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Palladium-Catalyzed Syntheses of Poly(amide-ols)–Poly(benzoxazole) Precursors

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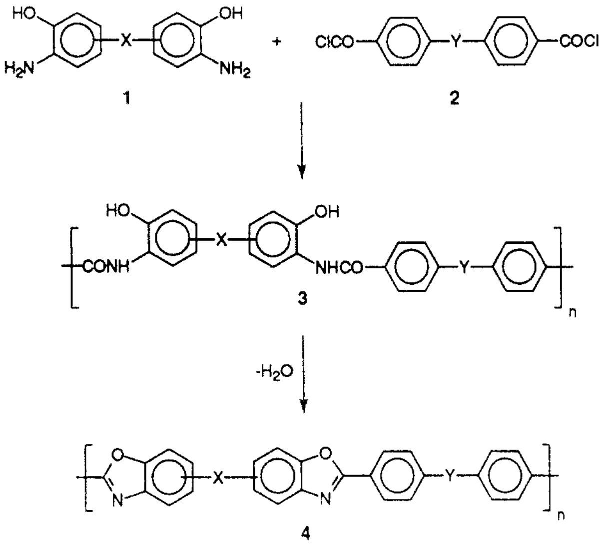
ABSTRACT: A new, synthetic procedure is described in which poly(amide-ols) can be formed from diiodoaromatics and bis(*o*-aminophenols) through a palladium-catalyzed carbonylation and coupling sequence. Optimum conditions found for this procedure were Pd(II) catalyst levels of 0.2–0.02% and associated phosphine ligands of twice this level, DMAc, NMP, or DMF as the solvent, a reaction temperature of 120 °C, 95 psig CO, and the use of DBU as the neutralizing agent. The poly(amide-ols) were characterized by inherent viscosity measurements, absolute molecular weight determinations, FT-IR, neutron activation analysis, and TGA. These intermediates were then subjected to cyclization temperatures of 325 °C to effect complete conversion to the desired benzoxazole polymers that were also characterized by TGA and FT-IR.

Introduction

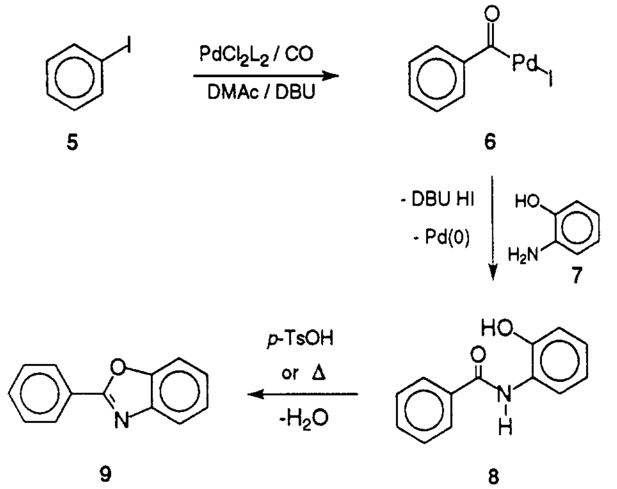
Aromatic poly(benzoxazoles) (PBOs) possess excellent thermal stability,[1,2] solvent resistance, light weight, and high strength, and the fibers are reported to have excellent mechanical properties suitable for a variety of applications.[3-8] Early synthetic efforts for the preparation of PBOs entailed two-step condensation reactions between bis(*o*-aminophenols) and acid chlorides (eq 1),[9]one-step melt condensations of bis(*o*-aminophenols) and aromatic diacid diphenyl esters,[10] or direct solution condensation reactions of bis(*o*-aminophenols) with aromatic diacids using poly(phosphoric acid) (PPA),[11] PPA/$MeSO_3H$,[12] or P_2O_5/$MeSO_3H$ mixtures.[13] More recently, nonacidic routes for PBO syntheses have been devised. Condensation of bis(azomethines) and bis(*o*-aminophenols) gave intermediate poly(azomethines),[14] and silylated aminophenol monomers were found to be effective in the preparation of high molecular weight poly(amide-ols) (**3**).[15-18] Poly(amide-ols) could also be made by direct coupling of aminophenols and aromatic carboxylic acids with triphenylphosphine and pyridine in hexachloroethane[19] and then cyclized in *o*-dichlorobenzene[20] or with trimethylsilyl polyphosphate (PPSE) in *o*-dichlorobenzene.[21] Many of these latter syntheses focus on the formation of soluble PBO precursors that can be subsequently cyclized to the desired rigid-rod polymer. These prepolymers have an advantage in that they can be processed (molded, spin-cast, or drawn) in ways not possible for the fully cyclized material.



