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Palladium-Catalyzed Formation of Poly(imide−amides). 2. Reactions with Chloroiodophthalimides and Diamines

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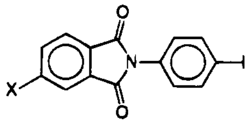
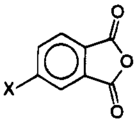
ABSTRACT: High molecular weight poly(imide−amides) can be readily formed by the palladium-mediated carbonylation and condensation reactions of activated chlorophthalimide monomers and aromatic diamines. The presence of iodide ion greatly accelerates the rate of reaction and increases the ultimate molecular weight of the polymer. Polymerizations proceed best using a protocol of high CO pressure (90 psig) for 2−4 h, followed by lower CO pressure (20 psig) in DMAc or NMP for 24−48 h at 100 °C using 0.3−3.0% $PdCl_2L_2$ (L = PPh_3) as the catalyst with 2−6 equiv of PPh_3/Pd and 0.3−1.0 equiv of an iodide/chloro group.

Introduction

We have reported on the use of palladium-catalyzed carbonylation and coupling reactions of iodinated aromatic compounds and diamines for the preparation of a variety of polymeric systems including aramids,[1] polyimides,[2] poly(amide-ols),[3] and, most recently, poly(imide−amides) (PIAs).[4] The latter report demonstrated that high molecular weight polymers could be prepared in a controlled manner with a well-defined ratio of imide/amide groups in the backbone. One of the monomers used in these polymerization reactions was 4-iodo-*N*-(4-iodophenyl)phthalimide (**1a**). A key intermediate in the synthesis of this monomer was 4-iodophthalic anhydride (**2a**), which was prepared in a three-step process with an overall yield of only 46%, based on 3,4-dimethylaniline. A commercially available alternative to this intermediate is the chloro analog **2b**,[5] which can be reacted directly with the appropriate iodoaniline or diamine to give the corresponding chlorinated monomers, such as **1b**.



1a X = I
1b X = Cl



2a X = I
2b X = Cl

However, oxidative addition reactions of Pd(0) complexes to chloroaromatic compounds are generally sluggish and severe conditions must usually be employed. Exceptions to this are activated aromatic chlorides, such as 2-chloropyrazine,[6] 4-chloronitrobenzene,[7] and $(\eta^6\text{-}C_6H_5Cl)Cr(CO)_3$.[8] The phthalimido group is also electron withdrawing, and to determine whether the chloro substituent in the phthalimide ring was reactive enough to undergo oxidative addition, and subsequent CO insertion and coupling, the reaction of aniline with 4-chloro-*N*-phenylphthalimide (**3**) was examined (Scheme 1).

It was found that the reaction proceeded readily in the presence of iodide ion and that lower CO pressures favored higher yields of product and faster rates of formation.[9] This discovery permitted the synthesis of a variety of poly(imide−amides) using appropriately substituted dichloro and chloroiodo imides as described below.

Experimental Section

General Procedures. Small-scale reactions were performed in a 120-mL pressure reaction vessel containing a Teflon-coated stirbar, fitted with a pressure gauge, a pressure release valve, a gas inlet, and a straight ball valve for degassing and sample withdrawal. Large-scale reactions (greater than 15 g) were performed in a Buchi, Model BEP 280, glass autoclave with a Pressflow gas control unit for CO delivery. All reactions were performed in a well-ventilated hood, behind safety shields. Fourier transform infrared spectra were recorded as KBr pellets. ^1H NMR and ^{13}C NMR spectra were acquired on a 300-MHz spectrometer using $CDCl_3$ or DMSO-d_6 as both solvent and reference. Size-exclusion chromatography (SEC) data were obtained in DMF containing 0.01 M $LiNO_3$ using two Jordi's DVB columns, which were calibrated with narrow molecular weight distribution poly(methyl methacrylate) (PMMA) standards between 2000 and 1 600 000. Absolute molecular weight data were obtained with viscosity detection in DMF using three Waters HT linear columns calibrated with narrow molecular weight distribution PMMA standards between 2000 and 1 600 000 after derivatizing the samples, if necessary, with methyl iodide.[12] Thermogravimetric analyses were performed on a Perkin-Elmer Series 7 thermal analysis system under nitrogen at a heating rate of 10.0 °C/min. Differential scanning calorimetry (DSC) results were obtained on a Du Pont 912 dual cell or 910 single cell calorimeter under nitrogen at a heating rate of 20 °C/min.

