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Palladium-Catalyzed Formation of Poly(imide-amides). 1. Reactions with Diiodo Imides and Diamines

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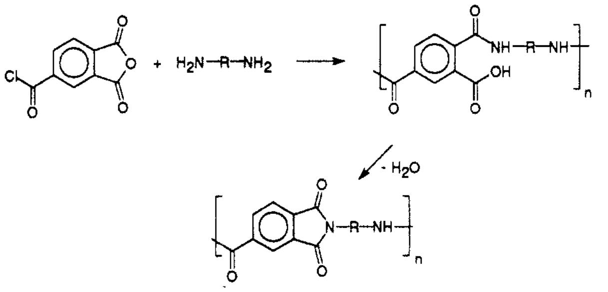
ABSTRACT: High molecular weight poly(imide-amides) can be readily formed by the palladium-mediated carbonylation and condensation reactions of diiodo imide monomers and aromatic diamines. Reaction conditions for polymerization are 100-120 °C, 90 psig CO, 3-6% $PdCl_2L_2$ (L = PPh_3), and 2.4 equiv of DBU for 2-4 h in DMAc or NMP. This route offers the flexibility of incorporating different ratios of amide and imide groups in the polymer backbone in a controlled manner. The imide moiety is preformed, which eliminates the possibility of postpolymerization curing.

Introduction

Poly(imide-amides) (PIAs) are amorphous, high-temperature engineering thermoplastics possessing excellent mechanical and thermal properties as well as solvent resistance and inherent nonflammability.[1] These polymers have also found use as adhesives and fibers and are under study as composite matrix materials.[2] PIAs are conventionally prepared by the condensation of trimellitic anhydride chloride and diamines (eq 1).[3] An alternate method involves the direct condensation of trimellitic anhydride with diisocyanates.[4] One problem present in the former approach is the incomplete conversion of the intermediate amic acid to an imide moiety. This leads to some of the uncontrollable postreaction curing commonly seen in commercial PIAs.[5] Preforming the imide linkage circumvents this problem, and PIAs have been made from imide diacid chlorides and diamines,[6] imide diacids and diisocyanates,[7] and imide diacids and diamines.[8] We recently reported on the preparation of poly(aromatic amides) by the palladium-mediated carbonylation and coupling of aromatic diiodides and diamines.[9] High molecular weight, linear polymers were readily prepared by this novel synthetic route. A similar procedure was also used to form polybenzoxazoles.[10] We believed that PIAs could also be prepared by the palladium-catalyzed carbonylation and coupling of aromatic diamines and aromatic diiodides containing a preformed phthalimide unit (eq 2). The mechanism by which amide bond formation occurs during polymerization is shown in Scheme 1 for model compound 4. Oxidative addition of a coordinatively unsaturated Pd(0) complex to iodo imide 1 gives the Pd(II) aryl intermediate 2, which is followed by CO insertion into the aryl-palladium bond to form acyl complex 3. Subsequent attack of aniline leads to the formation of imide-amide 4 and regeneration of the active Pd(0) catalyst. The PIAs prepared via this method have the advantage of a preformed imide linkage as well as provide for the option of a variable ratio of imide to amide groups. This variability may provide a method of controlling certain mechanical properties, such as modulus or elongation. In addition, no hydrolytically sensitive functionality is present in either of the monomers, eliminating the need for anhydrous storage conditions. Herein we report the initial results of our synthetic efforts.



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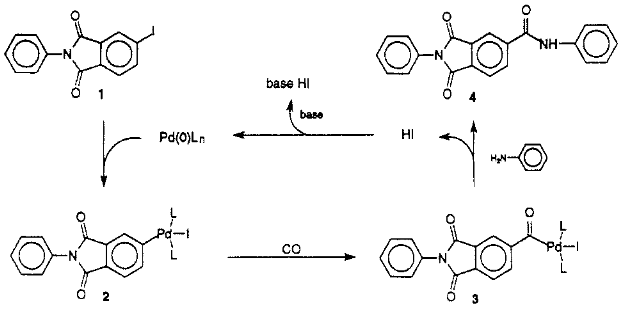
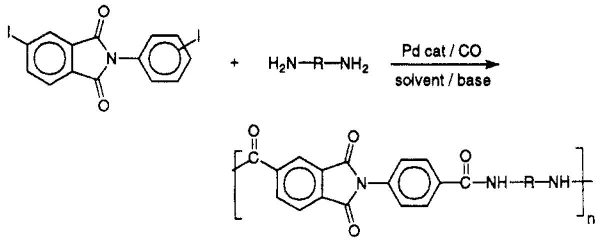
Scheme 1





