1014 *Macromolecules* **1996,** *29,* 1014−1020

Polyimide Formation through the Palladium-Mediated Carbonylation and Coupling of Bis(*o*-iodo amides) and Diamines

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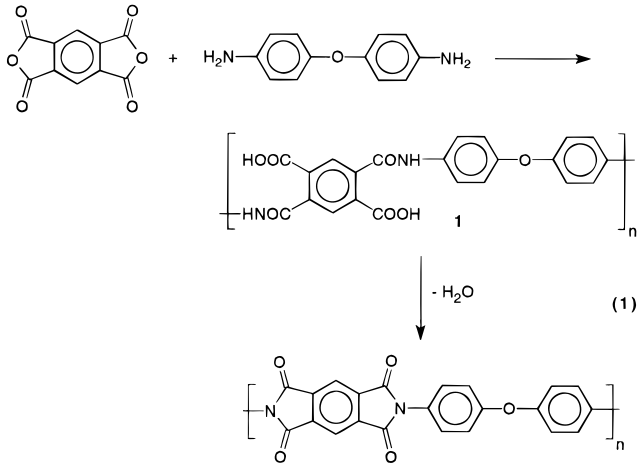
Received June 23, 1995; Revised Manuscript Received October 11, 1995[⊗]

ABSTRACT: Reactions between bis(*o*-iodo amides) and diamines in the presence of a palladium catalyst and a base at elevated (90 psig) carbon monoxide (CO) pressures give intermediate poly(amic amide) polymers which can be thermally ring-closed to the fully imidized polyimides. Model studies indicate that competing side reactions are suppressed and the intermediate *o*-diamide is stabilized when diisopropylamides are used.

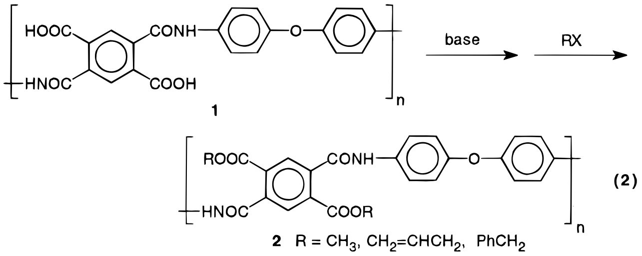
Introduction

Aromatic polyimides are an important class of compounds noted for their high use temperatures, toughness, good electrical properties, inherent flame resistance, and solvent resistance.[1] Conventionally, these materials are made through the condensation reaction of a primary diamine with a dianhydride (eq 1). The intermediate in this reaction is a poly(amic acid), **1**, which is soluble and processable. The poly(amic acid) is then thermally or chemically dehydrated to give the fully imidized polymer displaying the desired properties.

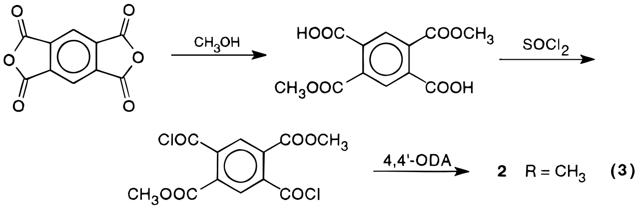


A disadvantage in this route is that the poly(amic acid) is hydrolytically unstable. On prolonged storage, a dramatic decrease in molecular weight is observed that is commensurate with loss of physical properties.[2] A procedure found to circumvent this hydrolysis involves the production of poly(amide esters). These intermediates are processable, like the poly(amic acids), but also exhibit long-term solution stability.

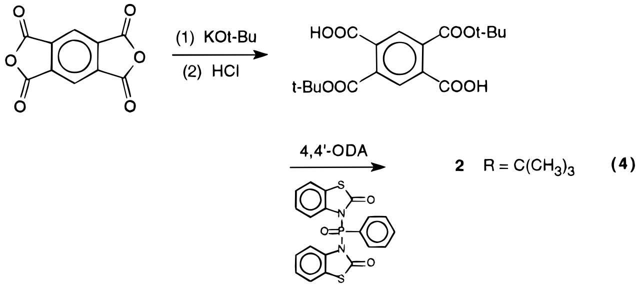
Several groups have reported on various syntheses of the poly(amide esters). One approach was to derivatize the conventionally prepared poly(amic acid) **1** (eq 2).[3]



Alternately, the dianhydride was ring-opened with the desired alcohol and then treated with thionyl chloride and the appropriate diamine. This approach allowed the preparation of regiopure isomers of the amide ester which showed varying degrees of reactivity (eq 3).[4]



A third route again involved the ring-opening of the dianhydride, but this time the diacid intermediate was directly reacted with the diamine using a peptide coupling agent (eq 4).[5]



In all of these cases, multiple steps are necessary in obtaining the poly(amic ester). We recently reported on attempts to make poly(amide esters) in a single step from the appropriate diiodo diester precursors and diamines.[6] In those cases, premature cyclization to the phthalimide ring was seen and a soluble, hydrolytically stable precursor was not obtained.

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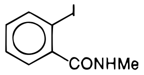
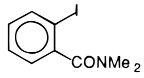
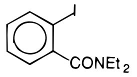
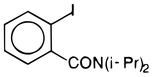
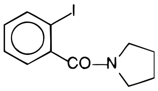
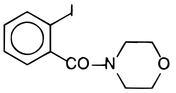
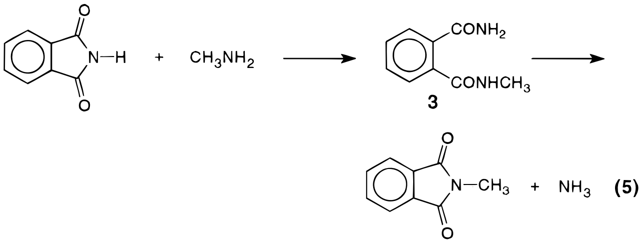
[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1995.

