Macromolecules **1995,** *28,* 3509−3515

Synthesis of Polyimides via the Palladium-Catalyzed Carbonylation of Bis(*o*-iodo esters) and Diamines

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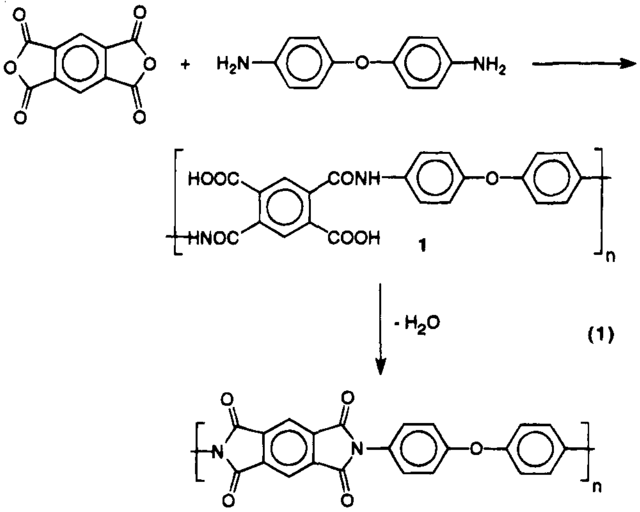
Received October 20, 1994; Revised Manuscript Received February 10, 1995®

ABSTRACT: A new method is described for the synthesis of polyimides utilizing bis(*o*-iodo esters) and primary diamines in the presence of carbon monoxide (CO) and a palladium catalyst. A goal of isolating the intermediate poly(amide esters) from these reactions was not realized. Under all conditions examined in the model systems, neutralizing bases suitable for promoting the carbonylation reaction also induced cyclization to the fully imidized product; intermediate amide esters were not observed. Hydrogen iodide traps such as olefins were also examined, but did not give the desired amide esters. Polyimides formed by this method were fully imidized and had thermal stability commensurate with conventionally prepared polymers. However, the synthetic scope of this method was limited to fully imidized polymers that were soluble in dipolar aprotic solvents.

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.

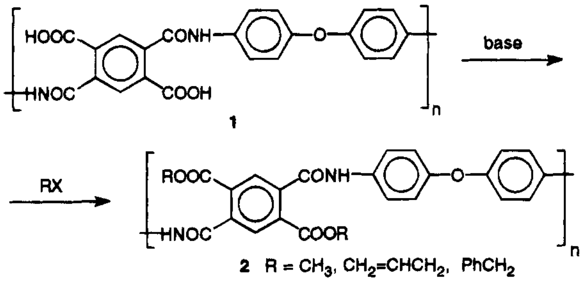


(1)

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, which 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.

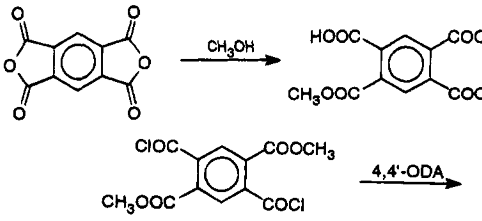
Several groups have reported on various syntheses of the poly(amide esters). One approach was to derivatize the conventionally prepared poly(amic acid) **1**, eq 2.[3]



2 R = CH_3, CH_2=$CHCH_2$, $PhCH_2$

(2)

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 that showed varying degrees of reactivity, eq 3.[4]



2 R = CH_3 (3)

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]

® Abstract published in *Advance ACS Abstracts,* April 1, 1995.

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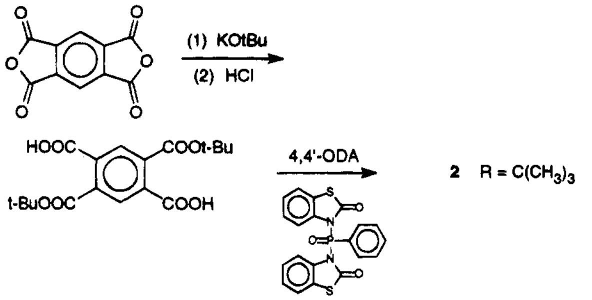
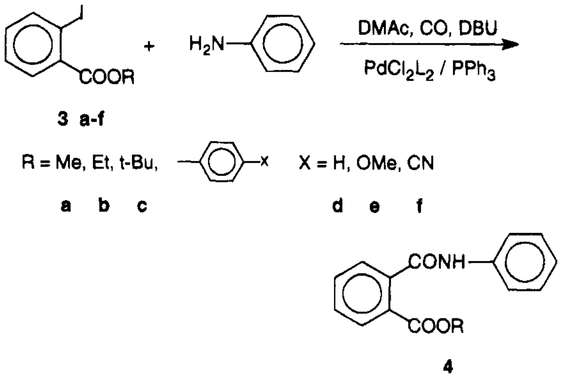


(4)

In all of these cases, multiple steps are necessary to obtain the poly(amic acid ester). We recently reported successful syntheses of linear, high molecular weight aramids,[6] poly(amide-ols),[7] and poly(imide amides)[8] based on the carbonylation and coupling reactions of diiodo compounds and aromatic diamines and felt that the same technology could be adapted to make poly(amide esters) in a single step from the appropriate diiodo diester precursors. Herein, we report the results of such an effort.

