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PREPARATION OF POLYIMIDES VIA THE PALLADIUM-CATALYZED CARBONYLATION AND CONDENSATION OF TETRAIODOAROMATICS AND DIAMINES

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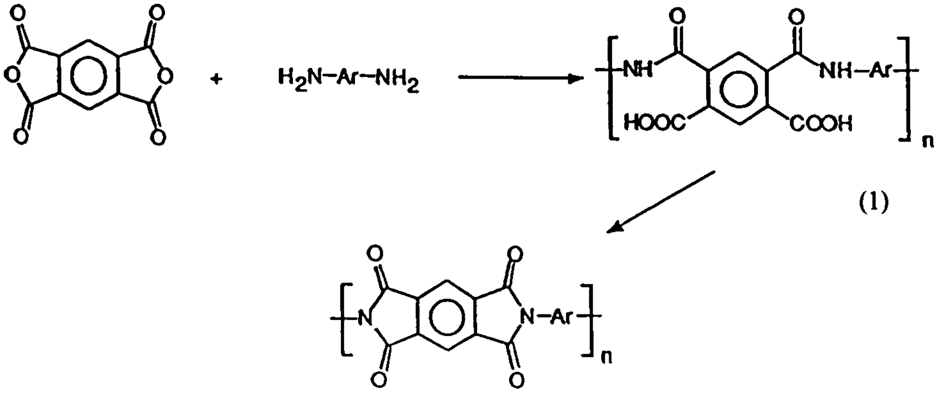
ABSTRACT

Several polyimides were prepared by the palladium-catalyzed carbonylation and condensation of tetraiodoaromatic compounds and diamines. This new reaction for preparing polyimides was verified in model compound work to be an efficient, high yield route to cyclic imides. Since fully imidized groups are formed during the polymerization, it was necessary to limit the diamines to those that would impart solubility to the polymer. In contrast to the model compound work, the polymerization reaction yielded an appreciable concentration of amide functional groups due to incomplete cyclization and/or branching reactions. Thermal characterization of the polyimides formed by this process is reported.

INTRODUCTION

Aromatic polyimides are a class of high-performance polymers that have outstanding thermal stability, inherent flame and chemical resistance, and good dielectric properties [1]. These characteristics have led to their widespread use as high temperature adhesives, matrices for advanced composites, and dielectrics in electronic applications. Because of this technological and commercial importance, there is ongoing synthetic research on polyimides generally directed at improving performance by the use of novel diamines or dianhydrides or by improving the postpolymerization cyclization step. The conventional method of preparation of polyimides involves the condensation of aromatic diamines with aromatic dianhydrides Eq. (1). One of the drawbacks of this method is the use of hydrolytically unstable dianhydrides. An alternate method for forming polyimides using dianhydrides and diisocyanates [2] has a double disadvantage in that both monomers are subject to hydrolysis.



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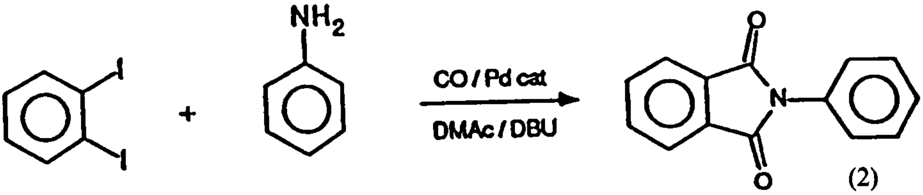
We recently reported [3] our discovery of a novel Heck reaction for forming the cyclic imide linkage through the palladium-catalyzed carbonylation and coupling of *o*-diiodoaromatics and primary amines. This reaction was found to be tolerant of a variety of functional groups and gave good yields of a wide range of phthalimide derivatives with no apparent side reactions. This reaction is represented in Eq. (2) with the formation of *N*-phenylphthalimide from *o*-diiodobenzene and aniline. In this report we describe a novel synthesis of polyimides based on this new imide-forming chemistry with the use of tetraiodoaromatic compounds and primary diamines.