0024-9297/96/2229-1014$12.00/0

Table 1. *o*-Iodobenzamides 4

compound	iodobenzamide	yield (%)	mp (°C) [bp (°C/torr)]
a		61	150–151
b		70	94–97/0.008
c		88	113/0.009
d		42	184–185
e		43	130–137/0.008
f		51	88.5–90

The transimidization reaction, first reported in 1946, proceeds through an *o*-(amidocarbonyl)benzamide, **3** (eq 5).[7] Takekoshi recently used this reaction to form polyimides.[8] The reaction proceeded through a poly(amic amide) intermediate, similar to **3**, which showed little propensity to undergo spontaneous ring closure under mild conditions. We have used this approach to generate poly(amic amides) from bis(*o*-iodobenzamides) and diamines and then subsequently ring-closed them to give polyimides. Herein are the results of the model compound and polymerization studies.



Model Studies

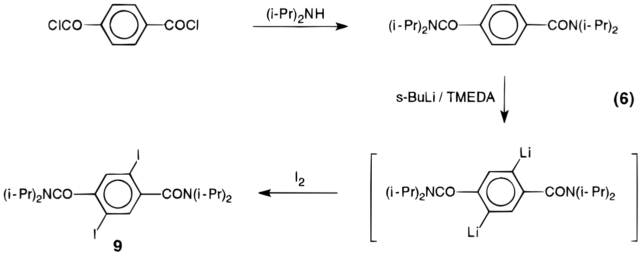
A variety of *o*-iodobenzamides were synthesized to examine their reactivity with aniline in the presence of a palladium catalyst and CO. Table 1 shows the amides made by the reaction of the appropriate amine with *o*-iodobenzoyl chloride.

Conditions used for the model reaction were the ones that were found to work well for amide formation in earlier experiments.[9] When **4a** and aniline were condensed in the presence of 3% catalyst and 95 psig CO, only 15% of the expected bis(amide) **7a** was formed (Scheme 1). The majority of the product was *N*-methylphthalimide, **6** (Table 2). Intramolecular ring-closure (path a) from the *N*-methylamide group was competitive with intermolecular bis(amide) formation (path b). If the N−H group is removed, the possibility of HI formation is eliminated and the reaction is forced to follow path b. This was seen when the N−H group was replaced with a N−Me group (entry **2**, Table 2). No N-methylated phthalimide was formed. However, a 3:1 ratio of **8:7b** was seen. Apparently, the small methyl groups were not large enough to prevent cyclization. More sterically demanding alkyl groups succeeded in suppressing premature imide formation (entries 3 and 4). Cyclic amides from pyrrolidine and morpholine (entries 5 and 6) were not as effective as the diisopropyl group in preventing phthalimide formation. When iododiisopropylbenzamide **4d** was used, no **8** was detected by GC. The diethyl derivative behaved similarly, but a small amount of **8** was seen by GC. Given these observations, the diisopropylamide group was determined to be the most likely candidate for extension into successful polymerizations.

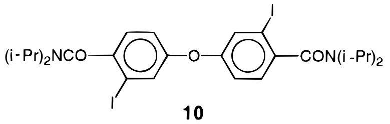
From the above reactions, it was apparent that the *N*-phenyl-*N′*-diisopropylbis(amide), **7d**, was stable to the carbonylation reaction conditions. It remained to be determined if cyclization to the phthalimide could be effected in a controlled manner. To this end, a solution of **7d** in DMAc was heated to 175 °C for 3 h. No conversion to **8** was detected by GC. Treatment of this solution with a catalytic amount of *p*-toluenesulfonic acid (TsOH) at 175 °C resulted in complete cyclization within 0.5 h.

Monomer Preparation

With a method in hand to prepare *o*-bis(amides), attention turned to the synthesis of the requisite monomers. Whereas *o*-iodobenzoyl chloride could be purchased commercially, the corresponding bis(*o*-iodobenzoic acid) derivatives were unavailable. Aromatic diacids can be readily obtained, and a number of acid derivatives have been used to direct ortho-metalation reactions.[10] Conversion of the diacid to the bis(diisopropylamide) and then treatment with *s*-BuLi/TMEDA in THF at −78 °C generated the dianion.[11] The dianion was then quenched with I_2[12] in THF to give the desired bis(*o*-iodo amide) product. An example is shown below (eq 6).



Monomers **10** and **11** were prepared in a similar manner and are shown below. In each case, greater than 90% yield of product was obtained. However, 3−7% of the monoiodo-substituted compound was present in the reaction mixture and could not be removed by recrystallization. Preparatory HPLC was used to obtain more pure monomers. In the case of **9**, 98.4% purity was achieved with 1.6% monoiodo compound remaining. Diiodiamide **10** was better than 99.9% pure, as determined by GC, but **11** was 92% diiodo, 6% monoiodo,



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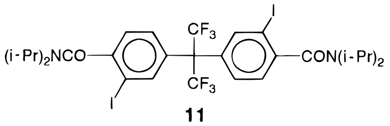

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Scheme 1

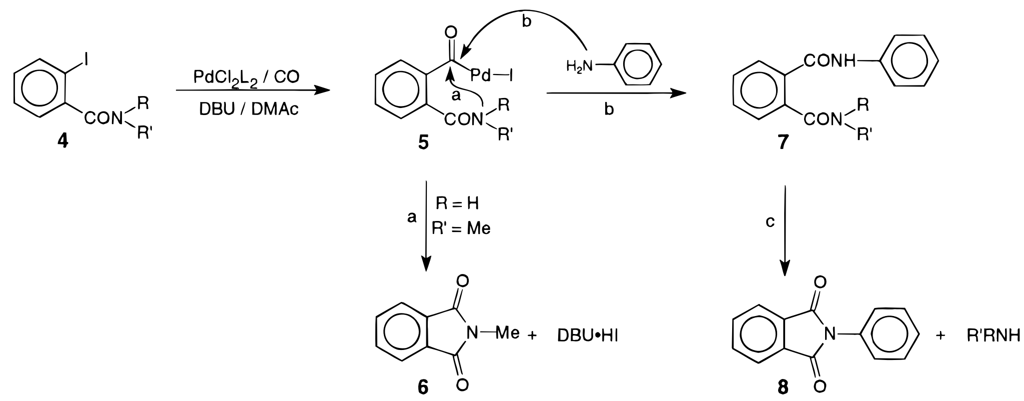


Table 2. Bis(amide) versus Imide Formation[a]