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Results and Discussion

Diiodophthalimide Preparation. Two classes of diiodophthalimides were used in order to give 2:1 and 2:2

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Scheme 2

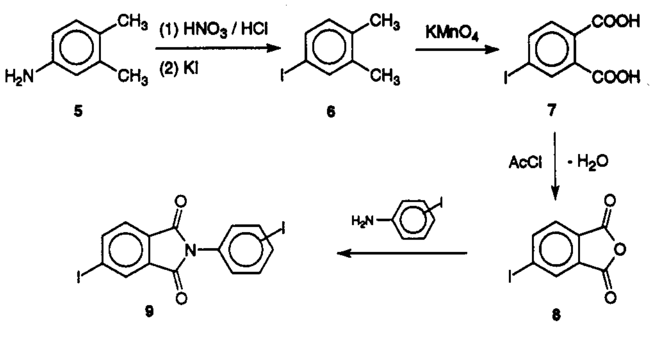
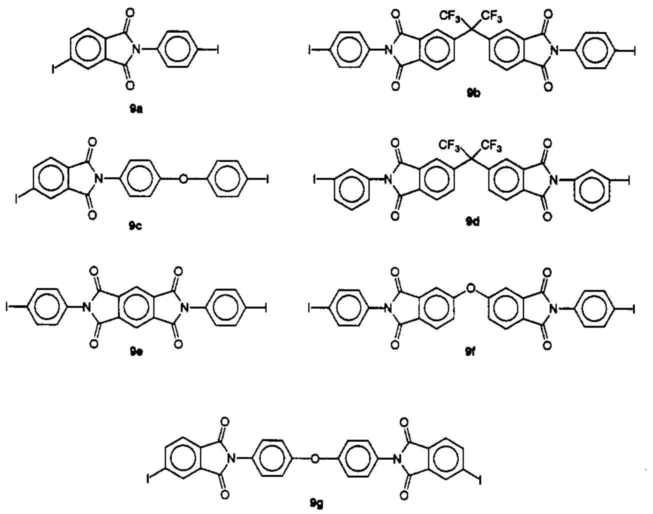
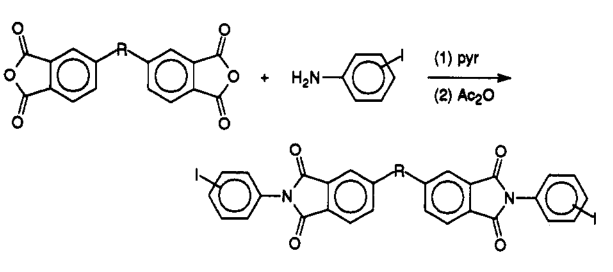


Chart 1



ratios of amide:imide groups. The first class was derived from 4-iodophthalic anhydride and iodoaniline derivatives (Scheme 2). Diazotization of 3,4-dimethylaniline (**5**), followed by treatment with KI, gave an 80% yield of 3,4-dimethyliodobenzene (**6**), which was oxidized with $KMnO_4$ to the corresponding phthalic acid **7** in 94% yield. Chemical cyclization of **7** gave 61% 4-iodophthalic anhydride (**8**). The reaction of iodo-substituted anilines with this anhydride formed the desired diiodophthalimides.

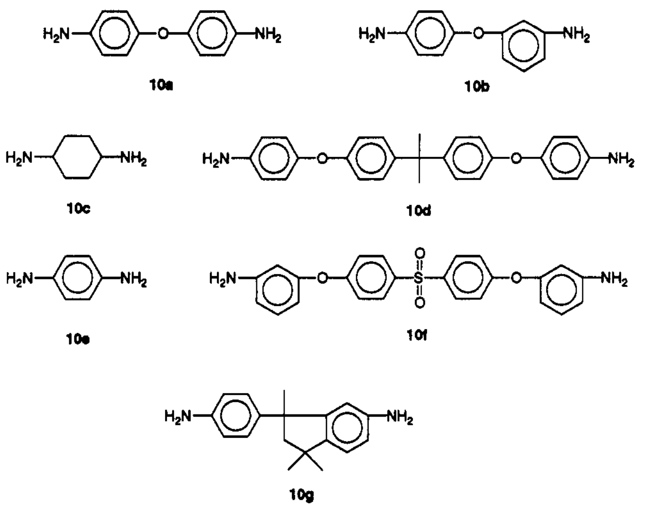
The second class could be prepared directly from commercially available dianhydrides and diamines (eq 3) and provided two preformed imide groups in the monomer. Charts 1 and 2 show the monomers used in this study.



