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# ISOMERIC OXYDIPHTHALIC ANHYDRIDE POLYIMIDES

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## INTRODUCTION

The objective of this structure-property study was to investigate the effect of isomeric attachment of the three oxydiphthalic anhydride (ODPA) polyimides on various polymer properties such as film forming ability, glass transition temperature ( $T_g$ ), crystallinity and thermooxidative stability. Polyimides were prepared from these three anhydrides and characterized by various methods. Polyimides containing the 4,4'-ODPA isomer are known<sup>1,2</sup>; however, the synthesis and polymerization of the 3,3'-ODPA and 3,4'-ODPA isomers have not yet been reported.

## EXPERIMENTAL

Chemicals were received from commercial sources except the 3,4'-ODPA and 1,3-bis (4-aminophenoxy-4'-benzoyl)benzene which were synthesized in-house. See Figure 1 for the structures of the

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dianhydrides and Figures 2 and 7 for the diamine structures. The name, acronym, source, DTA maximum melting point and method of purification are as follows: 2,3,2',3'-oxydiphthalic anhydride (3,3'-ODPA), experimental sample from Occidental Chemical Corporation, 237°C, recrystallized from acetic anhydride; 3,4,3'4'-oxydiphthalic anhydride (4,4'-ODPA), experimental sample purchased from Occidental Chemical Corporation, 221°C, used as received; 4,4'-bis(3-aminophenoxy)benzophenone, Mitsui Toatsu Chemical Corporation, 141°C, used as received; 3,3'-diaminobenzophenone (3,3'-DABP), Ash Stevens, Inc., 151°C, used as received; 3,3'-diaminodiphenylsulfone (3,3'-DDSO<sub>2</sub>), FIC Corporation, 173°C, recrystallized from water; 4,4'-oxydianiline (4,4'-ODA), Kennedy and Klim, Inc., 187°C, used as received; p-phenylenediamine (p-PDA), Aldrich Chemical Corporation, 136°C, used as received; N,N-dimethylacetamide (DMAc), used as received from Fluka Chemical Corporation; 1,3-bis(4-aminophenoxy-4'-benzoyl)benzene (1,3-BABB),<sup>3</sup> experimental sample prepared by Dr. Steve Havens of this laboratory, 165°C, used as received; 1,4-bis(3-aminophenoxy-4'-benzoyl)benzene, Mitsui Toatsu Chemical Corp., 156°C, used as received; and 1,3-bis(3-aminophenoxy-4'-benzoyl)benzene, Mitsui Toatsu Chemical Corp., 148°C, used as received. 2,3,3',4'-Oxydiphthalic anhydride (3,4'-ODPA) was synthesized via the following method. (Figure 3)

#### 4-Hydroxy-N-ethylphthalimide

4-Hydroxyphthalic anhydride was prepared from 4-hydroxyphthalic acid (Lancaster Synthesis, Ltd., England) in 88% yield by heating in a vacuum oven 0.75 h at 180°C, then slowly cooled

overnight. A small amount of product sublimed onto the glass wall of the oven. The m.p. was 162°C. Lit. reports m.p. 171-3°C.<sup>4</sup>

4-Hydroxyphthalic anhydride (5.48 g, 0.0334 mol) and ethylamine (2.22 ml, 0.0337 mol) were refluxed for 2 h in 30 ml DMAc. On cooling the product was precipitated in a blender from deionized water, filtered, reslurried in additional water and vacuum dried to afford 4.86 g (76.1%), m.p. 194°C. (DTA onset m.p.) Anal. Calcd. for C<sub>10</sub>H<sub>9</sub>NO<sub>3</sub>: C, 62.82; H, 4.74; N, 7.33. Found: C, 62.83; H, 4.70; N, 7.33%. FTIR (KBr): 3279 (phenolic OH); 3063 (aromatic C-H); 2986 (aliphatic C-H); 1762 and 1688 (imide I doublet); 1384 (imide II); 1078 (imide III); 720 cm<sup>-1</sup> (imide IV).

3-Fluorophthalic anhydride was prepared by reacting 3-nitrophthalic anhydride with Cl<sub>2</sub> in the melt, followed by fluorination of the resulting 3-chlorophthalic anhydride with anhyd. KF.<sup>5</sup> The melting points of the 3-chloro- and 3-fluorophthalic anhydrides were 125°C and 157°C respectively.