Results and Discussion

Model Studies. A model system was initially examined to test the efficacy of this process. Various esters of *o*-iodobenzoic acid were carbonylated and condensed with aniline in the expectation of forming the *ortho*-ester amide **4**, eq 5.



(5)

When the methyl ester **3a** was used, the reaction was over in 0.5 h at 115 °C (entry 1, Table 1). However, none of the expected ester amide was observed. Instead, 73% *N*-phenylphthalimide (**7**) was formed with 10% aniline still remaining. In addition, there was 17% of another product that was detected by gas chromatography (GC), which was subsequently found to be dimethyl phthalate. Believing that imide formation was promoted at 115 °C, a lower reaction temperature of 55 °C was examined. Entry 2 shows that about 67% phthalimide was still formed with 22% dimethyl phthalate being present.

Formation of this unwanted phthalate was thought to occur as outlined in Scheme 1. The methanol that was released on cyclization to the imide competitively reacted with the palladium acyl species to give the observed products. The slightly larger ethyl ester group had little effect on the outcome of the reaction, as seen in entries 3–5. Even the introduction of 4 Å sieves failed to bind the liberated ethanol and suppress phthalate formation. Use of the weaker base *N*-methylmorpholine (entry 6), only resulted in a much slower reaction occurring.

Table 1. Model Reactions of *o*-Iodo Esters in Scheme 1[a]

entry	iodo ester	PPh_3 (mol %)	*T* (°C)	reacn time (h)	imide (%)	phthalate (%)	aniline (%)
1	**3a**	12	115	0.5	73	17	10
2	**3a**	12	55	6.0	67	22	11
3	**3b**	12	115	0.25	79	15	6
4	**3b**	12	55	5.0	73	14	13
5	**3b**[b]	12	55	4.0	59	6	20
6	**3b**[c]		120	6.5	8		90
7	**3c**	12	115	0.25	100		
8	**3c**	12	55	5.0	100		
9	**3c**[d]		55	4.25	81		9
10	**3d**		115	0.33	100		
11	**3d**[e]		55	22	62		6
12	**3e**[f]		55	22	59	29	8
13	**3f**		55	22	32	54	14

[a] Conditions for reaction: iodo ester, 1.0 equiv; aniline, 1.0 equiv; DBU, 1.2 equiv; 95 psig (pounds/square inch gauge pressure) = 7.5 atm CO = 6.7 kg/cm^2 CO; 6 mol % $PdCl_2L_2$ (L = PPh_3); 0.33 M in DMAc. [b] 4 Å sieves used, 6% iodo ester remained. [c] 1.2 equiv of *N*-methylmorpholine used as base. [d] 1.0 equiv of DBU added. After an additional 10% DBU addition, 100% imide was formed. [e] 32% phenol formed. [f] 4% phenol formed.

Phthalate formation could be alleviated by use of a sterically demanding ester such as *tert*-butyl. Entries 7 and 8 show that 100% phthalimide formation occurred with no phthalate formation. Although *tert*-butyl alcohol was released, it was not nucleophilic enough to compete with aniline for the palladium acyl intermediate.

To address the problem of phthalimide versus amide ester formation, several approaches were taken. The first was to decrease the amount of base to exactly stoichiometric amounts. Entry 9 illustrates that this approach failed; only 81% phthalimide formed even after 4.25 h. When an additional 10% DBU was added, the reaction went to completion, but again, only phthalimide was formed, not the amide ester.

Using a phenyl ester as a sterically bulky group also succeeded in giving nearly quantitative yields of phthalimide at 115 °C, but not amide ester (entry 10). At 55 °C (entry 11), the same reaction was incomplete after 22 h. In an attempt to alter the rate at which intramolecular ring closure occurred, *p*-methoxy- and *p*-cyanophenyl esters were examined. *N*-Phenylphthalimide formation was still seen and phthalate formation was also noted.

In all cases cited above, the reactions were monitored by GC analysis. It was unclear whether imide formation was induced thermally when the sample was in contact with the injection port or that the intermediate amide ester was unstable, and under the reaction conditions, underwent spontaneous cyclization. To this end, (2-carboxyethyl)benzanilide was prepared by an independent route and was found to cyclize to *N*-phenylphthalimide when injected on the column.

An alternate means by which to analyze the reaction was by ^1H NMR. To determine the stability of the parent amide ester in solution, (2-carboxyethyl)benzanilide was dissolved in DMSO-d_6. Over the course of several hours, cyclization to some phthalimide was observed. After 4 days at ambient temperature, a ratio of 36:64 starting material to imide (as determined by the amount of ethanol released) was found (Figure 1). The same sample dissolved in acetone-d_6 was unchanged after 1 day at ambient temperature and several hours at 55 °C. It appeared that the basic DMSO solvent was promoting cyclization. To determine the effect that base had on the cyclization of (2-carboxyeth-