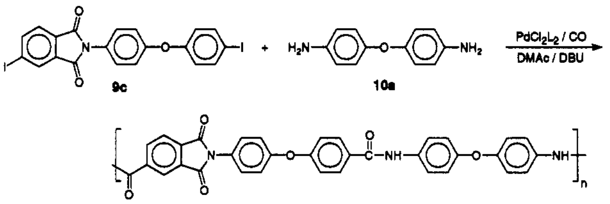
(3)

Polymerization Reactions. Following the stoichiometric ratio that worked best in the poly(aromatic amide) cases,[9] a 97% loading of the diiodophthalimide **9a** was allowed to react with diamine **10a** at 90–100 °C under 90–95 psig CO (Table 1, entry 1). We found that when an equivalent amount of iodo compound was used in aramid formation, some reduction to the free arene occurred resulting in lower molecular weights. If a slight excess of amine was present, decomposition of the iodo compound was suppressed and higher molecular weights were achieved. High molecular weight polymer having T_g = 244 °C was obtained that was stable in nitrogen to about 400 °C. Although not necessary to keep the polymer soluble in this particular reaction, the presence of LiCl may have had a slight deleterious effect on the polymerization, as seen in entry 2. This may have arisen from a small amount of residual water left on the LiCl or a combination of factors including a change of solvent and a more dilute reaction medium. When a slight excess of **9a** was used in the reaction, rather than the diamine, the molecular weight increased (entry 3). This was unexpected but illustrated that each reaction is subtly different and needs to be "fine-tuned" for optimal results. End-capping a similar reaction with aniline after 1 h gave a poly(imide–amide) with lower molecular weight and a slightly lower T_g (entry 4). Changing from **10a** to a more flexible diamine **10f** gave a polymer with a $\bar{M}_w$ greater than 150 000 (entry 5). Altering the stoichiometry of the reaction from a slight deficit of diiodo compound to exact equivalence resulted in lower molecular weight poly(imide–amide) being formed, consistent with earlier aramid observations[9] (entry 6). Aliphatic diamine **10c** used with diiodophthalimide **9a** gave a polymer that quickly gelled in the reaction vessel.

Chart 2



Diiodophthalimide **9c** also reacted with **10a** to give high molecular weight polymer with $\bar{M}_w$ = 151 000 and $\bar{M}_n$ = 45 000 (eq 4). Monomer **9c** was prepared from **4** and 4-amino-4′-iododiphenyl ether.



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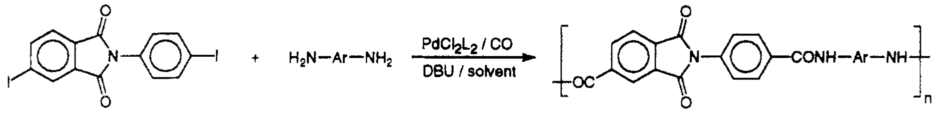
The first of the diimide monomers examined was the diiodo bisimide **9e**. In all cases, polymers with this monomer gelled or precipitated from solution with or without the presence of added salts to aid in solubility. To enhance the inherent solubility of the imide–amide polymers, monomer **9b** was used. Table 2 illustrates the polymers made from this diiodo compound. At 20% solids concentration, the reaction of **9b** and **10a** gave an insoluble precipitate (entry 1). However, if the reaction mixture was run more dilute (entry 2), soluble, high molecular weight polymer was obtained. Absolute molecular weight measurements indicated that the true molecular weight of the sample was about one-half that reported as PMMA

Table 1. Reaction of Diiodophthalimide 9a with Diamines[a]