#### 2,3,3',4'-Oxydiphthalic Anhydride (3,4'-ODPA)

4-Hydroxy-N-ethylphthalimide (4.60 g, 0.0241 mol) and aqueous NaOH (1.90 g, 0.0241 mol of 50.7%) were heated with 30 ml DMSO and 35 ml toluene. A Dean-Stark trap was used to remove the toluene-water azeotrope for 2 h until clear. After cooling to room temperature 3-fluorophthalic anhydride (4.00 g, 0.0241 mol) was added and the resulting solution was heated for 1 h at 73-75°C, then 1 h at 90-95°C before precipitation from water in a blender. Vacuum drying afforded 3.58 g (44.1%) of unrecrystallized anhydride-imide, DTA m.p. 197°C (slightly broad). IR (KBr): 1852 and 1790 (anhydride doublet); 1772 and 1710 (imide I doublet); 1260 cm<sup>-1</sup> (aryl ether). No carboxylic

acid absorption was detected. The entire sample was hydrolyzed in a refluxing solution of 6.66 g of 50.7% aqueous NaOH and 25 ml water for 20 h and filtered cold. The filtrate was acidified with excess 6N HCl and a white colloidal product was removed by centrifugation and rinsed with a small amount of water. Two additional crops were taken after the filtrate was evaporated under the hood for several weeks.

Vacuum drying at 110°C afforded 3.65 g (45.0%) of crude tetracarboxylic acid, m.p. 198-213°C (visual). IR (KBr): 2300-3500 (-CO<sub>2</sub>H dimer); 1692 (carboxylic carbonyl); 1288 cm<sup>-1</sup> (arom. ether). Cyclization with acetic anhydride toluene for 1 h at reflux afforded 3,4'-ODPA in 65.5% yield, m.p. 170°C. Anal. Calcd. for C<sub>16</sub>H<sub>6</sub>O<sub>7</sub>: C, 61.95; H, 1.95; O, 36.11. Found: C, 61.83; H, 2.13; O, 36.33%. FTIR (KBr): 1852, 1777 (anhyd. carbonyl); 1257 cm<sup>-1</sup> (arom. ether).

### Polymer Synthesis

Polymerizations were conducted at 15% solids in DMAc. The diamine was dissolved in the DMAc in an oven-dried serum bottle. Stirring was accomplished with a magnetic stirrer. Anhydride was added to the dissolved diamine, and the solution was allowed to stir at room temperature (RT) overnight (Figure 4). The poly(amic acid) was cast on a soda-lime glass plate at approximately 20 mil wet thickness, dried at RT to a tack-free film in a dust proof chamber and cured in a forced air oven 1 h each at 100°C, 200°C, and 300°C unless otherwise indicated. Cooled films were removed from plates using a razor blade.

### Characterization Methodology

Inherent viscosities were determined for the poly(amic acid) solutions in DMAc at 0.5% (wt./vol.) and 35°C. Differential scanning calorimetry (DSC) was performed on fully imidized films using a

DuPont 990 Thermal Analyzer at 20°C/min. Torsional braid analysis (TBA) was conducted at a heating rate of 3°C/min in air over the temperature range 50°C to 400°C.

Films were characterized as "creasable" when they could withstand a 180° fold followed by a 360° fold with a finger crease; "brittle" films snapped or tore at the crease line. Those that could not be removed from the glass plate in one piece were termed "brittle pieces."

Imidized films were tested for solubility at RT at approximately 1% by weight in methylene chloride, DMAc, and m-cresol. Films that were insoluble at 25°C in these solvents after several hours were also tested at the boiling point of each solvent for 15 minutes.

Wide Angle X-ray Scattering (WAXS) was performed on a Philips APD 3600, XRG 3100 at 45 kV and 40 mA using copper radiation with a flat sample holder and a graphite monochromator. Isothermal thermogravimetric analysis (ITGA) was performed on a Perkin Elmer TGS-2 thermogravimetric system at 325°C in flowing air for 100 h. Thermogravimetric analysis (TGA) was performed at a programmed heating rate of 2.5°C/min from 100°C to about 610°C.