Chemicals. 4-Chlorophthalic anhydride (Oxy Chem), 4-chloroaniline, 4-iodoaniline (both Kodak), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP), 2,2-bis[4-(3-aminophenoxy)phenyl] sulfone (m-BAPS; both Kennedy and Klim), *N,N*-dimethylacetamide (DMAc; anhydrous), *N*-methylpyrrolidinone (NMP; anhydrous), bis(triphenylphosphine)palladium(II) chlo-

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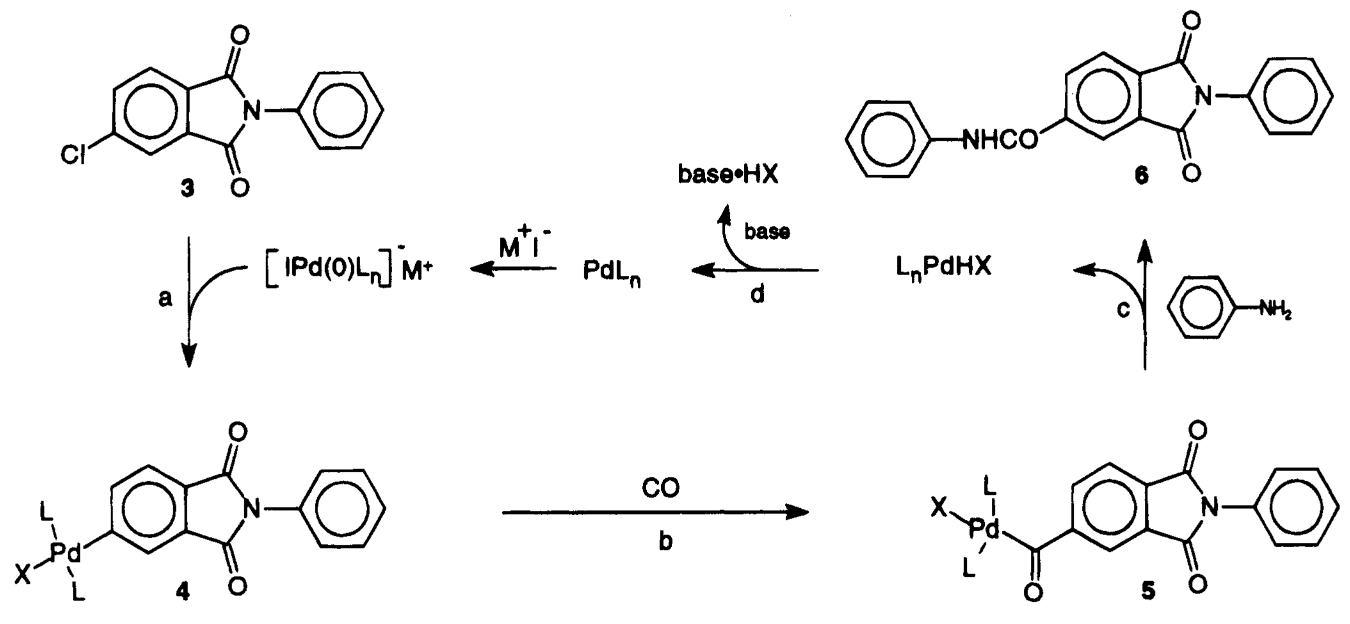
Scheme 1



ride ($PdCl_2L_2$; all Aldrich), and CO (Air Products; UPC grade) were used as received. Triphenylphosphine (PPh_3) was recrystallized from hexanes, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 3,4′-oxydianiline were distilled under reduced pressure, 4,4′-oxydianiline was sublimed, and NaI was dried in vacuo at 120 °C.