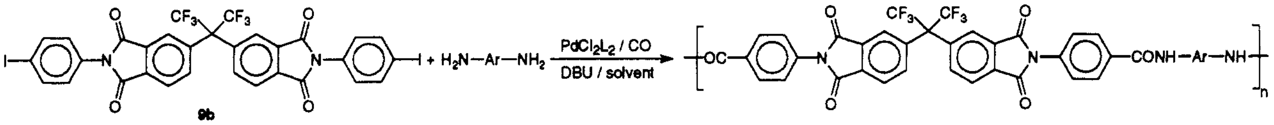


9a

entry	diamine	% cat.[b]	solvent (%)[c]	$\bar{M}_w$[d]	$\bar{M}_n$[d]	T_g[e] (°C)
1	**10a**[f]	6	DMAc (8)	82 300	35 700	244
2	**10a**[f,g]	6	NMP (12)	62 900	24 000	243
3	**10a**[h]	3	DMAc (10)	97 100	40 400	249
4	**10a**[h,i]	3	DMAc (10)	68 600	26 100	246
5	**10f**[j]	3	DMAc (13)	153 000	59 000	232
6	**10f**[k]	3	DMAc (13)	87 900	44 000	
7	**10c**[f]	3	DMAc (14)			

[a] Reactions were run at 90–100 °C for 2 h at 90 psig CO. [b] cat. = $PdCl_2L_2$ (L = PPh_3). [c] Percent solids concentration based on total weight of diamine + diiodo/solvent weight. [d] PMMA equivalent molecular weights. [e] Second heat in DSC at 20 °C/min. [f] 97% of the stoichiometric amount of **9a** was used relative to diamine. [g] 4.7 equiv of LiCl present. [h] 105% of the stoichiometric amount of **9a** was used relative to diamine. [i] Reaction was end capped with aniline after 1 h. [j] 98.6% of the stoichiometric amount of **9a** was used relative to diamine. [k] 100% of the stoichiometric amount of **9a** was used relative to diamine.

Table 2. Reaction of Diido Dimide 9b with Diamines[a]



9b

entry	diamine	solvent (%)[b]	time (h)	$\bar{M}_w$[c]	$\bar{M}_n$[c]
1	**10a**[d]	NMP (20)	2		
2	**10a**[d]	NMP (12)	1.5	147 000[e]	71 200[e]
3	**10a**[d]	NMP (12)	1.5	106 000	53 600
4	**10a**[f]	DMAc (13)	2	86 500	44 800
5	**10b**[d]	DMAc (10)	24	18 700[g]	5 800[g]
6	**10g**[h,i]	NMP (13)	2	86 000	44 000
7	**10d**[j,k]	DMAc (14)	1.5	102 000	43 600
8	**10d**[k,l]	DMAc (14)	1.5	96 000	44 000
9	**10d**[m]	DMAc (12)	18	78 700	43 600

[a] Reactions were run at 90–100 °C at 90 psig CO with 6% $PdCl_2L_2$ (L = PPh_3) as catalyst. [b] Percent solids concentration based on total weight of diamine + diiodo/solvent weight. [c] PMMA equivalent molecular weights. [d] 97% of the stoichiometric amount of **9b** was used relative to diamine. [e] Absolute M_w = 72 500, M_n = 33 800. [f] 96% of the stoichiometric amount of **9b** was used relative to diamine. [g] SEC on soluble fraction. [h] 95% of the stoichiometric amount of **9b** was used relative to diamine. [i] 5.9 equiv of LiCl added. [j] 99% of the stoichiometric amount of **9b** was used relative to diamine. [k] 3% catalyst. [l] 98% of the stoichiometric amount of **9b** was used relative to diamine. [m] 99.5% of the stoichiometric amount of **9b** was used relative to diamine; 5% catalyst, 11% PPh_3, 20 psig CO.

equivalent molecular weights. Reproducibility of entry 2 was demonstrated by a fourfold scale-up, to give 50 g of this material (entry 3).

When the ratio of diiodo compound to diamine was dropped from 97% to 96%, a concomitant decrease in molecular weight was also seen (entry 4). Using the 3,4′-isomer of ODA (entry 5) resulted in a less soluble polymer, which prematurely precipitated. Moderately high molecular weight polymer was formed in the presence of LiCl when diaminophenylindan **10g** was used (entry 6). High molecular weight poly(imide–amides) were also achieved with the BPA diamine **10f** (entries 7 and 8). Consistent with our previous work on aromatic polyamides,[3] lower molecular weight polymers were formed if the CO pressure was reduced and only 0.5% excess diamine was used during the reaction (entry 9). Decreased CO pressures resulted in the rate-determining CO insertion step decreasing (Scheme 1), thus giving more time for deleterious side reactions to occur.