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EXPERIMENTAL

Sample Analyses

TGA measurements were made on an Omnitherm Advantage II under 60 mL/min nitrogen at 10°C/min from 25 to 1000°C. SEC data were obtained from a Waters HPLC using three 10 μL PL Gel mixed bed columns and calibrated with PMMA standards. The samples were chromatographed in DMF. IR spectra were recorded on a Nicolet 5ZDX spectrometer as KBr pellets. Iodine analyses were obtained by neutron activation analysis. Inherent viscosities were determined in DMAc at 25.0°C at 0.25 wt% or in concentrated H_2SO_4 at 0.50 wt% with a Schott Gerate 526-10 viscometer.

Chemicals

$PdCl_2L_2$ (Aldrich), PPh_3 (Kodak), DMAc (anhydrous, Aldrich, sure seal), CO (UPC Grade, Air Products), Bis-P (Air Products) and *m*-toluidene were used as received. DBU (Aldrich), 1,6-diaminohexane, and *o*-diiodobenzene (Kodak) were distilled before use. ODA (Aldrich) was distilled or recrystallized from ethanol, and DPI (Kodak) was recrystallized from hexanes or heptane before use.

Preparation of Monomers

1,2,4,5-Tetraiodobenzene

This compound was prepared according to the literature and after recrystallization from 2-methoxyethanol gave light yellow needles (mp) 248–250°C, lit mp [4] 252–255°C.

2,3,5,6-Tetraiodoxylene

This compound was prepared by using a procedure similar to that used for tetraiodobenzene. A 500-mL 3-necked round-bottom flask was charged with 13.0 g (0.058 mol) periodic acid and 150 mL concentrated sulfuric acid. Iodine (43.54 g, 0.17 mol) was added and the mixture stirred with an overhead stirrer for 30 min. After this time the reaction flask was placed in an ice bath and after an additional 30 min of stirring, *p*-xylene (10.6 g, 0.1 mol) was slowly added to the reaction mixture. A fast reaction appeared to occur as considerable foaming was observed. The dark mixture was allowed to warm to room temperature and left stirring for 24 h. The mixture was slowly poured into an ice water sodium bisulfite solution. A brown powder was isolated (ca. 30 g). Recrystallization from 2-methoxyethanol using activated charcoal yielded 3.0 g of fluffy off-white needles. Mass spectrometry showed a parent ion at 610 and minor peaks at 483 and 356, in agreement with published data on this compound [5].

3,3′,4,4′-Tetraiododiphenylsulfone

o-Diiodobenzene (70.5 g, 0.21 mol) was dissolved in 150 mL dichloromethane and cooled to 10°C. To this solution, chlorosulfonic acid (52 g, 0.446 mol) was added slowly and the reaction was left to stir at room temperature overnight. A precipitate was formed which was redissolved with the addition of additional dichloromethane. The solution was washed with water and a solid came out of solution during the washing. This was isolated by filtration to yield 5.0 g (7.0%) of the sulfone as white needles mp 268–270°C. The organic layer contained predominately monoreacted chlorosulfone and the aqueous layer contained predominately the water soluble sulfonic acid. ^{1}H NMR (DMSO-d_6) 8.33(d,J = 2.0 Hz, 2), 8.11(d,J = 8.2 Hz, 2), 7.65(dd,J = 8.2, 2.0 Hz, 2). ^{13}C{^{1}H} NMR (DMSO-d_6) 140.8, 140.4, 136.6, 127.8, 117.7, 110.6. IR (Nujol) 1320, 1150 cm^{-1}. Calculated for $C_{12}H_6SO_2I_4$: C, 19.97; H, 0.84; S, 4.44; O, 8.49; I, 67.37. Found: C, 19.66; H, 0.93; S, 4.31.