Monomer Preparation. 4-Chloro-*N*-(4-iodophenyl)-phthalimide (1b). In a 3-L flask, a mixture of 4-chlorophthalic anhydride (183.3 g, 1.004 mol), 4-iodoaniline (222.11 g, 1.014 mol), pyridine (285 mL, 3.5 mol), and DMAc (1.0 L) was allowed to react for 3 h at 100 °C. The solution was then treated with acetic anhydride (380 mL, 4.0 mol) and heated at 100 °C for 17 h. The reaction mixture was cooled in an ice bath, and the crystalline solid collected by filtration and washed with cold DMAc and 0.1 N HCl, water, and MeOH. The solid was then dried in vacuo at 125 °C for 16 h to give 282.7 g (74%) of product. Mp: 202.5–204 °C. FTIR (KBr): 3240, 3087, 1721, 1608, 1491, 1399, 1169, 1127, 1092, 820, 746, 734 cm^{-1}. Anal. Calcd for $C_{14}H_7ClINO_2$: C, 43.84; H, 1.84; N, 3.65. Found: C, 43.41; H, 1.92; N, 3.76.

4-Chloro-*N*-(4-chlorophenyl)phthalimide (9). In a manner similar to that above, a mixture of 4-chlorophthalic anhydride (18.26 g, 0.10 mol), 4-chloroaniline (12.76 g, 0.10 mol), pyridine (41 mL, 0.51 mol), and DMAc (75 mL) was allowed to react for 20 min at room temperature. The solution was treated with acetic anhydride (56 mL, 0.59 mol) and heated at 70 °C for 17 h. The reaction mixture was cooled to room temperature and the crystalline solid collected by filtration, washed with water and MeOH, and dried in vacuo at 100 °C for 16 h to give 23.80 g (81%) of product. Mp: 198–200 °C. FTIR (KBr): 3470, 3090, 3045, 1721, 1708, 1491, 1398, 1127, 820, 734 cm^{-1}. Anal. Calcd for $C_{14}H_7Cl_2NO_2$: C, 57.56; H, 2.42; N, 4.79. Found: C, 57.19; H, 2.53; N, 4.77.

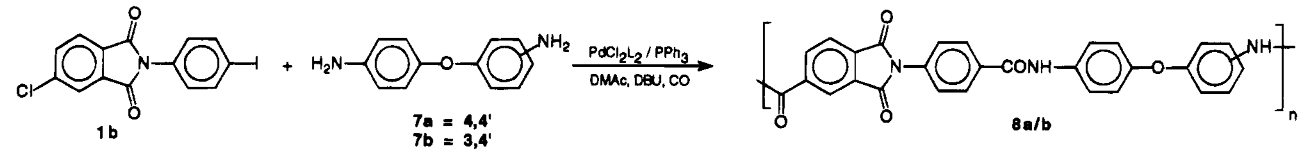
3,4′-Bis(4-chlorophthalimido)diphenyl ether (10). As above, 4-chlorophthalic anhydride (20.0 g, 110 mmol), 3,4′-oxydianiline (10.0 g, 50 mmol), pyridine (61 mL, 760 mmol), and DMAc (75 mL) were allowed to react for 30 min at 60 °C. The solution was treated with acetic anhydride (83 mL, 880 mmol) and heated at 70 °C for 17 h. The solid was isolated by filtration, washed with MeOH, water, acetone, and MeOH, and dried in vacuo at 80 °C to give 25.8 g (97%) of product. Mp: 243 °C. FTIR (KBr): 3480, 3100, 3070, 1784, 1714, 1591, 1508, 1387, 1249, 1168, 1115, 1097, 848, 747, 731 cm^{-1}. Anal. Calcd for $C_{28}H_{14}Cl_2N_2O_5$: C, 63.53; H, 2.67; N, 5.29. Found: C, 62.88; H, 2.78; N, 5.28.

Typical Polymerization Reaction. To a clean, dry pressure vessel under an argon atmosphere were added 4-chloro-*N*-(4-iodophenyl)phthalimide (**1b**; 1.89 g, 4.93 mmol), 4,4′-diaminodiphenyl ether (**7a**; 1.00 g, 4.99 mmol), $PdCl_2L_2$ (20 mg, 0.03 mmol), PPh_3 (50 mg, 0.19 mmol), DBU (1.80 mL, 12.0 mmol, 2.4 equiv), and NMP (25 g). The bottle was sealed, flushed with CO, and pressurized to 90 psig CO and then stirred and heated to 100 °C in a thermostated oil bath for 6 h. The pressure was then reduced to 20 psig, and the reaction, allowed to proceed for 48 h. The viscous solution was diluted with DMAc, filtered, and precipitated into MeOH, washed extensively with MeOH, and dried in vacuo to give a stringy white polymer. PMMA equivalent M_w = 89 600 and M_n = 47 800.