Scheme 1

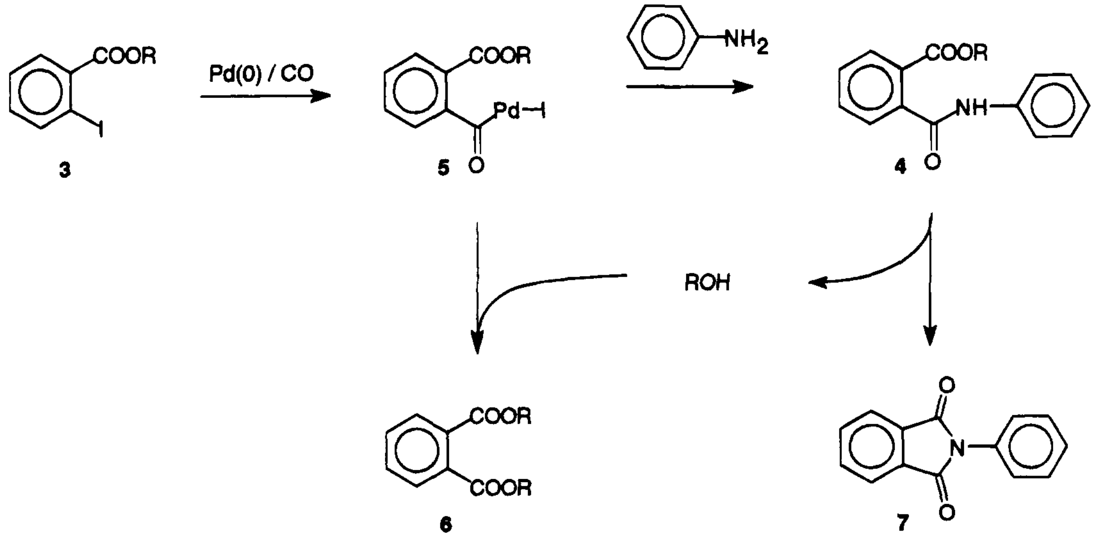
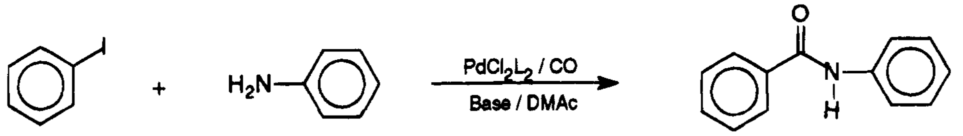


Table 2. Alternate HI Scavangers in Benzanilide Reaction[a]



entry	neutralizing agent	equiv	time (h)	PhCONHPh	PhNHCOMe	$PhCONMe_2$	PhI	$PHNH_2$
1	2-methyl-2-butene	1.2	4	26			37	37
2	2-methyl-2-butene	12.0	23	55	20	10	15	
3	1-methyl-1-cyclohexene	1.2	23	60	19	14	7	
4	β-pinene	7.0	23	55	8	23	14	
5	CaO	1.2	23	100				
6	CaO	6.0	4	78				22

[a] Conditions for reaction: iodobenzene, 1.0 equiv; aniline, 1.0 equiv; DBU, 1.2 equiv; 95 psig CO; 3 mol % $PdCl_2L_2$ (L = PPh_3); 6 mol % PPh_3, 0.33 M in DMAc.

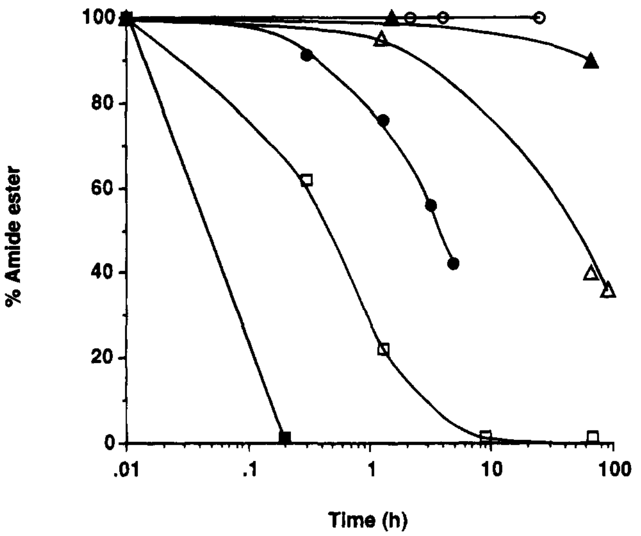


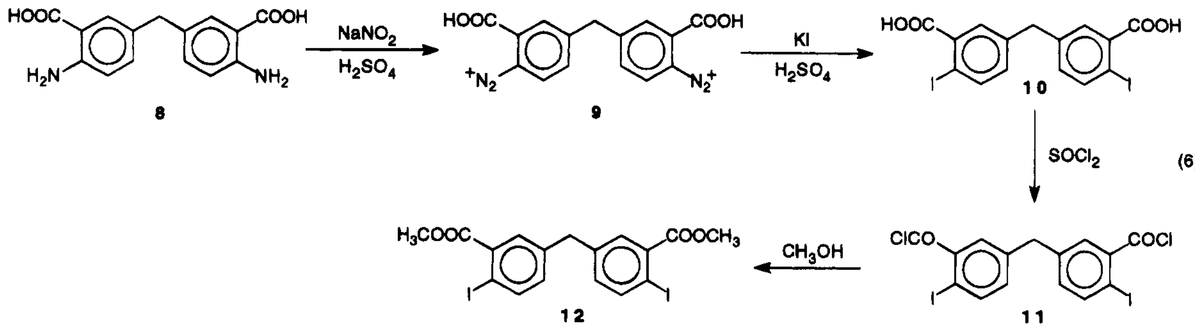
Figure 1. Cyclization of amide ester in the presence of base as determined by ^{1}H NMR: (△) DMSO-d_6; (○) acetone-d_7; (▲) NMM; (●) DABCO; (□) NH_3; (■) DBU.