(1)

Common to most of these synthetic methods is the use of aromatic diacids (or derivatives) as the electrophilic partner in the reaction. This is a limitation where such monomers are difficult to prepare or require a number of synthetic steps. Diiodinated aromatic compounds can be readily obtained by the direct iodination of a variety of available aromatic compounds.[22,23] We recently described several palladium-catalyzed routes to other high-performance polymer systems that were based on the carbonylation and condensation of aromatic iodides and amines.[24,25] Earlier, we reported that 2-arylbenzoxazoles could be easily synthesized through the palladium-catalyzed carbonylation of iodoaromatics and *o*-aminophenols (Scheme 1).[26] Oxidative addition of a Pd(0) complex to iodobenzene followed by carbon monoxide (CO) insertion gave a palladium acyl complex, **6** (ligands omitted for clarity). Nucleophilic attack by *o*-aminophenol formed intermediate *o*-hydroxybenzanilide (**8**), which showed no propensity to cyclize under the reaction conditions. Deliberate addition of *p*-TsOH or temperatures in excess of 200 °C were required for cyclization to **9** to occur.

Scheme 1



This same chemistry was applied to aromatic diiodides and bis(*o*-aminophenols) to generate soluble and process-

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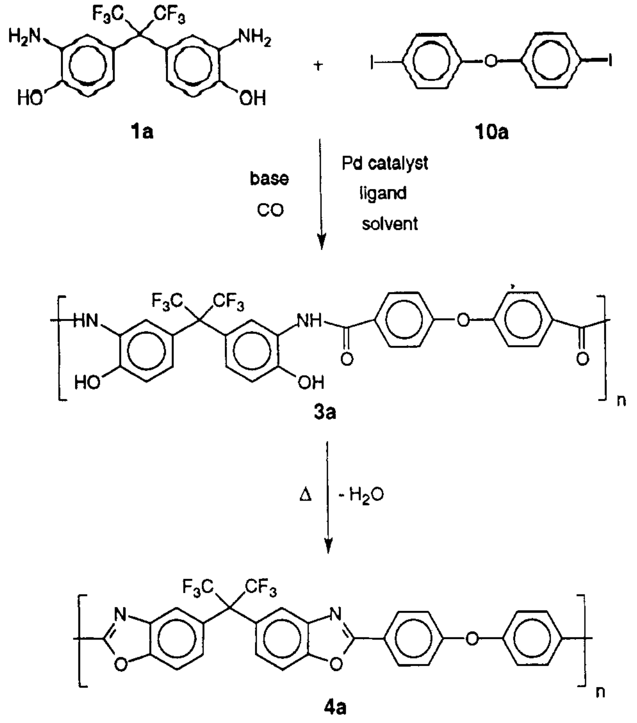
Scheme 2



able poly(amide-ols) (**3**). In this paper, we have examined variables affecting the polymerization process and report on the optimized formation of poly(amide-ols) and their conversion into poly(benzoxazoles). The effects of catalyst concentration and type, ligands, base, and solvent on the polymerization of 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (**1a**) and 4,4′-diiododiphenyl ether (**10a**) to give poly(amide-ol) (**3a**; Scheme 2) were explored and the results reported below.

Experimental Section

General Procedures. Polymerization reactions were performed in a Fischer–Porter bottle (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.

Sample Analyses. TGA measurements were made on an Omnitherm Advantage II under 50 mL/min of nitrogen or a PC Series TGA7 under 30 mL/min of nitrogen at 10 °C/min from 30 to 900 °C. SEC data were obtained from a Waters HPLC using three Waters HT linear columns and a 300-Å HT column and calibrated with PMMA standards between 2990 and 1 600 000. The samples were derivatized with methyl iodide and chromatographed in DMF. IR spectra were recorded on a Nicolet 5ZDX spectrometer as KBr pellets. Iodine, palladium, and chloride analyses were obtained by neutron activation analysis. Inherent viscosity's were determined in DMAc at 25.0 °C at 0.25 wt % with a Schott Gerate 526-10 viscometer.