Results and Discussion

As mentioned above, one feature of the chlorophthalimide reactions was their increased reactivity in the presence of iodide ion. One explanation for the iodide ion effect involves the formation of an ionic Pd(0) intermediate, which is more prone to undergoing oxidative addition reactions than neutral Pd(0) complexes (Scheme 1).[10] The iodide can be in the form of added NaI, or as the DBU·HI salt formed during the reaction of a mixed chloroiodo monomer such as **1b**. Although tetraalkylammonium iodide salts could be used, NaI is preferred as the added iodide source because of its comparatively low price. After oxidative addition occurs to generate Pd(II) intermediate **4**, CO insertion takes place to form the aroyl Pd(II) species, **5**. Attack by aniline liberates imide–amide **6** and a $Pd^{II}HX$ salt. The palladium salt reductively eliminates HX, which is neutralized by base and regenerates a neutral Pd(0) complex. In all the reactions of mixed chloroiodo monomers, the best results were obtained when the CO pressure was initially high (90 psig) and then lowered (20–30 psig) after several hours. At the higher pressures, the iodoaromatic moieties rapidly reacted, undergoing oxidative addition and CO insertion, while the chloroaromatic groups were sluggish. The aromatic chlorides exhibit the same decreased reactivity at high CO pressures as do aromatic bromides. This has been attributed to the ligation of a greater number of CO molecules to Pd which suppresses the already slow oxidative addition of Pd(0) complexes to aryl chlorides or bromides.[11] When all (or most) of the iodo groups had reacted, the pressure was decreased. The lower pressures favored carbonylation of the aromatic chloride, and the iodide ion, which was present as the salt, promoted the oxidative addition of the palladium catalyst to the chloride.

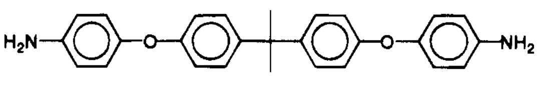
Table 1. Reactions of 1b with Oxydianilines[a]

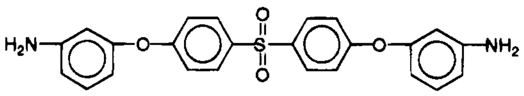


entry	diamine	% catalyst[b]	% L[c]	solvent[d]	M_w[e]	M_n[e]
1	**7a**[f]	5.6	12	DMAc (12)	126 000	65 200
2	**7a**[g]	0.6	4	NMP (12)	89 000	47 800
3	**7a**[h]	0.3	2	NMP (12)	66 500	33 000
4	**7b**[h]	0.3	2	NMP (12)	49 300	27 000
5	**7b**[i]	0.7	6	DMAc (18)	37 000	20 000

[a] Reactions run at 100 °C with 2.4 equiv of DBU starting at 90 psig CO. [b] Catalyst = $PdCl_2L_2$. [c] L = PPh_3. [d] DMAc = *N,N*-dimethylacetamide, NMP = 2-methylpyrrolidinone. Numbers in parentheses indicate % solids = g of monomers/g of solvent. [e] PMMA equivalent molecular weights. [f] 99% of the stoichiometric amount of **1b** was used relative to the diamine, and the reaction ran at 90 psig for 4 h and then at 20 psig for 16 h. Absolute M_w = 43 200. Absolute M_n = 23 100. [g] 99% of the stoichiometric amount of **1b** was used relative to the diamine, and the reaction ran at 90 psig for 6 h and then at 20 psig for 42 h. [h] 101.4% of the stoichiometric amount of **1b** was used relative to the diamine, and the reaction ran at 90 psig for 4 h and then at 20 psig for 44 h. [i] 99% of the stoichiometric amount of **1b** was used relative to the diamine, and the reaction ran at 90 psig for 2 h and then at 30 psig for 44 h.