## RESULTS AND DISCUSSION

Table I lists the inherent viscosities of the various polymer systems,  $T_g$  of the imidized films by DSC and film characteristics. The 3,3'-ODPA polyimides produced brittle films, while inherent viscosities of the corresponding poly(amic acids) ranged from 0.23 to 0.59 dl/g. Glass transition temperatures ranged from 198°-294°C. All

of these films examined by WAXS were amorphous. Three of the 3,4'-ODPA polyimides produced creasable films and the corresponding poly(amic acids) had viscosities of 0.97 to 1.45 dl/g. Two films were brittle and lower viscosities, 0.35 and 0.55 dl/g, were observed for these poly(amic acids). The 3,4'-ODPA-p-PDA polyimide film required a cure to 350°C in air to complete imidization. Glass transition temperatures were higher than in the corresponding 3,3'-ODPA polyimides and ranged from 207°C to 313°C. All of these films examined by WAXS were amorphous. The 4,4'-ODPA polyimide films were all creasable when fully imidized and the corresponding poly(amic acid) viscosities ranged from 0.34 to 0.95 dl/g. Glass transition temperatures which ranged from 204°C to 268°C showed an increase from the 3,3'-ODPA and 3,4'-ODPA polyimides in all but two cases, however, this may be a function of molecular weight as these two poly(amic acids) had unusually high viscosities. No  $T_g$  was observed by DSC or TBA for the 4,4'-ODPA-p-PDA polyimide, which was semicrystalline by WAXS.

Table II contains solubility data of the isomeric ODPA polyimides in three solvents. The 3,3'-ODPA polyimides appear to be the most soluble and the 4,4'-ODPA polyimides appear the least soluble.

The 100 h, 325°C isothermal thermogravimetric analysis (ITGA), of the three isomeric ODPA polyimides polymerized with 4,4'-bis(3-aminophenoxy)benzophenone (similar viscosities) is presented in Figure 5. The 3,3'-ODPA and 3,4'-ODPA polyimides showed 8.07% and 8.37% weight loss, respectively, after 100 h compared with the 4,4'-ODPA polyimide which experienced only 3.64% weight loss.

Dynamic TGA (Figure 6) showed a similar weight loss correlation to the ITGA curves. Once again the 4,4'-ODPA polyimide appeared most thermooxidatively stable.

Three additional polymers were synthesized using 3,3'-ODPA and three longer chain bis(aminophenoxy benzoyl)benzene isomers (Figure 7 compounds A, B and C). Two of these polyimides gave films that were creasable, indicating higher molecular weight. The inherent viscosities of these two poly(amic acids) were 0.82 and 0.48 dl/g, respectively. Cured films exhibited  $T_g$ s at 214°C and 194°C, respectively. However, the polyimide film synthesized from 1,4-bis(3-aminophenoxy-4'-benzoyl)benzene produced a brittle film. The inherent viscosity of its poly(amic acid) was 0.58 dl/g and the cured film had a  $T_g$  of 197°C. The long chain nature of the diamine seems to be an important component in producing high molecular weight creasable films in the 3,3' ODPA system.

## SUMMARY AND CONCLUSIONS

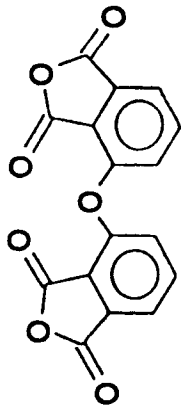
Two isomers of ODPA were procured as experimental samples, and one was synthesized in house for a structure - property study. Evaluation of polymers synthesized from the three isomers of ODPA indicated that all 4,4'-ODPA compositions produced high molecular weight creasable films; other isomeric ODPA compositions containing the 3-substituted ether linkage varied from low to high molecular weight as judged by their solution viscosities and flexibilities. A comparison of  $T_g$ s exhibited no significant trends. Polyimides based on 4,4'-ODPA were the least soluble in a range of organic solvents



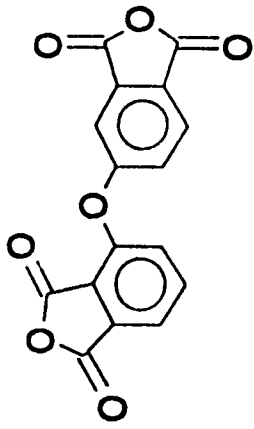
while polyimides based on 3,3'-ODPA were the most soluble. The 4,4'-ODPA/4,4'-bis(3-aminophenoxy)benzophenone polyimide exhibited the highest thermooxidative stability by dynamic TGA and 325°C -ITGA when compared with the other ODPA isomers. Additional polymers synthesized from 3,3'-ODPA and diamines with an increased chain length produced two flexible films.