Chemicals. The palladium catalysts $PdCl_2(PPh_3)_2$, $PdCl_2$(DPPE), $Pd(OAc)_2$, and $Pd(PPh_3)_4$ (Aldrich), PPh_3 (Eastman Kodak Co.), DMAc, NMP, and DMF (anhydrous; Aldrich, sure seal), CO (UPC grade; Air Products), TMBD (7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene; Fluka), DBN (1,5-diazabicyclo-[4.3.0]non-5-ene; Aldrich), DMPA [4-(dimethylamino)pyridine; Kodak], 2,6-lutidine (Kodak), *N*-methylmorpholine (Kodak), 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (Chriskev), 2,6-diiodonaphthalene (Kodak), 4,4′-diiodobiphenyl (Kodak), and 4,4′-diiododiphenyl sulfone (Kodak) were used as received. DBU (Aldrich) and triethylamine (Kodak) were distilled before use, 3,3′-dihydroxy-4,4′-diaminobiphenyl (Chriskev) was recrystallized from 5/1 dioxane/water, 4,4′-diiododiphenyl ether (Kodak) was recrystallized from ethyl acetate, 1,4-diiodobenzene (Kodak) was recrystallized from ethanol, and 2,8-diiododibenzofuran (Kodak) was recrystallized from 2/1 isopropyl alcohol/toluene.

Table 1. Effect of Catalyst Loading on Polymerization[a]

entry	mol % catalyst	yield (%)	η_{inh} (dL/g)[b]	$\bar{M}_w$[c]	$\bar{M}_n$[c]
1	3.00	70	0.34	32 000	20 000
2	1.00	97	0.44	45 500	24 400
3	0.17	87	0.57	52 000	27 700
4	0.05	86	0.60	53 400	29 700
5	0.02	74	0.51	45 600	28 500
6	0.01	31[d]			

[a] Conditions for polymerization were as follows: 3.00 mmol of **1a** and **10a**, 7.2 mmol of DBU, 17.8 mL of DMAc, 95 psig of CO, 120 °C, 6 h of reaction time, $PdCl_2L_2$ catalyst where L = PPh_3. [b] Measured as a 0.25 wt % solution in DMAc at 25.0 °C. [c] Absolute molecular weights. [d] A sticky goo was obtained on precipitation, which was not characterized.

Table 2. Effect of Catalyst and Ligands on Polymerization[a]

entry	catalyst[b]	ligand	yield (%)	η_{inh} (dL/g)[c]	$\bar{M}_w$[d]	$\bar{M}_n$[d]
1	$PdCl_2L_2$		87	0.57	52 000	27 700
2	$PdCl_2$(DPPE)		86	0.62	58 500	34 500
3	$Pd(OAc)_2$		87	0.42	42 900	22 900
4	$Pd(OAc)_2$	PPh_3	94	0.58	56 500	31 700
5	PdL_4		86	0.44	47 900	28 700
6	PS-Pd[e]		85	0.34	50 800	28 600

[a] Conditions for polymerization were as follows: 3.00 mmol of **1a** and **10a**, 7.2 mmol of DBU, 17.8 mL of DMAc, 95 psig of CO, 120 °C, 5–7 h of reaction time, 0.17% catalyst. [b] L = PPh_3. [c] Measured as a 0.25 wt % solution in DMAc at 25.0 °C. [d] Absolute molecular weights. [e] Cross-linked polystyrene containing 4 wt % Pd bound to *p*-(diphenylphosphino)styrene.

Polymerization Reactions. In a representative polymerization reaction the Fischer–Porter bottle was charged with 4,4′-diiodobiphenyl (1.266 g, 3.00 mmol), 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (1.099 g, 3.00 mmol), bis(triphenylphosphine)palladium(II) chloride ($PdCl_2L_2$; 3.5 mg, 0.005 mmol), and *N*,*N*-dimethylacetamide (DMAc; 17.3 mL). The mixture was stirred, degassed, placed under a carbon monoxide (CO) atmosphere, and heated to 115 °C. When the contents of the vessel had dissolved, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 1.08 mL, 7.2 mmol) was added and the vessel was charged to 95 psi of CO. The reaction was allowed to proceed for 6 h, after which time the contents of the bottle was filtered through a filter aid and precipitated into methanol. The polymer was washed extensively with methanol, dried and again dissolved in DMAc, refiltered, and reprecipitated into methanol to give a solid that was dried in vacuo to give 1.53 g of polymer with η_{inh} = 0.57 (0.25% in DMAc at 25 °C).