Polymers from three other diiodo imides examined are summarized in Table 3. Poly(imide–amides) with $\bar{M}_w$s in excess of 120 000 were readily formed, except when diamine **10g** was used. This observation was consistent with that seen in Table 2, in which the polymer with **10g** gave one of the lowest molecular weights. Entry 5 was an example of a diiodo imide in which the imide moieties were facing away from the iodo aromatic part of the monomer.

Table 3. Reaction of Various Diiodo Monomers with Diamines[a]

entry	diiodo	diamine	solvent (%)[b]	time (h)	$\bar{M}_w$[c]	$\bar{M}_n$[c]
1	**9d**	**10a**	DMAc (20)	1.5	163 000	72 300
2	**9d**[d,e]	**10e**	NMP (12)	2	128 000	59 000
3	**9d**[f]	**10g**	NMP (14)	2	76 900	45 400
4	**9f**[g]	**10d**	DMAc (10)	4	125 000	48 700
5	**9g**[h]	**10a**	DMAc (10)	3	121 000	49 900

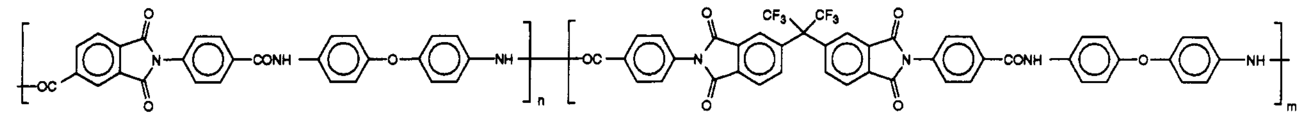
[a] Reactions were run at 90–100 °C at 90 psig CO with 6% $PdCl_2L_2$ (L = PPh_3) as catalyst. [b] Percent solids concentration based on total weight of diamine + diiodo/solvent weight. [c] PMMA equivalent molecular weights. [d] 97% of the stoichiometric amount of **9d** was used relative to diamine. [e] 5.9 equiv of LiCl added. [f] 95% of the stoichiometric amount of **9d** was used relative to diamine. [g] 100% of the stoichiometric amount of **9f** was used relative to diamine. [h] 99% of the stoichiometric amount of **9g** was used relative to diamine.

Several copolymers of **9a** and **9b** with **10a** were made with the charged ratio of monomers shown in Table 4. Reasonable molecular weight copolymers were made from this method in 3 h or less. All of these polymers were soluble and monomodal in the SEC.

Summary

High molecular weight poly(imide–amides) are readily formed by the palladium-mediated carbonylation and condensation reactions of diiodo imide monomers and aromatic diamines. This novel route offers the flexibility of incorporating different ratios of amide and imide groups

Table 4. Copolymers of 9a, 9b, and 10a[a]



entry	**9a**[b]	**9b**[b]	solvent (%)[c]	time (h)	$\bar{M}_w$[d]	$\bar{M}_n$[d]
1[e]	1	1	NMP (6)	1.5	68 000	30 900
2	3	1	DMAc (10)	2	65 900	33 800
3	1	3	NMP (7)	2	99 900	47 100
4	1	1	DMAc (6)	2	53 700	20 700
5	4	1	DMAc (9)	3	93 300	45 400

[a] Reactions were run at 90–100 °C at 90 psig CO with 6% $PdCl_2L_2$ ($L = PPh_3$) as catalyst. [b] Relative mole ratios of diiodo monomers charged. The total amount of diiodo monomers relative to **10a** was 97%. [c] Percent solids concentration based on total weight of diamine + diiodo/solvent weight. [d] PMMA equivalent molecular weights. [e] 5.9 equiv of LiCl added.

in the polymer backbone in a controlled manner. In contrast to the conventional method for preparing poly(imide–amides) from trimellitic anhydride, our procedure incorporates a preformed imide functionality.

Experimental Section

General Procedures. Small-scale reactions were performed in a 120 mL pressure reaction vessel containing a Teflon-coated stir bar, 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 (>15 g) were performed in a Büchi 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. 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 2100 thermal analyzer under 30 mL of N_2/min at 20 °C/min. 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 Da. ^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.

