of diodinated monomers with aromatic diamines. At elevated CO pressures, dramatic increases in molecular weight were observed for the iodoaromatic polymerizations as compared to the bromoaromatic ones. This process has been found to be broad in scope with a wide variety of diiodoaromatics successfully yielding high molecular weight aromatic polyamides. The attributes of this process make it a viable alternative to acid chloride chemistry for the preparation of high molecular weight aromatic polyamides.

## Experimental Section

**General Procedures.** Reactions at 1 atm to 100 psig CO were performed in a 120-mL pressure reaction vessel (containing a stirbar) from Aerosol Laboratory Equipment Corp. fitted with a pressure gauge, a pressure release valve, a gas inlet, and a straight ball valve for degassing and sample withdrawal. Reactions run at greater than 100 psig CO were performed in a 300-mL stirred autoclave (Parr No. 4561 M).

Model reactions were monitored on an HP 5890 gas chromatograph using a 15-m, 0.25-μm DB-5 column (0.32 mm i.d.) and a flame ionization detector. Helium flow rate through the column was 4.0 mL/min. The GC parameters employed for analysis were as follows: injection port, 300 °C; detector, 350 °C; temperature ramp from 50 °C (hold 1 min) to 300 °C (hold 10 min) at 20 °C/min. Viscosities were measured in *N,N*-dimethylacetamide (DMAc) at 25.0 °C at 0.25 wt % with an Ubbelohde viscometer (No. 38610). Size-exclusion chromatography (SEC) was performed on aromatic polyamide samples dissolved in *N,N*-dimethylformamide (DMF) containing 0.01 M LiBr or $LiNO_3$ using three 10-μm Waters HT linear columns and one 300-Å HT column. Some samples were insoluble in this solvent mixture. These samples were derivatized with methyl iodide as previously reported.[17] All samples were filtered prior to injection, and results were reported as poly(methyl methacrylate) (PMMA) equivalent molecular weights or absolute molecular weights as noted.

**Chemicals.** *N,N*-Dimethylacetamide (DMAc, anhydrous), *N*-methylpyrrolidinone (NMP, anhydrous), bis(triphenylphosphine)palladium(II) chloride ($PdCl_2L_2$), tetrakis(triphenylphosphine)palladium ($PdL_4$) (all from Aldrich), CO (Air Products, UPC grade), and *m*-toluidine (Kodak) were used as received. 4,4′-Diiododiphenyl sulfone, 2,6-diiodonaphthalene, 4,4′-diiodobiphenyl, and 2,8-diiododibenzofuran were prepared by known direct iodination techniques.

Triphenylphosphine was recrystallized from hexanes; 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was fractionally distilled under reduced pressure. 1,3-Diiodobenzene and 1,3-dibromobenzene were fractionally distilled before use, 1,4-diiodobenzene was recrystallized from ethanol, 4,4′-diaminodiphenyl ether (4,4′-ODA) was purified by sublimation or bulb-to-bulb distillation, 3,4′-diaminodiphenyl ether (3,4′-ODA) was distilled, and 1,3-diaminobenzene (*m*-PDA) was sublimed.

**Representative Polymerization Reaction.** To an oven-dried pressure vessel were added 3,4′-oxydianiline (1.00 g, 5.00 mmol), 4,4′-diiododiphenyl sulfone (2.28 g, 4.85 mmol), $PdCl_2L_2$ (0.21 g, 0.30 mmol), LiCl (0.40 g, 9.4 mmol), and DMAc (26.7 mL). The vessel was degassed and filled with argon three times and then degassed and filled to 30 psig with CO and lowered into an oil bath at 115 °C. After stirring for 1–2 min to effect dissolution of most of the reagents, the pressure was released and DBU (1.80 mL, 12.0 mmol) was added by syringe. The vessel was repressurized to 90 psig CO, and the reaction was allowed to proceed until CO uptake stopped (ca. 4 h). When the reaction was complete, the reaction mixture was diluted with DMAc, filtered through filter aid, and precipitated into methanol. The solid polymer was washed extensively with methanol, dried and then redissolved in DMAc, and then reprecipitated into methanol and dried at 90–110 °C under high vacuum (1 Torr) for 24–48 h.

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