Results and Discussion

We initially examined the effect of catalyst loading on the model polymerization. In previous investigations of palladium-catalyzed polymerizations,[24] we found that a 3% loading of catalyst was sufficient to permit high-yield formation of the amide bond. Decreasing the catalyst level to 1% or lower resulted in increased reaction times in small-molecule studies.[27] At the 3% level, in this system, a good yield of polymer with a modest viscosity was produced (Table 1, entry 1).

When the catalyst level was decreased by a factor of 3, the yield increased and the viscosity rose (entry 2). Decreasing the catalyst level again, to 0.17% (entry 3), gave a high yield of poly(amide-ol) with even greater viscosity. Even with 0.02% catalyst (entry 5), the reaction proceeded rapidly to give a high molecular weight polymer. This was evidently the lower limit as 0.01% catalyst (entry 6) did not result in high polymer formation. Subsequent polymerizations were performed with 0.17% catalyst.

Variation in the catalyst type and its associated ligands was also investigated. Table 2 shows that there was little difference between $PdCl_2L_2$ (entry 1) with the bound monodentate PPh_3 ligands and $PdCl_2$(DPPE) (entry 2)

Table 3. Effect of Solvent on Polymerization[a]

entry	solvent	yield (%)	η_{inh} (dL/g)[b]	$\bar{M}_w$[c]	$\bar{M}_n$[c]
1	DMAc	87	0.57	52 000	27 700
2	NMP	49	0.72	60 300	38 600
3	DMF	80	0.59	54 000	34 100
4	DMAc	74	0.51	45 600	28 500
5	NMP	70	0.49	41 800	27 800

[a] Conditions for polymerization were as follows: 3.00 mmol of **1a** and **10a**, 7.2 mmol of DBU, 17.8 mL of DMAc, 95 psig of CO, 120 °C, 5–6 h of reaction time, $PdCl_2L_2$ catalyst where L = PPh_3. Entries 1–3 are at 0.17% level. Entries 4 and 5 are at 0.02% level. [b] Measured as a 0.25 wt % solution in DMAc at 25.0 °C. [c] Absolute molecular weight.

Table 4. Effect of Base on Polymerization[a]

entry	base	pK_a[b]	yield (%)	η_{inh} (dL/g)[c]	$\bar{M}_w$[d]	$\bar{M}_n$[d]
1	MTBD	13.0	90	0.33	36 900	21 800
2	DBU	11.9	97	0.44	45 700	24 400
3	DBN	11.0	85	0.23	27 400	17 300
4	Et_3N	11.0				
5	DMAP	9.7				
6	*n*-methylmorpholine	7.5				
7	2,6-lutidine	6.6				

[a] Conditions for polymerization were as follows: 3.00 mmol of **1a** and **10a**, 7.2 mmol of base, 17.8 mL of DMAc, 95 psig of CO, 120 °C, 6 h of reaction time, 1.00% $PdCl_2L_2$ catalyst where L = PPh_3. [b] Reference 29. [c] Measured as a 0.25 wt % solution in DMAc at 25.0 °C. [d] Absolute molecular weight.

with the bidentate (diphenylphosphino)ethane ligand. When the phosphine ligands were absent, as with $Pd(OAc)_2$, the viscosity and the molecular weight of the resulting polymer were lower (entry 3). This indicated that the reaction proceeded more favorably in the presence of phosphine ligands. This was documented in the model study in which the formation of benzanilide from iodobenzene and aniline occurred more rapidly in the presence of phosphine ligands.[27] When 2 equiv of PPh_3 (based on Pd) were added to $Pd(OAc)_2$ (entry 4), the viscosity increased to the value obtained from the first two catalysts. The behavior of the preformed Pd(0) catalyst PdL_4 (entry 5) was indistinguishable from the Pd(II) catalysts used above. A polymer-bound catalyst PS–Pd (entry 6) also worked well and offered the added advantage of easy phosphine ligand removal.

The effect of several dipolar aprotic solvents on the polymerization reaction was also examined. As one can see from Table 3, there was little difference seen between DMAc, NMP, and DMF. At the 0.17% catalyst level (entries 1–3), NMP appeared to give a lower yield and higher viscosity polymer, but this may have been an artifact of the isolation technique. When NMP was again compared to DMAc (entries 4 and 5), at the 0.05% catalyst level, there was no noticeable difference between them.