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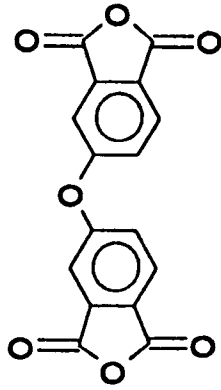
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**2,3,2',3'-oxydiphthalic anhydride  
(3,3'-ODPA)**

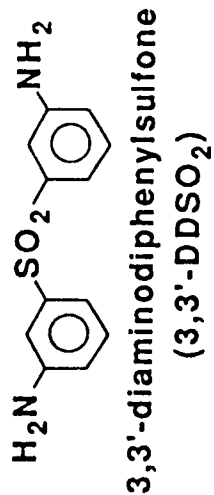


**2,3,3',4'-oxydiphthalic anhydride  
(3,4'-ODPA)**

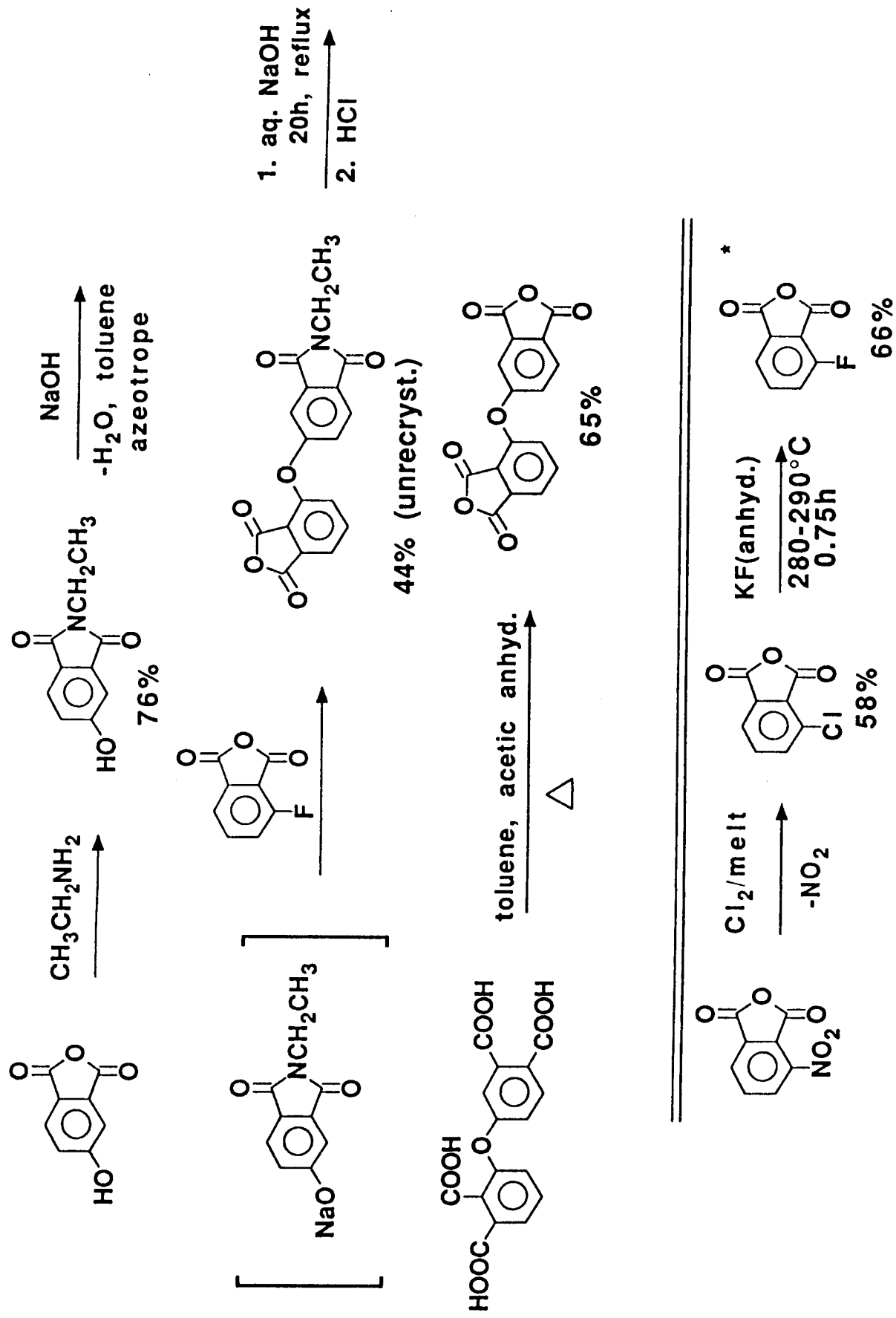


**3,4,3',4'-oxydiphthalic anhydride  
(4,4'-ODPA)**