yl)benzanilide to *N*-phenylphthalimide, several amine bases were examined. The amide ester was stable and soluble in DMF-d_7 and, after 1.5 h in the presence of *N*-methylmorpholine (NMM), showed no tendency to cyclize. Only on prolonged standing (3 days) did 10% of the ester cyclize. When DABCO was used as the base, cyclization was faster, with over 50% phthalimide formed in less than 5 h. Ammonia allowed rapid cyclization to occur, and 78% imide was formed in 1.3 h. The most rapid reaction occurred in the presence of DBU, the strongest base. Quantitative conversion of the amide ester was achieved in less than 0.2 h. During the course of this work, the base-catalyzed cyclization of *ortho*-aromatic alkyl esters was reported as a low activation energy process for chemical imidization.[9] This process was subsequently used for photosensitive polyimide applications.[10]

Finding that NMM did not promote cyclization of the amide ester, we then used NMM in the carbonylation reaction of iodobenzene and aniline. Although it was an efficient acid scavenger, NMM was not efficient in promoting the amidation reaction and, after 24 h, only 70% benzanilide was produced.

We then turned our attention to other substrates we thought would neutralize the hydrogen halide formed and also permit the amidation reaction to occur. Table 2 shows the results using three different olefins and an inorganic base in the amidation reaction.

The use of slightly more than 1 equiv of 2-methyl-2-butene allowed the formation of a small quantity of benzanilide (entry 1), but starting material was still present. Increasing the amount of olefin 10-fold (entry 2) increased the amount of product, but the reaction was still slow and byproducts from palladium-catalyzed solvent decomposition were seen.[11] The same results were seen for the other two olefins (entries 3 and 4). In the presence of 1.2 equiv of CaO, the reaction was slow (23 h) but showed no byproduct formation. This was promising and the reaction was extended to the ami-



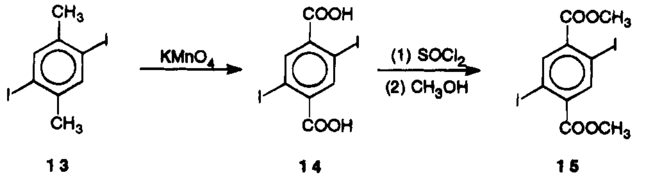
(6)

dation of *tert*-butyl *o*-iodobenzoate (eq 5, R = *t*-Bu). After 23 h, only 14% imide was detected, with the rest of the reaction consisting of starting material. No amide ester was seen.

Given these results, we concluded that amide esters were not stable under the conditions necessary for carbonylation and coupling to occur. Our attention, therefore, turned to forming fully ring-closed, high molecular weight polyimides.

Polymerization Reactions. The bis(*o*-iodo esters) used in these reactions were prepared as described below. 3,3′-Diiodo-4,4′-dicarbomethoxydiphenylmethane (**12**), was prepared as outlined in eq 6. Commercially available 5,5′-methylenebis(anthranilic acid) was diazotized with $NaNO_2$ in H_2SO_4 and then treated with KI to give the diiodo diacid intermediate, **10**. The diacid was refluxed with $SOCl_2$ and the resultant diacid chloride esterified with methanol to give the diiodo dimethyl ester.

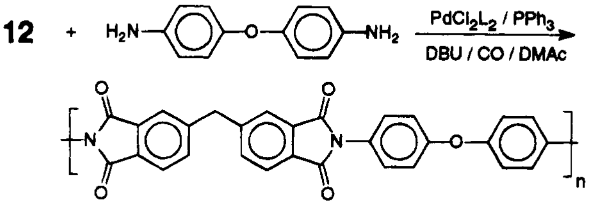
Preparation of dimethyl 2,5-diiodoterephthalate, **15**, followed the approach in eq 7. 2,5-Diiodo-*p*-xylene was oxidized with $KMnO_4$ and the subsequent diacid converted to the dimethyl ester in the fashion described above.



(7)

The di-*tert*-butyl 2,5-diiodoterephthalate **16**, was synthesized in a manner similar to that of **15**. In all three cases, yields of the intermediate iodo acids were poor to modest.

The initial polymerization reaction was performed with diiodo dimethyl ester **12** and 3.4% excess diaminodiphenyl ether **17** to give polyimide **18**, eq 8. As shown in entry 1 of Table 3, a modest molecular weight of 10 400 was achieved after 7 h. The residual iodine content was 0.26 wt %, which indicated most of the aromatic iodide bonds had reacted during the polymerization.