The choice of base was crucial in these reactions. Table 4 shows that, when the strongly basic amine DBU was employed as the HI scavanger, the polymerization reaction proceeded smoothly (entry 2). However, when DBU was replaced with a weaker base such as triethylamine, DMAP, *N*-methylmorpholine, or 2,6-lutidene, no reaction occurred. The stronger guanidine-like base MTBD (7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene) worked, as did the weaker base DBN. It is unclear why triethylamine failed to allow polymerization to occur while DBN, with the same basicity, did. Overall, these observations suggested that the amine base was doing more than just neutralizing the HI formed during the reaction. The amine may also be affecting the reactivity of the palladium by ligating to the metal. The stronger the base, the more electron density it will impart to palladium and the more reactive it will be toward oxidative addition and subsequent reactions. It was therefore important to use a strongly basic amine base for these reactions. Czernecki noticed similar effects in olefination reactions of aryl iodides and allylic alcohols and concluded that the amine served both as a neutralizing agent and as a ligand that helped form a highly reactive species in the oxidative addition step of the reaction.[28]

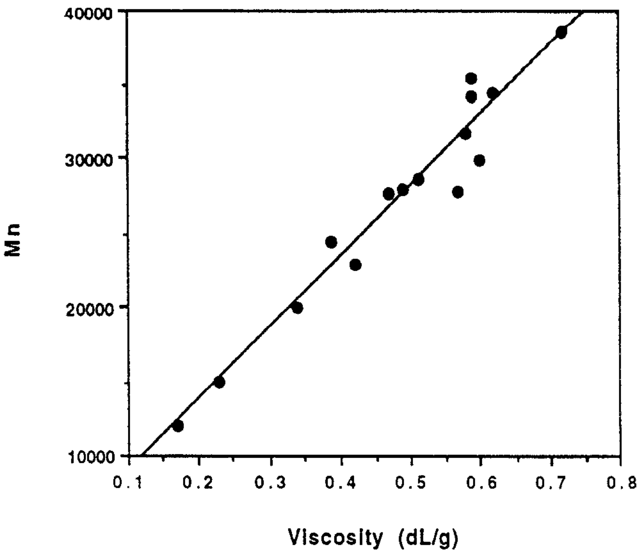


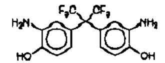
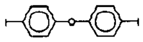
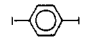
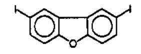
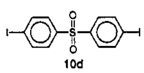
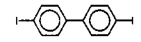
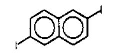
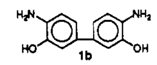
Figure 1. Correlation between η_{inh} measurements and $\bar{M}_n$ values.

While not a rigorous proof that high molecular weight has been obtained, inherent viscosity, η_{inh}, measurements had been used to assess the quality of the polymerization reaction. Figure 1 shows that there is a good correlation between the reported viscosity data and the absolute molecular weights of the poly(amide-ols). The absolute molecular weights were obtained by a novel derivatization method.[30] At higher viscosities, the plot shows more scatter around the linear fit because of varying amounts of residual solvent trapped in the polymer. Number-average molecular weights ($\bar{M}_n$s) of 30 000 or greater corresponded to degrees of polymerization (DPs) of 50 or more. These values are comparable to other rigid condensation polymers such as polyimides and polyamides.

Having optimized the polymerization reaction for **3a**, we wished to see if other monomers would form high molecular weight poly(amide-ols). Table 5 shows the polymers made by this method. The low yield of polymer **3b** in which 1,4-diiodobenzene was used as a monomer is a reflection of the insolubility of the poly(amide-ol) that formed. During the reaction, most of the polymer precipitated from solution. What remained in the DMAc solvent was precipitated and isolated to give the yield shown in Table 5. LiCl can commonly be employed to keep aramids from prematurely precipitating but was not effective in this case. The dibenzofuran monomer also gave a low yield of isolated polymer **3c**. The reason for this is unclear, as no solubility problem was encountered.