Chemicals. Diamines **10d** (Chriskev), **10f** (Chriskev), and **10e** (Aldrich, zone refined) were used as received, **10a** was recrystallized from ethanol, **10b** and **10d** were fractionally distilled, and **10g** was sublimed prior to use. Pyromellitic dianhydride (PMDA), 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), 4,4′-oxydiphthalic anhydride (ODPA) (all Chriskev), 3-iodoaniline, 4-iodoaniline, 3,4-dimethylaniline, NMP (anhydrous), DMAc (anhydrous), bis(triphenylphosphine)palladium(II) chloride ($PdCl_2L_2$) (all Aldrich), and CO (Air Products, UPC grade) were used as received. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was fractionally distilled under reduced pressure. Triphenylphosphine (PPh_3) was recrystallized from hexanes. LiCl and $CaCl_2$ were dried in vacuo at 100 °C.

Monomer Preparation. 4-Amino-4′-iododiphenyl Ether. In a 5 L flask were placed 4-iodophenol (300 g, 1.36 mol), 4-fluoronitrobenzene (18 g, 0.13 mol), DMF (1.5 L), and 50% NaOH (120 g, 1.5 mol). The mixture was stirred at 0 °C for 15 min, then the bulk of the 4-fluoronitrobenzene was added (200 g, 1.42 mol), and the reaction was allowed to stir 18 h at room temperature. The precipitated solid was isolated by filtration, washed with DMF, and recrystallized from isopropyl alcohol (IPA) to give 392 g (84%) of 4-iodo-4′-nitrodiphenyl ether. This intermediate (185 g, 0.542 mol) was hydrogenated in THF using a Ni/Co catalyst. The reaction solution was concentrated, dissolved in CH_2Cl_2, and chromatographed on silica gel (eluting with CH_2Cl_2) to give crude product that was recrystallized from ligroin to give 143 g (85%) of product, mp 91–92 °C. ^1H NMR (DMSO-d_6) δ 7.53 (m, 2), 6.84 (m, 2), 6.6 (m, 4), 3.61 (br s, 2).

4-Iodophthalic Anhydride (8). 3,4-Dimethylaniline (121 g, 1.0 mol), ice/water mixture (1.5 L), and concentrate HCl (215 mL) were cooled to 0 °C, and then a solution of $NaNO_2$ (69 g, 1.0 mol) in water (100 mL) was added rapidly. The reaction was stirred for 30 min at 5 °C, and then water (500 mL) and KI (170 g, 1.02 mol) were added. The mixture was allowed to stir at room temperature for 18 h. The aqueous layer was decanted from the heavy black layer and washed with CH_2Cl_2. The organic extract was combined with the black layer that was then washed with water. The organic layer was dried over $MgSO_4$, concentrated, and distilled (60 °C/0.1 Torr) to give 185 g (80%) of 3,4-dimethyiodobenzene, **6**, as a reddish oil. Intermediate **6** (185 g, 0.73 mol), pyridine (450 mL), and water (1.2 L) were heated to 80–90 °C, and then $KMnO_4$ (280 g, 1.8 mol) was added in portions over 3 h. (*Caution*: Reaction is exothermic.) Heating continued for 1 h after addition was complete, and then the excess $KMnO_4$ was destroyed with EtOH. The reaction mixture was filtered, and then the excess pyridine was removed by distillation. The aqueous layer was acidified with concentrate HCl and cooled, and the solid was collected by filtration. After washing extensively with water and drying, the yield of 4-iodophthalic acid, **7**, was 220 g (94%). The crude acid, **7** (220 g, 0.75 mol), was added over 30 min to warm (50 °C) AcCl (750 g). The mixture was heated to reflux. When dissolution was complete, the mixture was filtered, concentrated, and cooled. The crystalline solid was washed with cold Et_2O and then ligroin to give 125 g (61%) of product **8**, mp 123–125 °C. ^1H NMR (DMSO-d_6) δ 7.99 (s, 1), 7.90 (d, J = 8.1 Hz, 1), 7.48 (d, J = 7.9 Hz, 1).