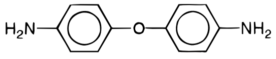
entry	iodo amide	bis(amide), **7**[b]	phthalimide, **8**[b]
1	**4a**	15	82[c]
2	**4b**	27	73
3	**4c**	90	10
4	**4d**	95[d]	0
5	**4e**	53	33
6	**4f**	35	21

[a] Reaction at 115 °C, 95 psig CO, 3% $PdCl_2L_2$, 0.22 M DMAc, 1.2 equiv of DBU, 7 h. [b] GC yields. [c] Yield of **6**. [d] Isolated yield.

and 2% unsubstituted. We were not able to obtain pure monomer.

Polymerizations

The initial polymerization reactions were run using 4,4′-diaminodiphenyl ether (ODA), **12**, and 2,5-diiodo-*N*,*N*′-bis(diisopropyl)terephthalamide, **9** with 3% $PdCl_2L_2$ catalyst under 95 psig CO. Under all conditions examined, an insoluble precipitate formed during the reaction. Variation in concentration and temperature and the presence of LiCl, known to help solubilize some H-bonding polymers, did not permit formation of soluble, high molecular weight polymer. Changing the diamine to (aminophenyl)aminoindan, **13**, one that would impart greater solubility to the poly(amic amide), also resulted in a material that was mostly insoluble.



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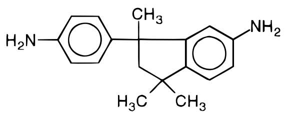

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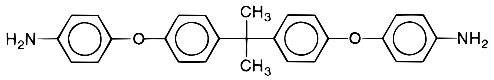

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Use of the other two diiodo diamide monomers resulted in more soluble prepolymers, as shown in Table 3.

The polymer made from unpurified diiodo diamide **10** (94.4% diiodo and 5.6% monoiodo) and ODA, **12**, gave a material with $M_w = 11\,000$ (polymer **17**). When the monomer was purified (>99.9% diiodo), the molecular weight increased 2-fold (polymer **18**). Use of purified (92.0% diiodo, 5.9% monoiodo, 2.1% unsubstituted) and unpurified (89.4% diiodo, 7.2% monoiodo, 3.4% unsubstituted) fluorinated monomer **11** with diamine **12** gave material of such low molecular weight that nothing precipitated from solution when poured into MeOH (polymers **20** and **21**). When **14** was employed as the diamine, only oligomeric materials were formed regardless of the diiodo diamide treatment (polymers **22** and **23**). It must be noted that a monomer with a 6% chain-stopper incorporated into the feed will only produce a polymer with a maximum DP = 32.[13] This calculates to an $M_n = 25\,900$ for polymer **21** and $M_n = 31\,600$ for polymer **23**. Since neither of these values is close to the actual numbers, it may be assumed that other processes are occurring to limit molecular weight buildup. Two of these processes may be coupling or reductive dehalogenation, as was seen under some conditions during aramid formation.[7b]

Imidization of Poly(amic amides)

The poly(amic amides) **18**, **19**, and **22** were cast as thin films from DMF on a glass plate and dried. The samples were analyzed by DSC and TGA to determine the temperature for thermal imidization (Figure 1). As shown, the onset of thermal imidization for all three poly(amic amides) was between 270 and 280 °C. Samples of poly(amic amides) were initially cured in a vacuum oven at 300 °C for 1 h. The resulting polyimides **24**–**26** were analyzed by DSC, TGA, and FTIR. Although TGA indicated a weight loss between 200 and 350 °C for all samples, FTIR showed complete conversion to polyimide for polymers **24** and **25** (Tables 4 and 5), as shown by imide carbonyl bands at 1779 and about 1723 cm^{-1} and the lack of an amide carbonyl band at 1676 cm^{-1}. Polymer **26** still had amide groups, as seen by FTIR. A second set of poly(amic amides) were cured at 300 °C for 3 h and again analyzed. The analysis indicated that 3 h/300 °C treated poly(amic amides) **18** and **19** were completely imidized to polyimides **24** and **25**, as before, with very little weight loss observed at less than 300 °C.

The 3 h/300 °C treated poly(amic amide) **22** was still incompletely imidized to polyimide **26**, as shown by the 3.8% wt loss between 275 and 335 °C and the 1676 cm^{-1} absorbance in the FTIR spectrum. Complete imidization may not be possible because of the monofunctional nature of the impurity in monomer **11** which would leave pendant amide groups. The T_g values of the polyimides of **24** and **25** were very close to the literature values of the same polyimides prepared by the classical method (dianhydride + diamine followed by thermal imidization).[14] The T_g of polyimide **26** was 40 lower than the literature value.[15] The difference can be rationalized by the low molecular weight of the poly(amic amide) precursor **22**.

Table 3. Poly(amic amide) Prepolymers[a]

polymer	diiodo diamide	diamine	yield (%)	M_w[b]	M_n[b]	M_w[c]	M_n[c]
15	**9**	**12**	insoluble				
16	**9**	**13**	28				
17	**10**[d]	**12**	71	11 000	8000	10 800	7600
18	**10**[e]	**12**	72	24 200	16 100	16 900	11 300
19	**10**[e]	**14**	93	16 000	9600		
20	**11**[d]	**12**	no precipitate				
21	**11**[e]	**12**	no precipitate				
22	**11**[d]	**14**	45	8200	5600	5700	3500
23	**11**[e]	**14**	49	8500	6200	6200	4600

[a] Reaction in DMAc (0.17 M) at 115 °C, 1.00:1.00 ratio of monomers, 3% $PdCl_2L_2$, 6% PPh_3, 2.4 equiv of DBU, 95 psig CO, 24 h. [b] PMMA equiv molecular weights. [c] Absolute molecular weights. [d] Unpurified monomer. [e] HPLC-purified monomer.