The last four poly(amide-ols) were isolated in nearly quantitative yields. In two cases, the precipitated polymer would not redissolve in DMAc without the addition of LiCl (**3e** and **3g**). Incomplete removal of this salt led to a greater than theoretical yield of polymer. In all cases, except the last one, $\bar{M}_n$ values were in the range of 20 000–30 000 with inherent viscosities of 0.34–0.46 dL/g. This indicated that a reasonably high molecular weight polymer had been formed. When 4,4′-diamino-3,3′-dihydroxybiphenyl (**1b**) was used as the monomer, a very viscous prepolymer was obtained.

Table 5. Synthesis and Properties of Poly(amide-ols)[a]

polymer	bis(aminophenol)	diiodoaromatic	yield (%)	η_{inh} (dL/g)[b]	$\bar{M}_w$[c]	$\bar{M}_n$[c]
3a	 1a	 10a	97	0.44	45 700	24 400
3b	1a	 10b	10	0.35	41 700	30 700
3c	1a	 10c	49	-	33 900	22 700
3d	1a	 10d	96	0.34	42 000	25 500
3e	1a	 10e	103[d]	0.34	39 100	19 500
3f	1a	 10f	95	0.46	49 400	28 700
3g	 1b	10a	103[d]	1.52	34 100	12 500

[a] Conditions for polymerization were as follows: 3.00 mmol of monomers, 1.00% $PdCl_2L_2$, 17.8 mL of DMAc, 95 psig of CO, 120 °C, 3–6 h of reaction time. [b] Measured as a 0.25 wt % solution in DMAc at 25.0 °C. [c] Absolute molecular weight. [d] LiCl was added to redissolve the polymer after the first precipitation.

Table 6. Neutron Activation Analysis of Poly(amide-ols)

polymer	wt % I	wt % Pd	wt % Cl
3a	0.17	0.045	
3c	0.02	0.179	
3d	0.05	0.012	
3e	0.19	0.033	0.08
3f	0.03	0.026	
3g	0.14	0.221	0.18

Neutron activation analysis of the polymers provided a way to analyze for remaining iodide in the polymer as well as for palladium or chloride contamination. Table 6 shows that iodide remained in the polymer to the extent of 0.02–0.2%. If all the remaining iodide was present as an aryl iodide, then the $\bar{M}_n$ of polymer **3e** should have been in excess of 66 000. The true $\bar{M}_n$ was about 19 500, which indicated that some iodide may have been consumed during the polymerization reaction that did not lead to monomer coupling. Most likely some of the aryl iodide was reduced to free arene during the reaction that would effectively act as a chain-stopping agent.

The effective synthesis of poly(benzoxazole) precursors had been achieved, and it remained to cyclize these materials to the desired final products. Rather than the chemical dehydrative ring-closure method employed in the small-molecule studies, a simple thermal cycle was used. Thermogravimetric analyses (TGAs) of the amide-ols **3a**–**g** (Figure 2) showed that all of the precursors lost water and began to cyclize between temperatures of 250 and 290 °C. The actual weight losses were slightly greater than the calculated weight losses (Table 7).

To effect cyclization, the poly(amide-ols) were dissolved in DMAc and cast on glass. After exposure to a temperature of 325 °C for 3 h under vacuum with a slight nitrogen purge, the thermal properties of the films were examined. Figure 3 and Table 7 show that the fully cyclized materials were thermally stable to greater than 450 °C. Figure 3 also shows that even at 900 °C a residue of 40–60% remained.

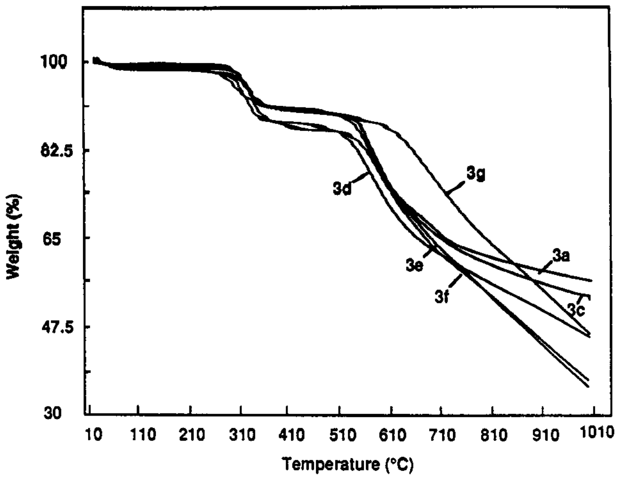


Figure 2. TGA of poly(amide-ols) in nitrogen.