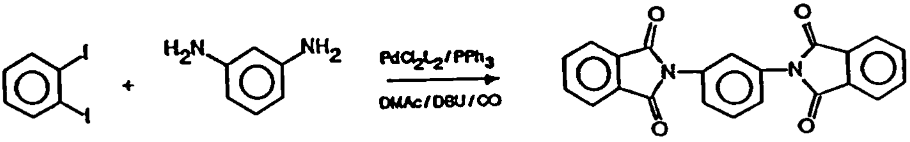
Polymerization Reactions

In a representative polymerization reaction a Fischer-Porter bottle (Aerosol Laboratory Equipment Corp.) fitted with a pressure gauge, a pressure release valve, a gas inlet, and a straight ball valve for degassing and sample withdrawl, was charged with 1,2,4,5-tetraiodobenzene (2.455 g, 4.22 mmol), 5-amino-3-(4-aminophenyl)-1,1,3-trimethylindane (1.124 g, 4.22 mmol), bis(triphenylphosphine) palladium(II) chloride ($PdCl_2L_2$, 178 mg, 0.253 mmol), triphenylphosphine (PPh_3, 133 mg, 0.506 mmol) and *N,N*-dimethylacetamide (DMAc, 21.1 mL). The mixture was stirred, degassed, placed under a carbon monoxide (CO) atmosphere, and heated to 115°C. When the contents of the vessel had dissolved, 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU, 3.03 mL, 20.26 mmol) was added and the vessel was charged to 95 psi CO. The reaction was allowed to proceed for 24 h, after which time the contents of the bottle were filtered through a filter aid and precipitated into methanol. The polymer was washed extensively with methanol, dried, and again dissolved in DMAc and reprecipitated into methanol to give a solid which was dried *in vacuo*. η_{inh} = 0.56 (0.25% in DMAc at 25°C).

RESULTS AND DISCUSSION

Our discovery of the efficient cyclic imide forming reaction between *o*-diiodoaromatic compounds and primary amines prompted us to investigate this reaction as a direct route to fully imidized polyimides. First, we extended the phthalimide reactions to model compounds **1** and **2** to demonstrate that bis-imides could be prepared. The conditions used were those that were optimized in our model phthalimide study [3]. The reaction between *o*-diiodobenzene and *m*-phenylene diamine (Eq. 3) produced bis-imide **1** in 63% isolated yield. As in the model study, GC analysis of the reaction mixture showed only the expected phthalimide, free of any products from side reactions.

In order to prepare bis-imide **2** or to prepare polymers via this chemistry, tetraiodo compounds were required with two sets of *o*-diiodo groups. Examples of these compounds were prepared by the direct iodination of benzene and *p*-xylene as described by Mattern [4]. The reaction of 1,2,4,5-tetraiodobenzene with *m*-toluidene (Eq. 4) gave **2** in 85% unoptimized yield and, as before, the reaction was free from any side products as determined by GC.



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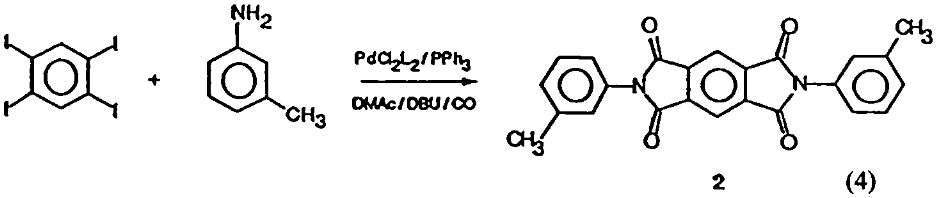