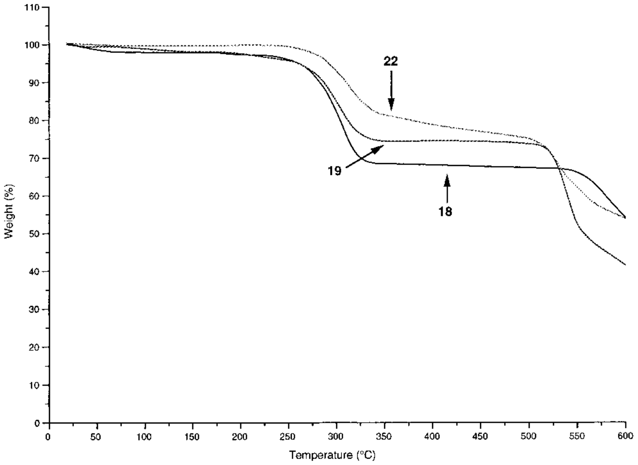


Figure 1. TGA of poly(amic amides) **18**, **19**, and **22**.

Summary

Reactions between bis(*o*-iodo amides) and diamines in the presence of a palladium catalyst and a base at 115 °C under 95 psig CO gave intermediate poly(amic amide) polymers that were thermally ring-closed at 300 °C to the fully imidized polyimides. Difficulty in monomer purification prevented high molecular weight polymers from being formed. Model studies indicated that competing side reactions during the carbonylation reaction are suppressed and the intermediate *o*-diamide is stabilized when diisopropylamides are used in the *o*-iodo amide monomers.

Experimental Section

General Procedures. Reactions were performed in a 120 mL pressure reaction vessel (containing a stir bar) fitted with a pressure gauge, a pressure release valve, a gas inlet, and a straight ball valve for degassing and sample withdrawal. All reactions were performed in a well-ventilated hood, behind safety shields. TGA measurements were made on an Omnitherm Advantage II under 50 mL/min nitrogen or a PC Series TGA7 under 30 mL/min nitrogen at 10 °C/min from 30 to 900 °C. DSC data were obtained on a DuPont 9900 thermal analyzer under 30 mL of N_2/min at 20 °C/min. Size exclusion chromatography (SEC) data were obtained from a Waters HPLC using two Jordi's DVB columns and calibrated with PMMA standards between 2000 and 1 600 000 Da. Samples were dissolved in DMF containing 0.01 M $LiNO_3$. All samples were filtered prior to injection and results are reported as poly(methyl methacrylate) (PMMA) equivalent molecular weights or absolute molecular weights, as noted. FTIR spectra were recorded on a Nicolet 60SX spectrometer 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. Elemental analyses were performed by the Analytical Technology Division of Eastman Kodak Co.

Chemicals. Morpholine, pyrrolidine, diethylamine, diisopropylamine, *o*-iodobenzoic acid, dimethylamine, terephthaloyl chloride, iodine, 5-amino-3-(4-aminophenyl)-1,1,3-trimethylindan (**13**) (all Eastman Kodak), Bisphenol A (Shell), 2,2-bis[4-(4-aminophenoxyl)phenyl]propane (**14**) (Kennedy and Klim), CO (Air Products, UPC grade), *N*,*N*-dimethylacetamide (DMAc, anhydrous), TMEDA, bis(triphenylphosphine)palladium(II) chloride ($PdCl_2L_2$), triphenylphosphine (PPh_3), and *s*-BuLi (all Aldrich) were used as received. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was fractionally distilled under reduced pressure, and 4,4′-diaminodiphenyl ether (ODA, **12**) was purified by sublimation.

Preparation of *o*-Iodobenzamides. A representative example for 2-iodo-*N*-methylbenzamide, **4a**, is described. To a solution of 40% aqueous methylamine (100 mL, 1.16 mol) in water (200 mL) was added a solution of 2-iodobenzoyl chloride (12.5 g, 46.9 mmol) in MeCN (50 mL). The reaction mixture was allowed to stir for 0.5 h and was then extracted with CH_2Cl_2, dried with $MgSO_4$, and concentrated and recrystallized from toluene to give 7.5 g (61%) of product. Mp: 150−151 °C. Lit. mp: 153−154 °C.[16] ^1H NMR ($CDCl_3$): δ 7.79 (d, $J = 7.9$ Hz, 1), 7.29 (m, 2), 7.04 (m, 1), 6.14 (br s, 1), 2.92 (d, $J = 5.0$ Hz, 3).

2-Iodo-*N*,*N*-dimethylbenzamide, 4b. In a manner similar to that described above, 2-iodobenzoyl chloride (75 g, 281 mmol) was added to a precooled (−5 °C) solution of anhydrous dimethylamine (100 g, 2.22 mol) in THF (500 mL). The mixture was allowed to stir at room temperature for 1 h and then concentrated, diluted with CH_2Cl_2, washed with water, passed through a short column of silica gel, and distilled (94−97 °C/0.008 Torr) to give 54 g (70%) of product. Lit. bp: 120 °C/0.5 Torr.[17] Lit. mp: 33−36 °C.[16] ^1H NMR ($CDCl_3$): δ 7.74 (d, $J = 8.0$ Hz, 1), 7.33 (t, $J = 7.4$ Hz, 1), 7.14 (d, $J = 7.4$ Hz, 1), 7.00 (t, $J = 8.0$ Hz, 1), 3.07 (s, 3), 2.78 (s, 3).