**Figure 1. ODPA isomer structures.**

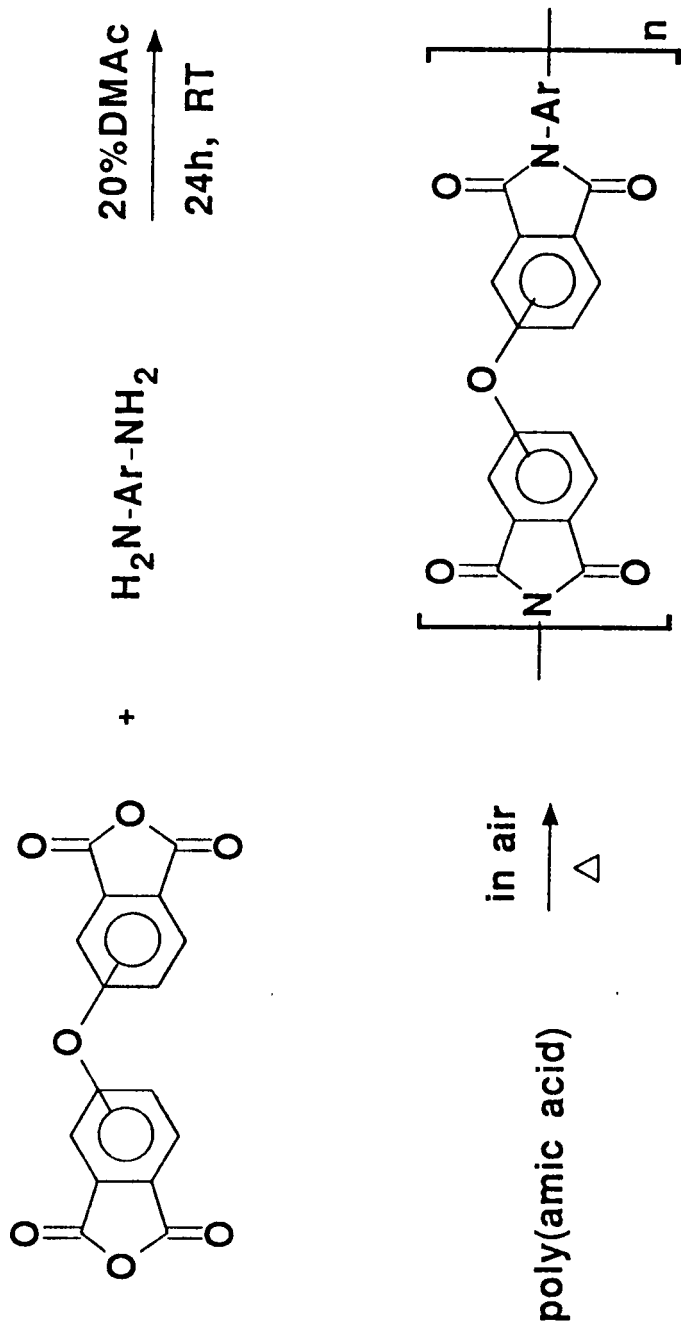


**Figure 2. Diamine structures.**



\*A. Heller, *J. Org. Chem.*, **25**, 834 (1960).

Figure 3. Synthesis of 2,3,3',4'-oxydiphthalic anhydride (3,4'-ODPA).



Films cast 20 mil wet thickness on soda lime glass plates,  
 Heat treated in air 1h at 100°, 200° and 300°C unless otherwise indicated.

Figure 4. Synthesis of ODPA polyimides.