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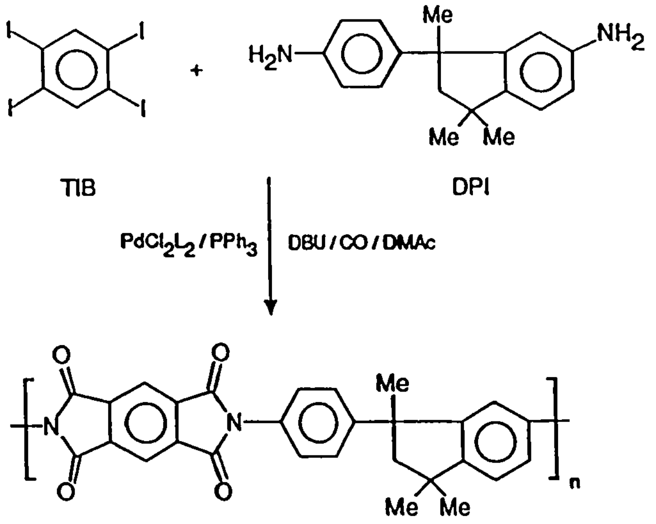
Since fully imidized polymers are produced via this method, it was necessary to choose comonomers that form polyimides soluble in the polymerization solvent, *N*,*N*-dimethylacetamide (DMAc). We found that 1,2,4,5-tetraiodobenzene (TIB) was the most readily available tetraiodo compound for polymerization studies. Since the TIB in this reaction leads to a pyromellitic dianhydride replacement in the backbone, a very rigid insoluble polymer is formed with common diamines such as oxydianiline. In order to impart solubility to the polymer, a flexible diamine such as 5-amino-3-(4-aminophenyl)-1,1,3-trimethylindane (DPI) was used.

In an initial experiment, TIB was allowed to react with DPI in DMAc at 115°C under 95 psi CO in the presence of 6% $PdCl_2L_2$ and 12% PPh_3 (Eq. 5). After 24 h the reaction mixture was moderately viscous. The polymer solution was filtered and precipitated twice into methanol and dried. The inherent viscosity of **3** was 0.56 dL/g in DMAc. A portion of the polymer was cast on glass as a DMAc solution. After drying overnight at 100°C a dark film had formed. Tables 1, 2, and 3 (entry 1) show some of the characteristics of this polyimide.



3

(5)

The M_w of this polymer was found to be 281,000 but the M_n was much smaller by a factor of 16. The SEC trace (Fig. 1) indicates the material was trimodal with a very broad polydispersity. Infrared analysis of the polymer (Fig. 2) showed a doublet at 1778 and 1726 cm^{-1} and an absorbance at 1371 cm^{-1} characteristic of the phthalimide group. The

TABLE 1. Polymerization Reactions of Tetraiodoaromatics with Diamines

Entry	Ioda[a]	Amine[b]	η_{inh}	Yield, %	M_w[c]	M_n[c]	Iodine, wt%
1	TIB	DPI	0.56	95	281,000	17,000	0.12
2	TIB	DPI	–	86	115,000	12,600	8.6
3	TIB	DPI	–	88	57,600	9,200	0.08
4	TIB	DPI	–	Extensive crosslinking			0.22
5	TIX	DPI	–	128	4,100	2,600	2.1
6	$TiSO_2$	DPI	0.09	55	12,600	5,700	0.05
7	TIB	Bis-P	–	25	4,300	3,300	28.0
8	TIB	C_6	0.42	79	13,200	5,900	0.01

[a] TIB = 1,2,4,5-tetraiodobenzene; TIX = 2,3,5,6-tetraiodoxylene; $TiSO_2$ = 3,3′,4,4′-tetraiododiphenylsulfone.

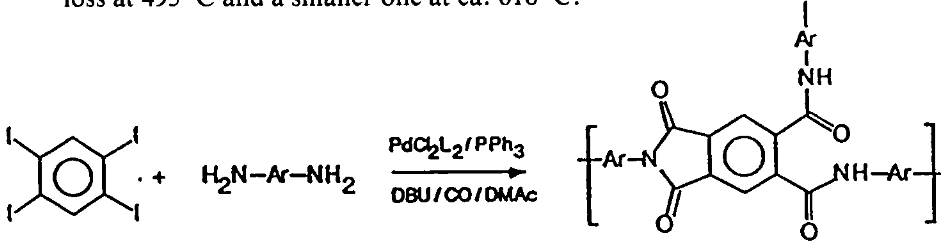
[b] DPI = 5-amino-3-(4-aminophenyl)-1,1,3-trimethylindane; Bis-P = 1,4-[2-(4-aminophenyl)-2-propyl]benzene; C_6 = 1,6-diaminohexane.