Table 7. Thermal Data for Poly(amide-ols) and Poly(benzoxazoles)

polymer	% wt loss		dehyd onset (°C)[a]	decomp onset (°C)[b,c]	residue at 900 °C (wt %)[b]
	theory[a]	observed[a]			
3/4a	6.1	9.0	276	460	53
3/4b	7.3	8.5	285	480	51
3/4c	6.1	8.9	285	485	33
3/4d	5.7	6.1	270	450	51
3/4e	6.3	6.8	276	500	57
3/4f	6.6	9.3	275	520	57
3/4g	8.2	7.1	249	540	47

[a] For poly(amide-ols) (**3**). [b] For poly(benzoxazoles) (**4**). [c] Temperature at which 5% weight loss was recorded.

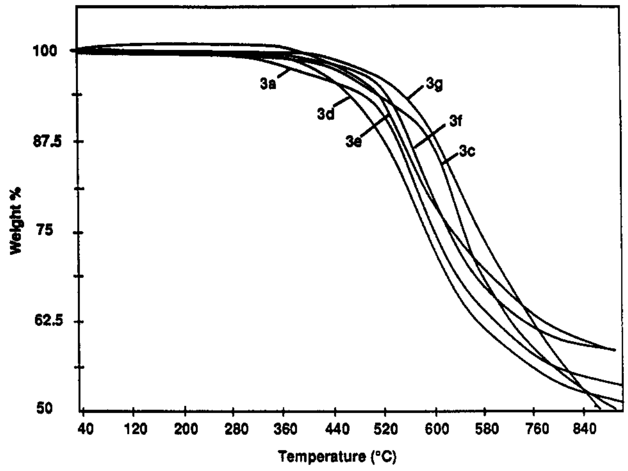


Figure 3. TGA of poly(benzoxazoles) in nitrogen.

To confirm that cyclization to the desired benzoxazole nucleus had taken place, FT-IR spectra of the cyclized and uncyclized polymers were obtained. Figure 4 shows the expanded spectra of polymers **3a** and **4a**. The amide I and II carbonyl bands at 1648 and 1515 cm^{-1} are quite distinct in **3a**. After heating at 325 °C for 3 h, the bands are gone in polymer **4a**. Also absent was the broad band centered around 3200 cm^{-1}, indicative of OH and NH resonances. This is in good agreement with observations reported by others.[19]

Summary

We have demonstrated a new synthetic procedure in which poly(amide-ols) can be formed from diiodoaromatics and bis(o-aminophenols) through a palladium-catalyzed carbonylation and coupling sequence. Optimum condi-

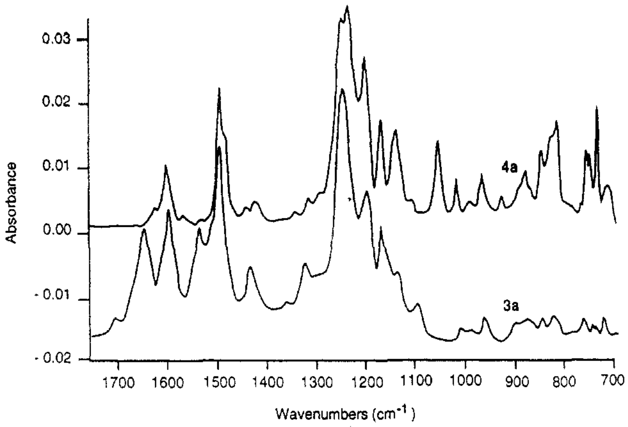


Figure 4. FT-IR comparison between poly(amide-ol) **3a** and poly(benzoxazole) **4a**.

tions found for this procedure were Pd(II) catalyst levels of 0.2–0.02% and associated phosphine ligands of twice this level, DMAc, NMP, or DMF as the solvent, a reaction temperature of 120 °C, 95 psig of CO, and the use of DBU as the neutralizing agent. SEC data indicate high molecular weight poly(amide-ols) are formed that readily cyclize at elevated temperatures to give poly(benzoxazoles). This synthesis offers alternatives to conventionally employed routes to form these materials. Three advantages to this route are the hydrolytic stability of the monomers, the processability of the intermediate poly(amide-ol), and the diverse numbers of diiodinated materials that are available as monomers.

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