2-Iodo-*N*,*N*-diethylbenzamide, 4c. As above, 88% product was obtained after distillation. Bp: 113 °C/0.009 Torr. Lit. bp: 120 °C/0.3 Torr.[17] ^1H NMR ($CDCl_3$): δ 7.77 (d, $J = 8.0$ Hz, 1), 7.33 (t, $J = 7.5$ Hz, 1), 7.15 (d, $J = 7.4$ Hz, 1), 7.01 (t, $J = 8.0$ Hz, 1), 3.81 (m, 1), 3.25 (m, 1), 3.08 (m, 2), 1.24 (t, $J = 7.1$ Hz, 3), 1.02 (t, $J = 7.1$ Hz, 3).

2-Iodo-*N*,*N*-diisopropylbenzamide, 4d. As above, 42% product was obtained after recrystallization from toluene. Mp: 184−185 °C. ^1H NMR ($CDCl_3$): δ 7.76 (d, $J = 8.0$ Hz, 1), 7.31 (t, $J = 7.3$ Hz, 1), 7.09 (d, $J = 7.4$ Hz, 1), 6.98 (t, $J = 8.0$ Hz, 1), 3.50 (m, 2), 1.55 (d, $J = 6.8$ Hz, 3), 1.52 (d, $J = 6.8$ Hz, 3), 1.22 (d, $J = 6.8$ Hz, 3), 1.02 (d, $J = 6.8$ Hz, 3). Anal. Calcd for $C_{13}H_{18}NOI$: C, 47.15; H, 5.48; N, 4.23; I, 38.32. Found: C, 46.97; H, 5.51; N,4.42.

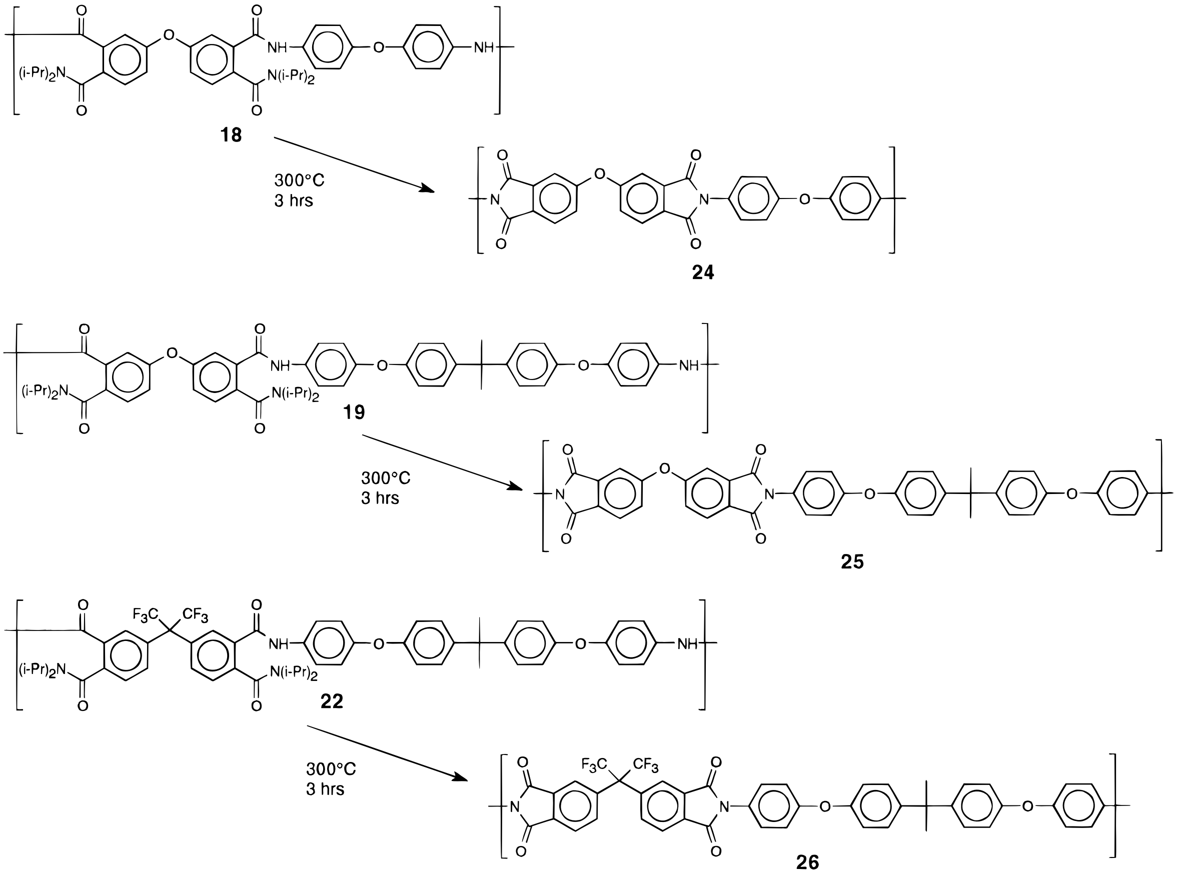
2-Iodo-*N*-(tetramethylene)benzamide, 4e. As above, 43% product was obtained after distillation. Bp: 130−137 °C/0.008 Torr. ^1H NMR ($CDCl_3$): δ 7.72 (d, $J = 8.0$ Hz, 1), 7.30 (t, $J = 7.9$ Hz, 1), 7.14 (dd, $J = 7.6$, 1.4 Hz, 1), 6.97 (td, $J = 7.6$, 1.4 Hz, 1), 3.56 (t, $J = 6.7$ Hz, 2), 3.06 (t, $J = 6.5$ Hz, 2), 1.86 (m, 4). Anal. Calcd for $C_{11}H_{12}NOI$: C, 43.88; H, 4.02; N, 4.65; I, 42.14. Found: C, 43.76; H, 3.99; N, 4.77.