(8)

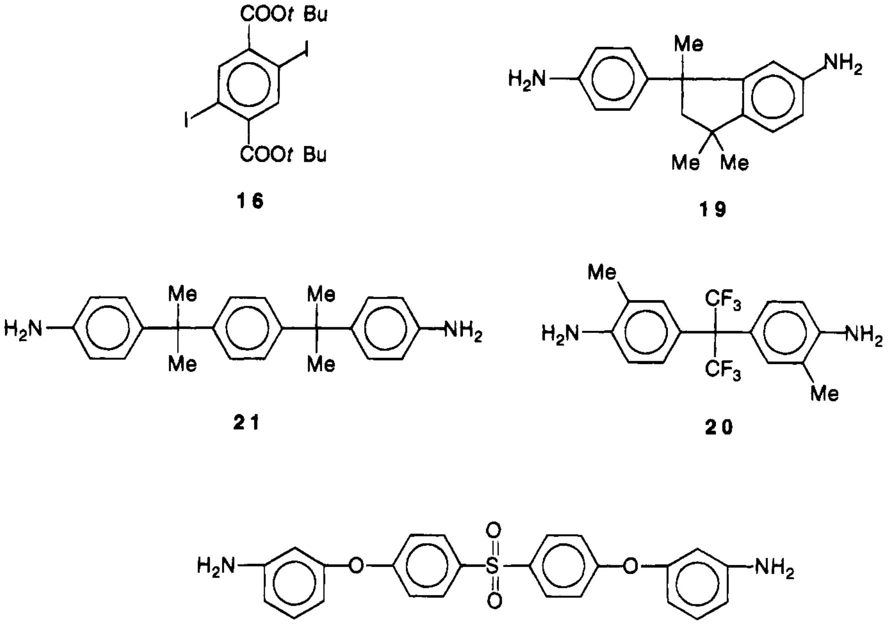
Changing to the diamino phenylindan monomer **19** resulted in a polymer with substantially lower molecular weights and a lower isolated yield (entry 2, Table 3). That these latter two polymers were indeed polyimides, and not the poly(amide esters), was confirmed by FTIR analysis, which showed the presence of the two strong imide C=O stretches at 1775 and 1720 cm^{-1}. Complete cyclization and low molecular weights were also obtained when dimethyl diiodoterephthalate (**15**) was employed as one of the monomers (Table 3, entries 3 and 4). The low yields were likely due to the soluble nature of the oligomers formed which did not precipitate in methanol.

While it was clear that cyclization to the imide could not be avoided under these conditions, we anticipated that higher molecular weight polyimides would be formed from the iodo *tert*-butyl ester derivatives. The use of the bulky ester should permit clean formation of the imide group without the side reaction of phthalate formation seen in the model systems. To this end,di-*tert*-butyl diiodoterephthalate (**16**) and diamine **19** were allowed to react together. A polymer with *4 times* greater molecular weight was achieved (entry 5, Table 3).

When **16** and diamine **20** were used, low molecular weight polymer was again formed. This may be due to the steric interference of the *o*-methyl groups. Two other diamine monomers, without the steric encumbrance of ortho substituents, were used and relatively high molecular weights were achieved. Entry 7 (Table 3) indicates that 3 h into the reaction, some polymer precipitation occurred with diamine **21**. This may account for the bimodal distribution seen in the SEC data. No premature precipitation was seen in the sulfone diamine **21** reaction which formed a polyimide with 27 000 molecular weight (entry 8, Table 3). Intrinsic viscosity (IV) data tracks with increasing molecular weight with the exception of entry 7. The bimodal distribution and lower IV is consistent with branching.

TGAs of the resulting polymers indicated that occluded solvent was lost at low temperatures (150−250 °C). After treatment at these temperatures, the polymers were thermally stable to greater than 450 °C and had correspondingly high T_g values (Table 4). The fourth heats from DSC data were reported because the first two scans were noisy due to solvent loss. Infrared analysis of the carbonyl region of the polymers showed some trace of amide functionality in several of the polymers, in addition to the imide stretches. This suggests that either residual solvent remained in the polymer or that some amide ester was formed which had not cyclized. However, no evidence for an ester band was seen in the infrared spectra. The reason for the large difference in T_g values for polymer entries 3 and 5, which should be structurally identical, is unclear at this time.

Chart 1



16 **19** **21** **20** **22**

Table 3. Polymerization Reactions[a]

entry	bis(*o*-iodo ester)	diamine	yield (%)	IV[b]	M_w[c]	M_n[c]
1	**12**	**17**	78	0.10	10400	7150
2	**12**	**19**	48	0.07	6650	5250
3	**15**	**19**	21	0.07	8250	6200
4	**15**	**20**	24	0.04	6250	4600
5	**16**	**19**	38	0.15	46500	21000
6	**16**	**20**	47	0.04	7500	5200
7	**16**	**21**	83	0.12	76900	19500
8	**16**	**22**	82	0.12	27200	13900

[a] Reactions were run at 115–120 °C, 95 psig CO in DMAc, using 3 mol % $PdCl_2L_2$ (L = PPh_3) and 6 mol % PPh_3 as the catalyst system. *b* Intrinsic viscosity reported in dL/g at 35 °C in DMF. [c] PMMA equivalent molecular weights.