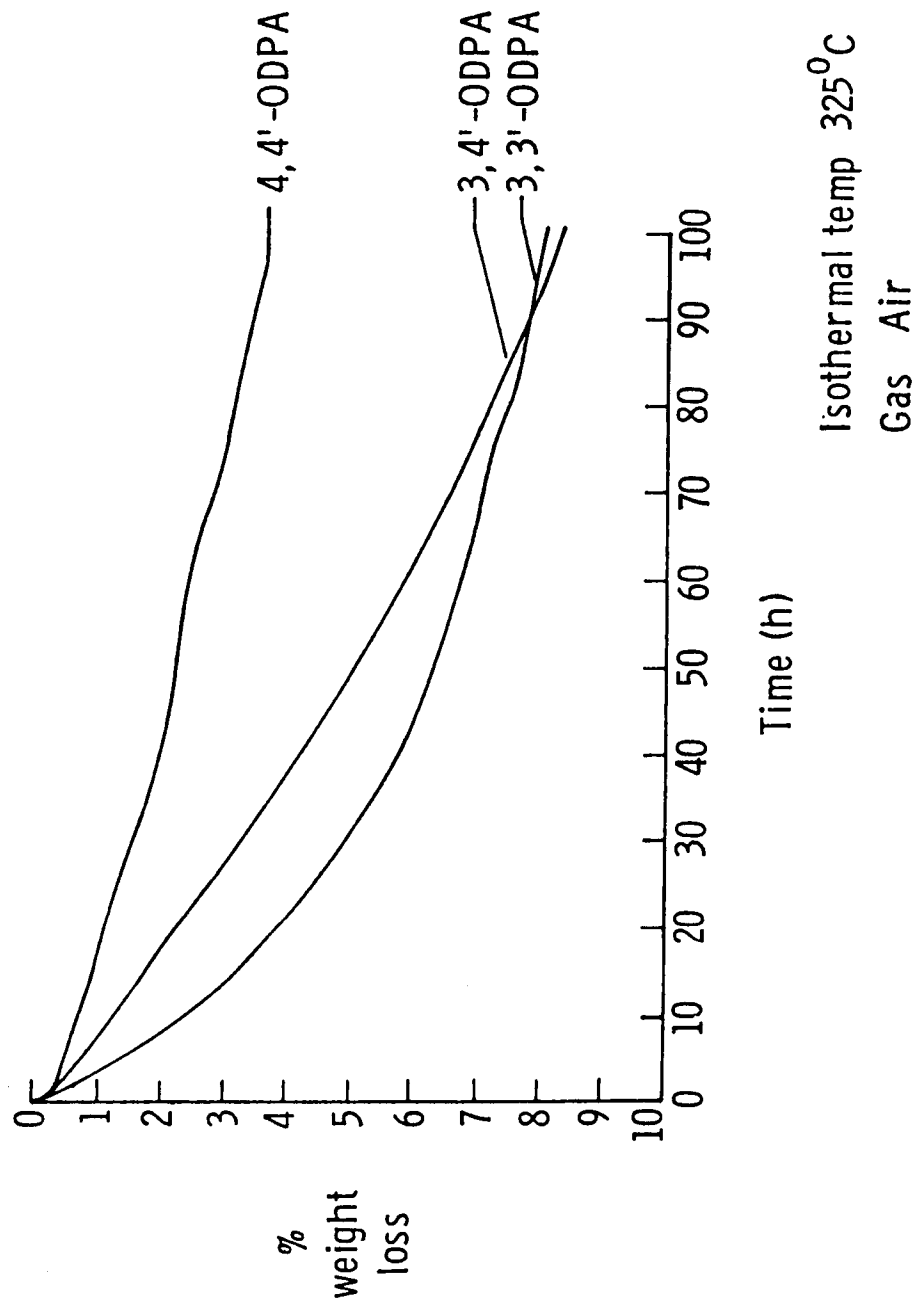


Figure 5. Isothermal thermogravimetric analysis of oxydipthalic anhydride-4,4'-bis(3-aminophenoxy)benzophenone polyimides.