2-Iodo-*N*,*N*-(oxydiethylene)benzamide, 4f. As above, 51% product was obtained after recrystallization from toluene. Mp: 88.5−90 °C. Lit. mp: 86−87 °C.[16] ^1H NMR ($CDCl_3$): δ 7.81 (d, $J = 7.9$ Hz, 1), 7.38 (t, $J = 7.5$ Hz, 1), 7.18 (d, $J = 7.5$ Hz, 1), 7.06 (t, $J = 7.6$ Hz, 1), 3.77 (m, 5), 3.56 (m, 1), 3.24 (m, 1), 3.17 (m, 1).

A representative amidation reaction is described below.

Table 4. Thermal Data for Poly(Amic Amides)

		TGA % weight loss between 200 and 350 °C			DSC T_g (°C)	
poly(amic amide)	calcd[a]	as prepared[b]	1 h @ 300 °C	3 h @ 300 °C	obsd	lit.
18	29.9	28.9	4.3	0.4	249	252[14]
19	22.8	22.0	2.8	0.4	221	212[14]
22	19.8	18.2	12.4	3.8	210	249[15]



[a] Weight loss calculated on the basis of the loss of two diisopropylamine molecules/repeat unit. [b] Actual weight loss observed.

Table 5. FTIR Data from Imidization of Poly(amic amides)

poly (amic amide)	$\nu_{C=O}$ (cm^{-1})	polyimide (1 h)	$\nu_{C=O}$ (cm^{-1})	polyimide (3 h)	$\nu_{C=O}$ (cm^{-1})
18	1676	**24**	1779, 1721	**24**	1779, 1721
19	1676	**25**	1779, 1725	**25**	1779, 1725
22	1676	**26**	1784, 1728, 1676	**26**	1784, 1728, 1676

***N*,*N*-Diisopropyl-*N*′-phenylphthalamide, 7d.** 2-Iodo-*N*,*N*-diisopropylbenzamide, **4d** (1.822 g, 5.5 mmol), aniline (500 μL, 5.50 mmol), $PdCl_2L_2$ (117 mg, 0.17 mmol), DBU (1.00 mL, 6.67 mmol), and DMAc (25 mL) were added to a pressure vessel, degassed, pressurized to 95 psig CO, and heated to 115 °C. After 24 h, the reaction mixture was filtered, concentrated, dissolved in toluene, and passed through a small column of silica gel (eluting with 3:1 hexanes/toluene). The product fractions were collected and concentrated to give 1.65 g (93%) of product which was recrystallized from MeOH/water (2:1). Mp: 146−147 °C. ^{1}H NMR ($CDCl_3$): δ 10.28 (br s, 1), 7.68 (d, J = 7.9 Hz, 3), 7.49 (m, 2), 7.27 (m, 3), 7.05 (t, J = 7.3 Hz, 1), 3.58 (sept, J = 6.5 Hz, 1), 3.47 (sept, J = 6.6 Hz, 1), 1.36 (br s, 6), 1.10 (br s, 3), 1.05 (br s, 3). {^{1}H}^{13}C NMR ($CDCl_3$): δ 168.6, 165.3, 138.7, 138.1, 133.3, 129.8, 128.0, 127.5, 127.3, 125.1, 123.0, 119.5, 50.2, 44.1, 19.8, 19.7, 19.6, 19.5. Anal. Calcd for $C_{20}H_{24}N_2O_2$: C, 74.05; H, 7.46; N, 8.63. Found: C, 74.22; H, 7.38; N, 8.71.

***N*-Methyl-*N*′-phenylphthalamide, 7a.** 2-Iodo-*N*-methylbenzamide, **4a** (1.436 g, 5.5 mmol), aniline (500 μL, 5.50 mmol), $PdCl_2L_2$ (117 mg, 0.17 mmol), DBU (1.00 mL, 6.67 mmol), and DMAc (25 mL) were treated as above. After 7 h, the reaction mixture was filtered, concentrated, dissolved in toluene, and passed through a small column of silica gel (eluting with 2:1 toluene/hexanes). Two fractions were collected and concentrated to give 210 mg (15%) of **4a** (lit. mp: 228 °C dec[18]) and 724 mg (82%) of *N*-methylphthalimide, **6**. Mp: 132−134 °C. Lit. mp: 126−128 °C.[19] ^{1}H NMR ($CDCl_3$): δ 7.81 (m, 2), 7.68 (m, 2), 3.15 (s, 3).

***N*,*N*-Dimethyl-*N*′-phenylphthalamide, 7b.** 2-Iodo-*N*,*N*-dimethylbenzamide, **4b** (1.513 g, 5.5 mmol), aniline (500 μL, 5.50 mmol), $PdCl_2L_2$ (117 mg, 0.17 mmol), DBU (1.00 mL, 6.67 mmol), and DMAc (25 mL) were treated as above. After 24 h, the reaction mixture was filtered, concentrated, dissolved in toluene, and passed through a small column of silica gel (eluting with 3:1 hexanes/ toluene) to give two product fractions. The first was 739 mg (60%) of *N*-phenylphthalimide, **8**. Mp: 201−204 °C. Lit. mp: 206−207 °C.[20] ^{1}H NMR ($CDCl_3$): δ 7.96 (m, 2), 7.79 (m, 2), 7.46 (m, 5). {^{1}H}^{13}C NMR ($CDCl_3$): δ 167.0, 134.7, 131.9, 131.5, 128.8, 128.0, 127.4, 123.4. The second was 697 mg of a mixture of 25% **8** and 75% **7b**. The total yield of **8** was 73%. The yield of **7b** was 27%. Mp: 183−184 °C. Lit. mp: 182 °C.[18] ^{1}H NMR ($CDCl_3$): δ 10.36 (br s, 1), 7.72 (d, J = 7.0 Hz, 1), 7.66 (d, J = 8.0 Hz, 2), 7.52 (m, 2), 7.29 (m, 3), 7.06 (t, J = 7.3 Hz, 1), 2.91 (s, 3), 2.78 (s, 3). {^{1}H}^{13}C NMR ($CDCl_3$): δ 169.6, 165.5, 138.7, 136.9, 133.8, 129.9, 128.1, 127.8, 127.3, 126.2, 123.2, 119.8, 39.7, 38.7.