Table 4. Thermal and FTIR Data for Polymers

entry	T_g (°C)[a]	TGA (°C)[b]	imide ν_{CO} (cm^{-1})	amide ν_{CO} (cm^{-1})
1	219	500	1775, 1720	
2	251	490	1776, 1720	
3	261	490	1776, 1726	
4	235	535	1781, 1729	
5	221	495	1778, 1725	1685
6	213	520	1781, 1729	1687
7	223	490	1776, 1725	
8	216	480	1777, 1725	1685

[a] Determined by DSC at 20 °C/min in N_2; fourth heat after cycling through 300 °C. [b] Temperature at 5% wt loss from baseline adjusted for low-temperature solvent loss. Heating rate of 10 /min in N_2.

Summary

A novel method has been described for the preparation of polyimides derived from bis(*o*-iodo esters) and primary diamines in the presence of carbon monoxide (CO) and a palladium catalyst. The original goal of utilizing the carbonylation and coupling reactions of diiodo compounds and aromatic diamines to make poly(amide esters) in a single step from the appropriate diiodo diester precursors was not achieved, as none of the poly(amide esters) could be isolated. Under the conditions examined, premature ring closure of the amide esters resulted in the formation of polyimides. This limited the class of imides to those that were soluble in dipolar aprotic solvents. In addition, monomer synthesis was lengthy and low yielding. The conventional condensation of dianhydrides and diamines is a more preferred method for polyimide formation.

Experimental

General Procedures. Reactions were performed in a 120 mL pressure reaction vessel (containing a Teflon-coated stir-bar), fitted with a pressure gauge, pressure release valve, gas inlet, and a straight ball valve for degassing and sample withdrawal in a well-ventilated hood, and behind safety shields.

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. The 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. ^{1}H 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. Fourier transform infrared spectra were recorded as KBr pellets. 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 2990 and 1 600 000 after derivitizing the samples 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 DuPont 912 dual cell or 910 single-cell calorimeter under nitrogen at a heating rate of 20 °C/min.

Chemicals. Iodobenzene was fractionally distilled and stored in the presence of copper wire. Aniline. 1,8-

diazabicyclo[5.4.0]undec-7-ene (DBU), and *N*-methylmorpholine (NMM) were fractionally distilled under reduced pressure. Triphenylphosphine (PPh_3) was recrystallized from hexanes. 1,4-Diazabicyclo[2.2.2]octane (DABCO), CaO, and 2-methyl-2-butene (all Kodak), ammonia (Air Products, anhydrous) and CO (Air Products, UPC grade), 1-methyl-1-cyclohexene, β-pinene, and bis(triphenylphosphine)palladium(II) chloride ($PdCl_2L_2$) (all Aldrich), and 5,5′-methylenebis(anthranilic acid) (TCI America) were used as received.

Methyl 2-Iodobenzoate (3a). 2-Iodobenzoic acid (7.73 g, 31.2 mmol) was dissolved in anhydrous MeOH (150 mL) to which was added concentrated HCl (10 drops). The solution was heated to reflux and, after 16 h, was concentrated in vacuo. The residue was dissolved in Et_2O, passed through a silica gel column (elute with 9:1 hexanes:EtOAc), concentrated, and distilled (140 °C/5 Torr) to give 4.2 g (51%) of product. ^1H NMR ($CDCl_3$): δ 7.94 (d, $J = 8.0$ Hz, 1), 7.75 (dd, $J = 7.8$, 1.3 Hz, 1), 7.35 (t, $J = 7.7$ Hz, 1), 7.10 (dt, $J = 7.6$, 1.4 Hz, 1), 3.88 (s, 3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 166.7, 141.1, 134.9, 132.5, 130.7, 127.7, 93.9, 52.3.

Ethyl 2-Iodobenzoate (3b) was synthesized in the same manner as described above to give a 62% yield of product (120 °C/0.5 Torr). ^1H NMR ($CDCl_3$): δ 7.93 (d, $J = 8.0$ Hz, 1), 7.75 (dd, $J = 7.7$, 1.6 Hz, 1), 7.35 (t, $J = 7.5$ Hz, 1), 7.09 (dt, $J = 7.5$, 1.4 Hz, 1), 4.35 (q, $J = 7.1$ Hz, 2), 1.37 (t, $J = 7.1$ Hz, 3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 166.4, 141.0, 135.2, 132.3, 130.6, 127.7, 93.8, 61.5, 14.1.

***tert*-Butyl 2-Iodobenzoate (3c).** A toluene solution (60 mL) of 2-iodobenzoic acid (12.49 g, 50.4 mmol) was treated with $SOCl_2$ (5.5 mL, 75.6 mmol) and refluxed for 2 h. Excess $SOCl_2$ and solvent were removed by distillation, and the oily residue was dissolved in THF and added to a cooled (−78 °C) slurry of KO-*t*-Bu (5.85 g, 52 mmol) in THF (50 mL). When addition was complete, the mixture was allowed to stir for 1 h at room temperature and then was diluted with Et_2O and filtered. The filtrate was concentrated, dissolved in Et_2O, washed with water (3 × 50 mL) and brine (1 × 50 mL), dried over $MgSO_4$, concentrated, and distilled (123 °C/1.8 Torr) to give 5.3 g (34%) of product as an oil which slowly solidified. ^1H NMR ($CDCl_3$): δ 7.92 (d, $J = 8.1$ Hz, 1), 7.66 (dd, $J = 7.7$, 1.5 Hz, 1), 7.35 (t, $J = 7.5$ Hz, 1), 7.08 (dt, $J = 7.7$, 1.5 Hz, 1), 1.61 (s, 9). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 166.0, 140.8, 137.3, 131.8, 130.3, 127.7, 93.3, 82.5, 28.0.