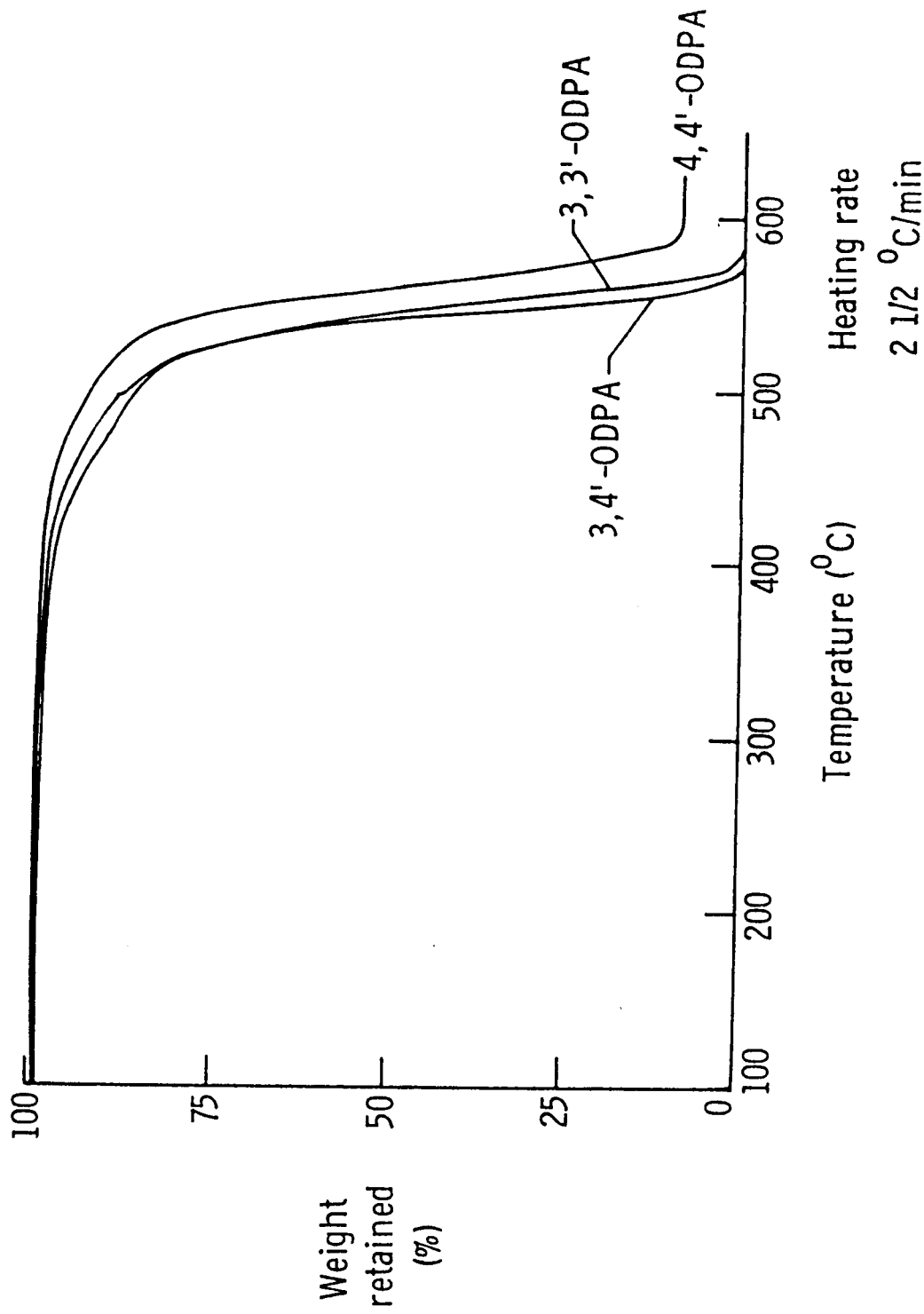
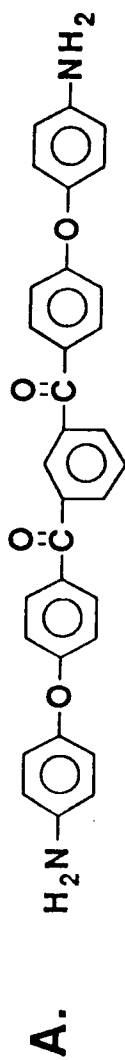
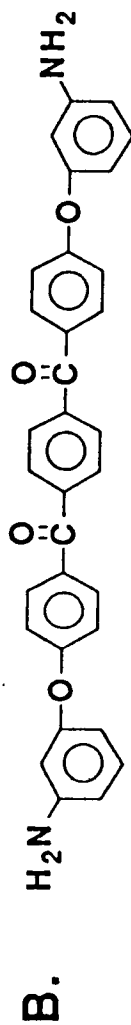


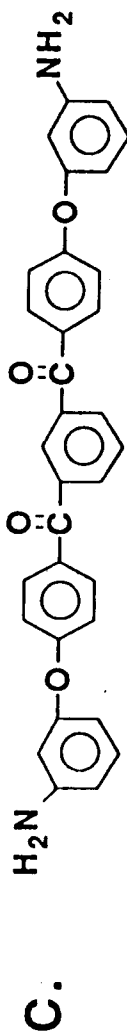
Figure 6. Dynamic thermogravimetric analysis of oxydiphthalic anhydride-4,4'-bis (3-aminophenoxy)benzophenone polyimides.