***N,N*-Diethyl-*N′*-phenylphthalamide, 7c.** 2-Iodo-*N,N*-diethylbenzamide, **4c** (1.667 g, 5.5 mmol), aniline (500 μL, 5.50 mmol), $PdCl_2L_2$ (117 mg, 0.17 mmol), DBU (1.00 mL, 6.67 mmol), and DMAc (25 mL) were treated as above. After 24 h, the reaction mixture was filtered, concentrated, dissolved in toluene, and passed through a small column of silica gel (eluting with 3:1 hexanes/toluene) to give 118 mg (10%) of **8** and 1.46 g (90%) of **7c**. Mp: 121−122 °C. Lit. mp: 124 °C.[18] ^{1}H NMR (DMSO-d_6): δ 10.33 (br s, 1), 7.69 (m, 3), 7.51 (m, 2), 7.31 (m, 3), 7.05 (t, J = 7.2 Hz, 1), 3.36 (q, J = 7.0 Hz, 2), 3.10 (q, J = 7.0 Hz, 2), 1.06 (t, J = 7.0 Hz, 3), 1.00 (t, J = 7.0 Hz, 3) . {^{1}H}^{13}C NMR (DMSO-d_6): δ 169.0, 165.4, 138.8, 137.0, 133.8, 129.8, 128.1, 127.8, 127.4, 125.9, 123.1, 119.6, 42.2, 37.8, 13.1, 11.9.

***N*-Tetramethylene-*N′*-phenylphthalamide, 7e (2-(Pyrrolidinocarbonyl)benzanilide).** 2-Iodo-*N*-tetramethylenelbenzamide, **4e** (1.656 g, 5.5 mmol), aniline (500 μL, 5.50 mmol), $PdCl_2L_2$ (117 mg, 0.17 mmol), DBU (1.00 mL, 6.67 mmol), and DMAc (25 mL) were treated as above. After 22 h, the reaction mixture was filtered, concentrated, dissolved in toluene, and passed through a small column of silica gel (eluting with 3:1 hexanes/toluene) to give two fractions: 322 mg of **8** and 946 mg of a mixture of 9% **8** and 88% **7e** for an overall yield of 33% **8** and 53% **7e**. Mp: 189−190.5 °C. ^{1}H NMR (DMSO-d_6): δ 10.39 (br s, 1), 7.69 (m, 3), 7.51 (m, 2), 7.31 (m, 3), 7.06 (t, J = 7.2 Hz, 1), 3.37 (m, 2), 3.17 (m, 2), 1.78 (m, 4). {^{1}H}^{13}C NMR (DMSO-d_6): δ 167.8, 165.5, 138.6, 137.5, 133.7, 129.8, 127.9, 127.8, 127.3, 126.1, 123.0, 119.7, 47.6, 44.5, 24.9, 23.5. Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.32; H, 5.98; N, 9.71.

***N,N*-(Oxydiethylene)-*N′*-phenylphthalamide, 7f (2-(Morpholinocarbonyl)benzanilide).** 2-Iodo-*N,N*-(oxydiethylene)benzamide, **4f** (1.744 g, 5.5 mmol), aniline (500 μL, 5.50 mmol), $PdCl_2L_2$ (117 mg, 0.17 mmol), DBU (1.00 mL, 6.67 mmol), and DMAc (25 mL) were treated as above. After 7 h, the reaction mixture was filtered, concentrated, dissolved in toluene, and passed through a small column of silica gel (eluting with toluene) to give two fractions: 258 mg of **8** (21%) and 596 mg of **7f** (35%). Mp: 177.5−178.5 °C. ^{1}H NMR (DMSO-d_6): δ 10.38 (br s, 1), 7.71 (m, 3), 7.53 (m, 2), 7.32 (m, 3), 7.07 (t, J = 7.3 Hz, 1), 3.55 (m, 6), 3.17 (m, 2). {^{1}H}^{13}C NMR (DMSO-d_6): δ 168.4, 165.4, 138.7, 136.0, 134.2, 129.9, 128.1, 128.0, 127.3, 126.3, 123.2, 119.8, 65.3, 48.1. Anal. Calcd for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.42; H, 5.81; N, 8.92.

Preparation of Monomers. 2,5-Diiodo-*N,N,N′,N′*-tetraisopropylterephthalamide, 9. To a solution of diisopropylamine (225 mL, 1.6 mol) in THF (1500 mL) was added a solution of terephthaloyl chloride (73 g, 360 mmol) in THF/MeCN (500 mL/100 mL). The reaction mixture was allowed to stir for 1 h at room temperature and then at reflux for 2 h. The solid product was removed by filtration, slurried with EtOH, filtered out, and washed extensively with water and EtOH to give intermediate *N,N,N′,N′*-tetraisopropylterephthalamide (85 g, 71%). Mp: 282−284 °C. Lit. mp: 283−284 °C.[21] ^{1}H NMR ($CDCl_3$): δ 7.28 (s, 4), 3.60 (m, 4), 1.38 (m, 12), 1.11 (m, 12). A 1.3 M cyclohexane solution of *s*-BuLi (5.3 mL, 6.9 mmol) was added over 35 min to a precooled (−78 °C) solution of TMEDA (1.0 mL, 6.6 mmol) in THF (10 mL). This mixture was allowed to stir at −78 °C for 0.3 h, and then a THF solution (50 mL) of the intermediate (997 mg, 3.00 mmol) was added dropwise over 10 min. The mixture was allowed to stir for 3.25 h, and then iodine (3.05 g, 12 mmol) in THF (30 mL) was added over 6 min. After a 1 h reaction time, water (25 mL) was added and the reaction was warmed to room temperature. The reaction mixture was precipitated into water, filtered, washed with aqueous MeOH and dried to give 1.593 g (91%) of **9** which was recrystallized from $MeNO_2$. After multiple recrystallizations, the product still contained 1.6% of the monoiodo compound. Mp: 327 °C dec. ^{1}H NMR ($CDCl_3$): δ 7.50 (s, 2), 3.54 (m, 4), 1.56 (d, J = 6.6 Hz, 6), 1.53 (d, J = 6.6 Hz, 6), 1.24 (d, J = 6.6 Hz, 6), 1.06 (d, J = 6.6 Hz, 6). {^{1}H}^{13}C NMR ($CDCl_3$): δ 167.8, 145.6, 136.6, 92.0, 51.4, 46.4, 20.8, 20.5, 20.2, 20.1. Anal. Calcd for $C_{20}H_{30}N_2O_2I_2$: C, 41.11; H, 5.18; N, 4.79; I, 43.44. Found: C, 41.42; H, 5.21; N, 4.66.