Phenyl 2-Iodobenzoate (3d). 2-Iodobenzoic acid chloride (30.5 g, 115 mmol) was made as described above and dissolved in 1,4-dioxane (150 mL), and the solution was treated with phenol (10.7 g, 115 mmol) and Et_3N (13 g, 128 mmol). After stirring at room temperature overnight, the solution was diluted with water, extracted with CH_2Cl_2, dried over $MgSO_4$, concentrated, and distilled (152−155 °C/0.1 Torr) to give 26.5 g (71%) of product. ^1H NMR ($CDCl_3$): δ 8.05 (d, $J = 7.8$ Hz, 2), 7.44 (m, 3), 7.31 (d, $J = 7.3$ Hz, 2), 7.18 (dt, $J = 7.7$, 1.2 Hz, 1). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.5, 150.4, 141.2, 133.8, 132.9, 131.1, 129.2, 127.8, 125.8, 121.3, 94.4.

4-Methoxyphenyl 2-Iodobenzoate (3e) was made as described for phenyl 2-iodobenzoate above, except that the reaction was heated to 60 °C. The product was obtained in 90% yield after recrystallization from MeCN. Mp: 106−108 °C. ^1H NMR ($CDCl_3$): δ 8.02 (m, 2), 7.45 (t, $J = 7.2$ Hz, 1), 7.20 (m, 1), 7.18 (d, $J = 9.0$ Hz, 2), 6.94 (d, $J = 9.0$ Hz, 2), 3.80 (s, 3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.1, 157.3, 144.0, 141.4, 134.2, 133.0, 131.3, 127.9, 122.2, 114.4, 94.4, 55.5.

4-Cyanophenyl 2-Iodobenzoate 3f was made as described for phenyl 2-iodobenzoate above, except that the reaction was heated to 60 °C. The product was obtained in 90% yield after recrystallization from *i*-PrOH. Mp: 88−89 °C. ^1H NMR ($CDCl_3$): δ 8.02 (m, 2), 7.69 (d, $J = 8.6$ Hz, 2), 7.46 (t, $J = 7.3$ Hz, 1), 7.37 (d, $J = 8.6$ Hz, 2), 7.22 (dt, $J = 7.7$, 1.4 Hz, 1). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 163.6, 153.6, 141.6, 133.6, 133.5, 132.8, 131.5, 128.0, 122.6, 118.0, 109.7, 94.6.

3,3′-Diiodomethylenebis(benzene-4,4′-dicarboxylic Acid) (10). An aqueous solution of $NaNO_2$ (15.0 g, 217 mmol, 70 mL) was added to a cooled (0 °C) solution of **8** (28.6 g, 100 mmol) in water (150 mL) and concentrated H_2SO_4 (25 mL). The mixture was stirred for 1 h at 0 °C and then urea (2 g) was added and the mixture slowly poured into a solution of water (900 mL), concentrated H_2SO_4 (100 mL), and KI (50 g, 30 mmol). The temperature was raised to 100 °C, and the reaction was allowed to proceed for 18 h. The solid that had formed was removed by filtration, dissolved in aqueous NH_4OH, treated with decolorizing charcoal, acidified with concentrated HCl, reisolated by filtration, and air dried. The crude product was dissolved in MEK, washed with aqueous $NaHSO_3$, dried with $MgSO_4$, reduced to ca. half volume, and diluted with toluene, and the remainder of the MEK was removed by distillation. The solution was cooled (0 °C) and the solid slurried with toluene and air dried to give 10 g (20%) of product. Mp: 248 °C. ^1H NMR ($CDCl_3$): δ 13.1 (br s, 2), 7.85 (d, $J = 8.1$ Hz, 2), 7.56 (d, $J = 1.5$ Hz, 2), 7.07 (dd, $J = 8.0$, 1.9 Hz, 2), 3.92 (s, 2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 168.1, 140.9, 140.7, 137.1, 132.9, 130.4, 130.3, 91.4, 21.1.

3,3′-Diiodo-4,4′-dicarbomethoxydiphenylmethane (12). Diacid **10** (9 g, 17.8 mmol) was refluxed with $SOCl_2$ (100 mL) and DMF (2 drops) for 3 h. Excess was removed by distillation and the oily residue treated with MeOH at reflux for 3 h. The mixture was cooled to room temperature over 18 h and then filtered, air dried, and recrystallized from MeOH to give 7.0 g (73%) of product. Mp: 83.5−84.5 °C. ^1H NMR ($CDCl_3$): δ 7.85 (d, $J = 8.1$ Hz, 2), 7.56 (d, $J = 1.8$ Hz, 2), 6.90 (dd, $J = 8.1$, 1.8 Hz, 2), 3.88 (s, 8). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 166.6, 141.4, 139.9, 135.3, 133.1, 131.2, 91.5, 52.4, 40.2.