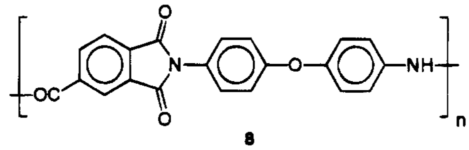
Table 2. Reaction of 1b with 7c/d[a]


7c


7d

entry	diamine	% catalyst[b]	% L[c]	solvent	M_w[e]	M_n[e]
1	**7c**[f]	2.8	12	DMAc (13)	90 100	43 900
2	**7c**[g]	1.4	3.8	DMAc (14)	90 600	42 100
3	**7c**[h]	0.6	3.6	NMP (14)	83 000	41 300
4	**7c**[i]	0.3	1.9	NMP (14)	71 000	35 500
5	**7d**[j]	2.5	5.0	DMAc (10)	43 500	20 900
6	**7d**[k]	0.3	1.9	NMP (14)	82 400	34 100
7	**7d**[l]	0.6	3.6	NMP (14)	44 400	23 600
8	**7d**[m]	0.6	3.6	NMP (14)	48 200	25 700
9	**7d**[n]	0.6	3.6	NMP (14)	64 400	32 000
10	**7d**[o]	0.6	3.6	NMP (14)	45 500	24 100

[a] Reactions run at 100 °C with 2.4 equiv of DBU under 90 psig CO for 2 h and then at 20 psig CO for 22 h unless otherwise noted. [b] Catalyst = $PdCl_2L_2$. [c] L = PPh_3. [d] DMAc = *N,N*-dimethylacetamide, NMP = 2-methylpyrrolidinone. Numbers in parentheses indicate % solids = g of monomers/g of solvent. [e] PMMA equivalent molecular weights. [f] 99.6% of the stoichiometric amount of **1b** was used relative to the diamine. [g] 104% of **1b** was used relative to the diamine. [h] 103% of **1b** was used relative to the diamine. [i] 103% of **1b** was used relative to the diamine, and the reaction ran for 46 h at 20 psig CO. [j] 98% of **1b** was used relative to the diamine. [k] 98% of **1b** was used relative to the diamine, and the reaction ran for 70 h at 20 psig CO. [l] 100% of **1b** was used relative to the diamine. [m] 98% of **1b** was used relative to the diamine. [n] 94% of **1b** was used relative to the diamine. [o] 102% of **1b** was used relative to the diamine.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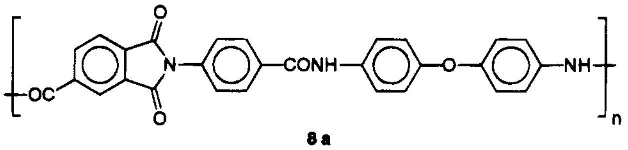

8a

Polymerization of **1b** with **7a** gave PIA **8a** that was analogous to commercially available poly(imide–amide) **8**. PIA **8a** contained an extra benzamide linkage which could provide additional sites for intermolecular H-bonding and thus might alter physical properties such as modulus and tensile strength. The properties will be discussed in a subsequent report. The results of the polymerization reactions with **1b** and oxydianilines (**7a,b**) are summarized in Table 1.

After 4 h at 90 psig CO and then 16 h at 20 psig CO, the reaction of **1b** and 4,4'-oxydianiline (**7a**) in the presence of 6% catalyst (entry 1) gave a PIA with a PMMA equivalent M_w = 126 000. The absolute M_w was found to be about 43 000. Reducing the catalyst level an order of magnitude (entry 2) still gave a polymer with high molecular weight. Scale-up of this reaction to make 50 g of polymer for physical testing was successful, with a molecular weight of 66 000 being achieved (entry 3). Molecular weights of the poly(imide–amides) derived from the 3,4'-isomer, **7b**, were slightly lower (entries 4 and 5).

The use of other diamines such as BAPP (**7c**) or *m*-BAPS (**7d**), also produced high molecular weight poly(imide–amides) as shown in Table 2. Polymers with M_w greater than 70 000 were made with the BAPP monomer, **7c**, even at 0.3% catalyst loading (entries 1–4). Again, the CO pressure was reduced to 20 psig after several hours to allow reaction of the chloroimide to proceed at a reasonable rate. Even so, reactions took 24–48 h for completion. Also interesting was the wide variability in the stoichiometry tolerated by these reactions. Entry 1 used a 99.6% theoretical loading of **1b** relative to **7c** and entry 2 used 104% **1b**, and yet both gave M_w = 90 000. This was in direct constrast to sulfone diamine **7d** in which the highest molecular