[c] Polystyrene equivalent molecular weights.

presence of amide bonds was also noted by the absorbance at 1675 cm^{-1} (Table 3).

The polydispersity of the sample and the amide linkages suggested that a competing side reaction leading to branching was present. This could be explained by the reaction of the TIB not as a difunctional monomer but as a tri- or tetrafunctional one capable of forming amide bonds (Eq. 6). Other side reactions are possible but our studies to date do not permit us to discriminate among these other possibilities.

Thermal data (Table 2, Entry 1) showed a major weight loss at 480°C with a subsequent smaller one at ca. 600°C. This is similar to that found for a polyimide sample with the same viscosity (η_{inh} = 0.56 dL/g) prepared by a conventional process which showed the onset major weight loss at 495°C and a smaller one at ca. 610°C.



(6)

TABLE 2. Thermal Data for Polyimides. TGA in N_2

Entry	Decomposition onsets in °C	% weight loss	Residue at 1000°C, %
1	481 (30.3)	606 (10.6)	43.9
2	355 (21.7)	495 (20.9)	53.1
3	203 (17.6)	513 (12.2)[a]	55.2
4	212 (12.9)	499 (11.1)[b]	59.1
5	238 (9.9)	372 (26.6)[c]	40.3
6	233 (7.8)	432 (56.3)	31.0
7	193 (1.4)	305 (66.8)	28.1
8	285 (6.4)	451 (54.7)	36.1

[a] A third transition was seen at 610°C with 12.8% weight loss.
[b] A third transition was seen at 581°C with 11.3% weight loss.
[c] A third transition was seen at 500°C with 16.6% weight loss.

Removal of the additional phosphine ligand from the reaction mixture (Table 1, Entry 2) resulted in a drop in M_w and an increase in residual iodine content of the polymer. Repeating entry 1 twice more (Table 1, Entries 3 and 4) gave materials with low iodine content. This indicated more complete reaction of the aryl-iodine bonds but not in a reproducible manner. Entries 2–4 also exhibited much lower decomposition onset

TABLE 3. FTIR Analysis of Polyimides (values in cm^{-1})

Entry	N—H	C=O imide	C=O amide	C—N imide	Other
1	3426	1778, 1726	1628	1371	
2	3391	1777, 1724	1671	1376	
3	3423	1777, 1726	1676	1371	
4	3420	1777, 1725	1675	1371	
5	3417	1766, 1714	1673[a]	1379	
6	3375	1780, 1724	1661	1322	1155 (SO_2)
7	3384	1766, 1714	1670	1320	
8	3404	1771, 1714	[b]	1394	

[a] A weak shoulder was seen.
[b] No amide bond was detected.

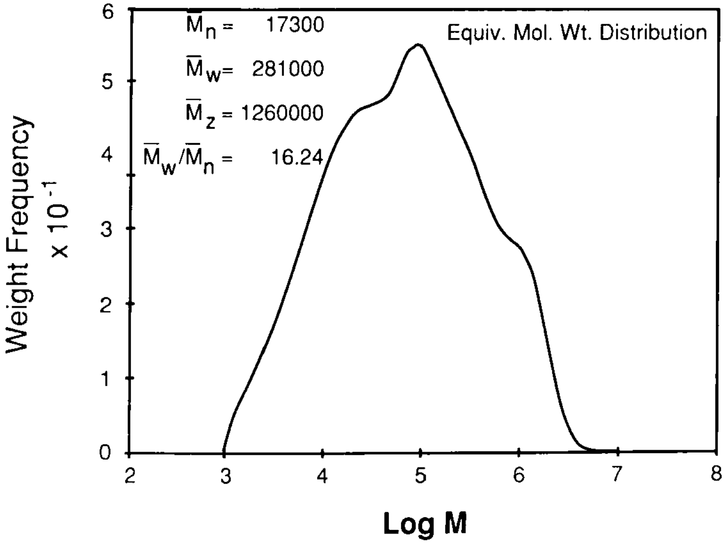


FIG. 1. SEC of polyimide **3**.