2,5-Diiodo-*p*-xylene (13). A mixture of *p*-xylene (35.4 g, 334 mmol), periodic acid dihydrate (30.4 g, 133 mmol), iodine (68.0 g, 268 mmol), acetic acid (160 mL), water (32 mL), and concentrated H_2SO_4 (5 mL) were stirred at 70 °C. An exothermic reaction occurred at 65 °C, and the reaction was allowed to cool to 70 °C before heating again to 70 °C for 4 h. The reaction mixture was poured into a $NaHSO_3$ solution (50 g in 1 L water). The brown-violet solid was collected, washed with water (200 mL), slurried in methanol (250 mL), collected, and again washed with methanol. The product was recrystallized from heptanes to give 53.9 g (56%) of product. Mp: 101−103 °C. Lit. mp: 104−105 °C.[13] A second crop was obtained from the heptane filtrate (17 g, 18%). ^1H NMR ($CDCl_3$): δ 7.58 (s, 2), 2.32 (s, 6).

2,5-Diiodoterephthalic Acid 14. A refluxing solution of **13** (45.9 g, 128 mmol), water (1.65 L), and *tert*-butyl alcohol (920 mL) was treated with four portions of $KMnO_4$ (4 × 60.7 g, 384 mmol). The first portion was added at the beginning of the reaction, the second after 3 h, the third after 6 h, and the last after 2 h. The reaction was allowed to stir 18 h at reflux, after which time the colorless mixture was filtered hot. The filtrate was concentrated to ca. 600 mL and then diluted with water (600 mL), extracted with ether (1 × 200 mL), and acidified with concentrated HCl. The precipitated solid was heated to 70 °C, filtered hot, and washed with warm water to give 25.0 g (53%) of crude product as a colorless solid. The solid was slurried with ether, collected, washed with ether, and then shaken with ether (150 mL) and 5% Na_2CO_3. The aqueous layer was extracted with ether (2 × 100 mL) and then acidified. The solid that formed was washed with water to give 9 g of material. This was dissolved in THF, chromatographed on silica gel (Bodman), and eluted with THF to give 5.5 g (10%) of product. An analytically pure sample was obtained by recrystallization from 95% EtOH. Mp: 140–144 °C.

Dimethyl Diiodoterephthalate (15). Diiodoterephthalate **14** (30.0 g, 72 mmol) was added in portions to $SOCl_2$ (100 mL), and the mixture was heated until gas evolution ceased. The reaction mixture was concentrated, dissolved in CH_2Cl_2, reconcentrated, and dissolved in MeOH. After stirring at room temperature for 18 h, the precipitated product was collected, washed with MeOH, and dried to give 23.0 g (72%) of product. ^1H NMR ($CDCl_3$): δ 8.16 (s, 2), 3.84 (s, 6). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.7, 141.2, 138.8, 93.5, 52.7.

Di-*tert*-butyl Diiodoterephthate (16). A solution of **14** (20.0 g, 48 mmol), oxalyl chloride (200 mL), and DMF (3 drops) was stirred for 0.5 h at room temperature and then 2 h at reflux. The reaction mixture was then concentrated in vacuo and the solid redissolved in CH_2Cl_2 (300 mL). The mixture was again concentrated and the residue treated with *t*-BuOH (28.0 g, 250 mmol) and MeCN (300 mL) and allowed to stir 0.5 h at room temperature. Pyridine (20.0 g, 250 mmol) was added dropwise over 15 min and the resulting solution stirred at room temperature for 1 h and then at reflux for 1 h. The reaction mixture was added to 1.5 L of water, and the solid was collected, dissolved in CH_2Cl_2, washed with water, dried, concentrated, and chromatographed on silica gel, eluting with 1:1 heptane/CH_2Cl_2. The product collected was recrystallized from MeOH to give 11.2 g (44%). Mp: 142–146 °C. ^1H NMR ($CDCl_3$): δ 8.09 (s, 2), 1.58 (s, 18). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.0, 141.7, 140.2, 92.2, 83.6, 28.0.

Typical Polymerization Reaction. To a clean, dry pressure vessel under an argon purge was added **16** (1.590 g, 3.00 mmol), **22** (1.298 g, 3.00 mmol), PPh_3 (47 mg, 0.18 mmol), $PdCl_2L_2$ (63 mg, 0.09 mmol), and DMAc (18 mL). The bottle was sealed and flushed with CO. The contents of the bottle were then degassed and filled with argon three times. The final degassing was followed by the introduction of CO, which saturated the solution. The contents of the reactor were then stirred and heated to 120 °C in a thermostated oil bath until all the solids had dissolved. At this time any pressure in the reactor was released and DBU (1.08 mL, 7.2 mmol, 2.4 equiv) was added by syringe through the ball valve. The flask was again flushed with CO and pressurized to 90 psig. After 24 h the contents of the flask were filtered through Celite, concentrated to ca. 10 mL, and then precipitated into 4:1 MeOH/water. The polymer was washed extensively with MeOH and dried in vacuo to give 1.88 g (82%) of polymer.

Acknowledgment. We thank C. Maggiulli and J. Ford for the synthesis of the iodo monomers and model compounds, D. Margevich and D. Motyl for FTIR spectra, R. Moody and P. Sciotti for thermal analyses, T. Bryan and T. Mourey for SEC data, and J. Lugert and P. Keogh for GC/MS data.

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MA9461355