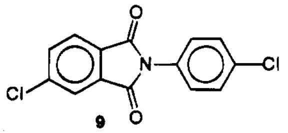
Table 3. Reactions of 10 and Diamines[a]

entry	diamine	% catalyst[b]	% L[c]	NaI[d]	time (h)	M_w[e]	M_n[e]	CO pressure (psig)
1	**7b**[f,h]	6.0	12	0.5	7	15 900	11 300	20
2	**7b**[g,i]	6.0	12	0.5	28	36 600	29 900	20
3	**7c**[g,i]	3.0	12		48	15 900	8 900	90
4	**7c**[g,k]	3.0	12	0.33	30	72 100	38 600	20
5	**7c**[g]	3.0	12	0.33	24	36 400	18 400	90

[a] Reactions run in DMAc at 100 °C with 2.4 equiv of DBU under CO pressures noted. [b] Catalyst = $PdCl_2L_2$. [c] L = PPh_3. [d] Number of equivalents/aryl chloride unit. [e] PMMA equivalent molecular weights. [f] 99.6% of the stoichiometric amount of **10** was used relative to the diamine. [g] 100% of **10** was used relative to the diamine. [h] Absolute M_w = 8800. Absolute M_n = 6300. [i] Absolute M_w = 33 400. Absolute M_n = 19 000. [j] Absolute M_w = 8800. Absolute M_n = 5200. [k] Absolute M_w = 59 800. Absolute M_n = 30 500.

weights were seen with 94–98% of **1b** relative to **7d** (entries 7–10). These four reactions were only allowed to proceed for 24 h, and the highest possible molecular weights were not obtained. A polymer with M_w = 82 000 could be made if the polymerization was allowed to go to completion (72 h, entry 6).

Other chloroimides could be used as monomers for the preparation of poly(imide–amides) provided they were appropriately activated. Dichloroimide **9** was not reactive enough to undergo polymerization, and only a single reaction occurred at the 4-position on the phthalimide ring.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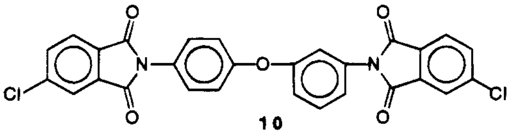
10

Dichlorodiimide **10** did react with diamines to produce polymers as shown in Table 3. Entry 1 shows that a modest molecular weight polymer was formed in 7 h under 20 psig CO. Allowing the reaction to proceed for longer times resulted in a higher molecular weight poly(imide–amide) (entry 2). With monomer **10**, it was necessary to add iodide to the reaction in the form of NaI to get substantial molecular weight buildup. Entry 3 shows that, although some polymerization did occur without NaI, the polymerization reaction was greatly facilitated in the presence of the iodide ion and at low CO pressure (entry 4). If higher CO pressures were used (entry 5), a lower molecular weight polymer was formed, even in the presence of NaI.

With one exception, all the polymers exhibited T_gs greater than 200 °C. The single example that did not display a T_g was the rigid polymer made from monomers **1b** and **7b**. Thermal stabilities of these polymers were found to be consistent with those observed for other poly(imide–amides), with onset of degradation occurring beyond 400 °C (Table 4). Infrared spectra of these polymers all showed the characteristic imide and amide stretches associated with the carbonyl groups.

Table 4. Thermal and FTIR Data for PIAs

entry	monomers	T_g[a] (°C)	TGA[b] (°C)	imide ν(CO) (cm^{-1})	amide ν(CO) (cm^{-1})
1	**1b** + **7a**	218	457	1777, 1716	1664
2	**1b** + **7b**	*c*	404	1777, 1719	1664
3	**1b** + **7c**	216	449	1778, 1718	1666
4	**1b** + **7d**	238	429	1779, 1724	1669
5	**10** + **7b**	211	454	1778, 1720	1667
6	**10** + **7c**	207	456	1778, 1720	1664

[a] Determined by DSC after third heat. [b] Temperature at onset of decomposition. [c] No T_g detected.

Summary

We have demonstrated that high molecular weight poly(imide–amides) can be readily formed by the palladium-mediated carbonylation and condensation reactions of chlorophthalimide monomers and aromatic diamines. The presence of iodide ions greatly accelerates the rate of reaction and the ultimate molecular weight of the polymers. When mixed haloaromatic monomers are used, a sequence of high and then low CO pressures gives the highest molecular weight materials.

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