***N*-(4-Iodophenyl)-4-iodophthalimide (9a).** In a dry, three-necked flask equipped with a mechanical stirrer, thermometer, condenser, and argon gas inlet were placed 4-iodophthalic anhydride (13.7 g, 0.05 mol), 4-iodoaniline (10.95 g, 0.05 mol), pyridine (19.9 mL, 0.25 mol), and DMAc (35 mL). The solution was heated at 100 °C for 4 h, and then Ac_2O (10.3 mL, 0.11 mol) was added and the mixture was allowed to react for 16 h. The reaction mixture was poured into water, and the precipitate was filtered and washed with methanol. After drying in vacuo at 60 °C, 22.1 g (93%) of product was obtained, mp 235 °C. Anal. Calcd for $C_{14}H_7NI O_2$: C, 35.40; H, 1.49; N, 2.95. Found: C, 35.47; H, 1.59; N, 2.94.

A representative example of a diiodo diimide preparation from a dianhydride is given below.

2,2-Bis[4-{*N*-(4-iodophenyl)phthalimidyl}]hexafluoropropane (9b). In a dry, 2 L, three-necked flask equipped with a mechanical stirrer, thermometer, condenser, and argon gas inlet were placed 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane (199.91 g, 0.45 mol), 4-iodoaniline (197.13 g, 0.900 mol), pyridine (255 mL, 3.15 mol), and DMAc (500 mL). The solution was heated for 4 h at 100 °C with stirring, and then acetic anhydride (Ac_2O, 340 mL, 3.60 mol) was added. The mixture was allowed to stir at 80 °C for 16 h and then cooled to 10 °C, and the precipitate was collected by filtration. Extensive washing with methanol and air-drying gave 305.4 g (80%) of the product, mp 308–310 °C. Anal. Calcd for $C_{31}H_{14}N_2F_6I_2O_4$: C, 44.00; H, 1.67; N, 3.31. Found: C, 43.70; H, 1.82; N, 3.28.

The other diiodo diimides were prepared in a similar manner.

4-Iodo-*N*-(4-(4-iodophenoxy)phenyl)phthalimide (9c): mp 244–246 °C. Anal. Calcd for $C_{20}H_{11}NI_2O_3$: C, 42.36; H, 1.96; N, 2.47. Found: C, 42.43; H, 2.00; N, 2.31.

2,2-Bis[4-{*N*-(3-iodophenyl)phthalimidyl}]hexafluoropropane (9d): mp 242 °C. Anal. Calcd for $C_{31}H_{14}N_2F_6I_2O_4$: C, 44.00; H, 1.67; N, 3.31. Found: C, 43.76; H, 1.77; N, 3.30.

***N,N′*-Bis(4-iodophenyl)pyromellitimide (9e)**: mp >350 °C. Anal. Calcd for $C_{22}H_{10}N_2I_2O_4$: C, 42.61; H, 1.63; N, 4.52. Found: C, 42.47; H, 1.67; N, 4.30.

Bis[4-{*N*-(4-iodophenyl)phthalimidyl}] ether (9f): mp 332 °C. Anal. Calcd for $C_{28}H_{14}N_2I_2O_5$: C, 47.22; H, 1.98; N, 3.93. Found: C, 47.21; H, 2.08; N, 3.91.

4,4′-Bis[*N*-(4-iodophthalimidyl)]diphenyl ether (9g): mp 247 °C. Anal. Calcd for $C_{31}H_{14}N_2F_6I_2O_4$: C, 47.22; H, 1.98; N, 3.93. Found: C, 47.29; H, 2.11; N, 3.99.

Typical Polymerization Reaction. To a clean, dry pressure vessel under argon were added 2,2-bis[4-{*N*-(4-iodophenyl)-phthalimidyl}]hexafluoropropane (**9b**; 1.65 g, 1.95 mmol), 4,4′-diaminodiphenyl ether (**10a**; 0.40 g, 2.00 mmol), $PdCl_2L_2$ (84 mg, 0.12 mmol), DBU (740 μL, 4.96 mmol, 2.4 equiv), and NMP (16 g). The bottle was sealed, flushed with CO, and pressurized to 90 psig CO, the mixture was stirred and heated to 90 °C in a thermostated oil bath, and the reaction was allowed to proceed for 1.5 h. The viscous solution was diluted with DMAc (40 mL), filtered, and precipitated into MeOH, washed extensively with MeOH, and dried in vacuo to give a stringy white polymer. η_{inh} = 1.18 dL/g in DMAc at 25.0 °C at 0.25 wt %.

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References and Notes

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