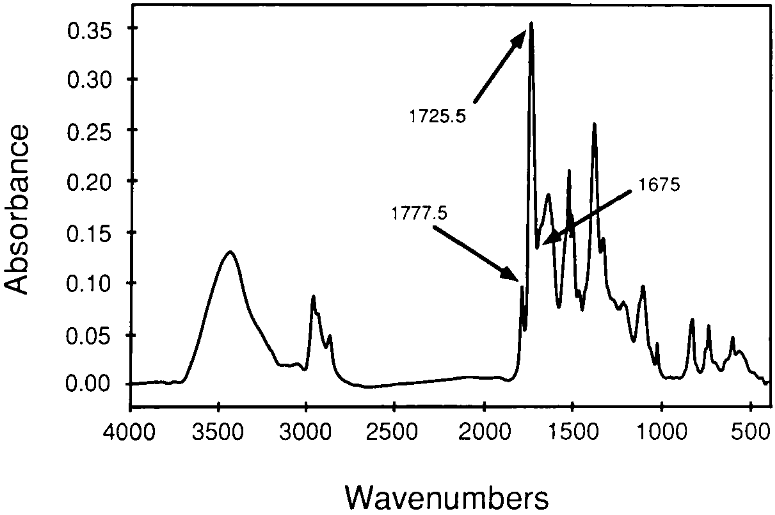
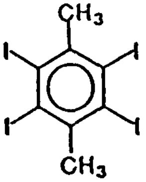


FIG. 2. FTIR of polyimide **3**.

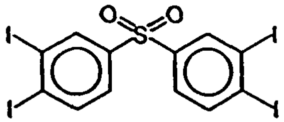
temperatures which supported the SEC evidence of lower molecular weights.

The reaction of DPI with other tetraiodo monomers such as the xylyl derivative TIX (Table 1, Entry 5) and sulfone $TISO_2$ (Table 1, Entry 6) gave low molecular weight polymers with more narrow dispersities. The large amount of iodine remaining in the sulfone polymer accounted for greater than theoretical yield.

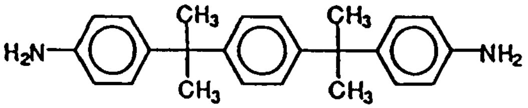
A low yield of iodine rich oligomeric material was isolated when the diamine was changed to Bis-P (Table 1, Entry 7). Residual iodine of 28% corresponds to a dimer. When the aliphatic diamine C_6 was used with TIB, the solution viscosity increased. After precipitation, most of the material was insoluble in DMAc. The soluble fraction showed only modest molecular weight build-up.



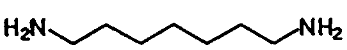
TIX



TISO2



Bis-P



C_6

CONCLUSION

We have demonstrated a new reaction for the preparation of polyimides that is based on the palladium-catalyzed carbonylation, condensation, and cyclization of tetraiodoaromatic compounds and primary diamines. At this time the chemistry appears to have several limitations in its efficacy for preparing high molecular weight polyimides. The polymerization reaction was found to be less efficient than the corresponding model compound reactions in forming the imide linkages. A significant number of amide units were identified via infrared, and a very broad multimodal polydispersity was observed. Double amide group formation is proposed as the most probable side reaction. This side reaction is believed to lead to branched polymer and to significantly lower the degree of polymerization by disturbing the monomer feed stoichiometry. A second factor limiting the scope of the polymerization reaction is the difficulty in obtaining bis(*o*-diiodoaromatic) compounds. Further studies to optimize the formation of linear high molecular weight polyimides by this and related methods are in progress.

ACKNOWLEDGMENTS

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