3,3′-Diiodo-4,4′-bis[(diisopropylamino)carbonyl]diphenyl Ether, 10. In a manner similar to that above, a THF solution of 4,4′-oxybis(benzoic acid) was treated with thionyl chloride. The crude diacid chloride was then treated with diisopropylamine to give the intermediate bis(amide). Recrystallization from petroleum ether gave a solid with mp 104.5−105.5 °C. ^{1}H NMR ($CDCl_3$): δ 7.29 (d, J = 8.4 Hz, 4), 6.99 (d, J = 8.4 Hz, 4), 3.71 (br s, 4), 1.33 (br s, 24). The bis(amide) was dissolved in THF, the solution was added to a cooled solution of TMEDA and *s*-BuLi in THF, and the resulting mixture was treated with iodine as above. The isolated product (containing 15% of the monoiodinated compound) was purified by column chromatography (silica gel, eluting with 1:1 hexanes/CH_2Cl_2) to give material that still contained 5.6% monoiodo material. This was subjected to preparative HPLC to give material that was >99.9% **10**. Mp: 208−210 °C. ^{1}H NMR ($CDCl_3$): δ 7.42 (dd, J = 5.0, 2.1 Hz, 2), 7.07 (d, J = 7.7 Hz, 2), 6.97 (dd, J = 5.0, 2.1 Hz, 2), 3.58 (sept, J = 6.8 Hz, 2), 3.48 (sept, J = 6.8 Hz, 2), 1.55 (d, J = 6.8 Hz, 6), 1.51 (d, J = 6.8 Hz, 6), 1.24 (d, J = 6.8 Hz, 6), 1.05 (d, J = 6.8 Hz, 6). {^{1}H}^{13}C NMR ($CDCl_3$): δ 169.2, 156.1, 140.4, 129.7, 127.0, 118.6, 92.6, 51.3, 46.1, 20.9, 20.7, 20.6, 20.2. Anal. Calcd for $C_{26}H_{34}N_2O_3I_2$: C, 46.17; H, 5.07; N, 4.14; I, 37.52. Found: C, 45.96; H, 5.11; N, 4.23.

2,2-Bis[3-iodo-4-((diisopropylamino)carbonyl)phenyl]hexafluoropropane, 11. As above, 4,4′-(hexafluoroisopropylidene)bis(benzoic acid) was converted into the bis(amide). Mp: 227−230 °C. ^{1}H NMR ($CDCl_3$): δ 7.38 (d, J = 8.2 Hz, 4), 7.30 (d, J = 8.2 Hz, 4), 3.82 (br s, 2), 3.55 (br s, 2), 1.51 (br s, 12), 1.17 (br s, 12). The bis(amide) was dissolved in THF, the solution was added to a cooled solution of TMEDA and *s*-BuLi in THF, and the resulting mixture was treated with iodine as above. The product was a mixture of noniodinated bis(amide) (5.7%), monoiodinated material (7.5%), and **11** (86.8%). After HPLC purification, 2.2% noniodinated and 5.9% monoiodinated materials remained. Mp: 161−164 °C. ^{1}H NMR ($CDCl_3$): δ 7.42 (d, J = 4.8, 2.1 Hz, 2), 7.25 (d, J = 8.4 Hz, 2), 7.08 (d, J = 8.2, 2.1 Hz, 2), 3.49 (m, 4), 1.53 (d, J = 6.8 Hz, 6), 1.49 (d, J = 6.8 Hz, 6), 1.25 (d, J = 6.6 Hz, 6), 1.03 (d, J = 6.6 Hz, 6). {^{1}H}^{13}C NMR ($CDCl_3$): δ 168.6, 145.6, 140.6, 133.8, 130.1, 129.9, 125.6, 123.6 (q, J = 281 Hz), 91.9, 51.2, 46.1, 20.8, 20.7, 20.5, 20.0.

Typical Polymerization Reaction Described for Polymer 18. A pressure vessel was charged with **10** (2.109 g, 3.00 mmol), **12** (2.008 g, 3.00 mmol), $PdCl_2L_2$ (63.2 mg, 0.09 mmol), and DMAc (18 mL), degassed, charged with DBU (1.08 mL, 7.2 mmol), pressurized to 95 psig CO, and heated to 115 °C for 27 h. After this time, the contents of the vessel were diluted with DMAc, filtered, concentrated, precipitated into MeOH, and washed extensively with MeOH to give 1.456 g (72%) of polymer **18** as a white solid.

Sample Preparation and Thermal Imidization of Poly(amic amides) 18, 19, and 22. A 10% wt/vol solution of the poly(amic amide) in DMF was cast on a glass plate and dried under reduced pressure at 100 °C. Poly(amic amides) **18** and **19** gave films that were brittle, and poly(amic amide) **22** shattered on drying. The samples were heated in a Fisher vacuum oven from room temperature to 300 °C over approximately 2 h, held at 300 °C for either 1 or 3 h, and then allowed to cool to 50 °C. All samples foamed and darkened. Samples were analyzed by DSC, TGA, and FT-IR.

Acknowledgment. We thank R. Moody for thermal analyses, D. Motyl for FTIR spectra, and T. Mourey and T. Bryan for SEC analyses.

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MA950890G