1,3-bis(4-aminophenoxy-4'-benzoyl)benzene



1,4-bis(3-aminophenoxy-4'-benzoyl)benzene



1,3-bis(3-aminophenoxy-4'-benzoyl)benzene

	$\eta_{inh}$ (dl/g)	T <sub>g</sub> (°C)	Film Nature
<b>A.</b>	0.82	214	creasable
<b>B.</b>	0.58	197	brittle
<b>C.</b>	0.48	194	creasable

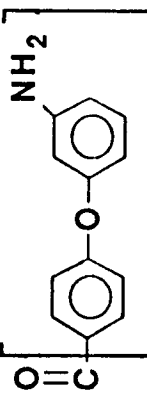
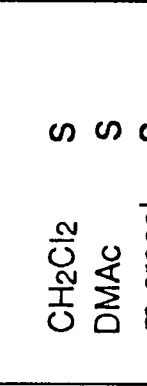
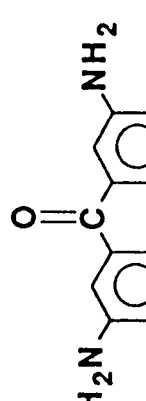
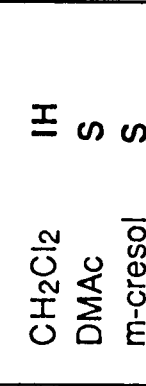
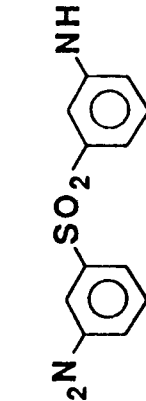
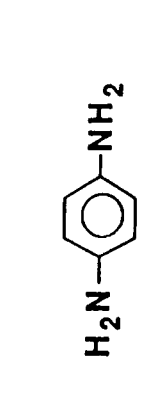
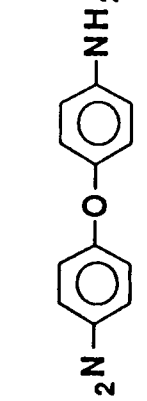
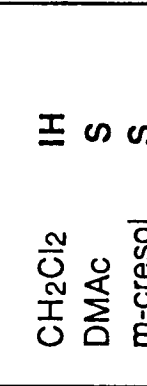
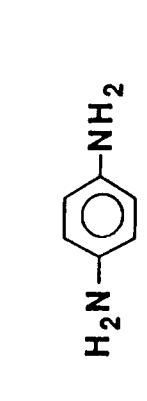
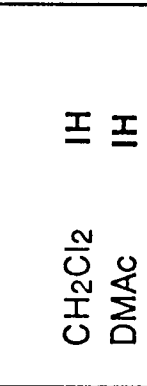
Figure 7. Additional diamines polymerized with 3,3'-ODPA.



DIAMINE	DIANHYDRIDE			
		$\eta_{inh} = 0.52$ dl/g <sup>1</sup> $T_g = 198^\circ\text{C}$ <sup>2</sup> brittle film	$1.14$ $207^\circ\text{C}$ creasable film	
		$0.44$ $234^\circ\text{C}$ brittle pieces	$0.95$ $235^\circ\text{C}$ creasable film	
		$0.23$ $241^\circ\text{C}$ brittle pieces	$0.34$ $253^\circ\text{C}$ creasable film	
		$0.59$ $246^\circ\text{C}$ brittle pieces	$0.82$ $268^\circ\text{C}$ creasable film	
		$0.43$ $294^\circ\text{C}$ brittle pieces	$0.69$ no $T_g$ observed creasable film <sup>3</sup>	

<sup>1</sup> $\eta_{inh}$  35°C, .5%wt/vol in DMAc      <sup>2</sup> $T_g$  by DSC      <sup>3</sup>cured to 350°C

Table I. Characteristics of isomeric ODPA polyimides.

DIAMINE	DIANHYDRIDE		
		S S S	CH <sub>2</sub> Cl <sub>2</sub> DMAC m-cresol
		IH S S	CH <sub>2</sub> Cl <sub>2</sub> DMAC m-cresol
		IH S SH	CH <sub>2</sub> Cl <sub>2</sub> DMAC m-cresol
		IH S S	CH <sub>2</sub> Cl <sub>2</sub> DMAC m-cresol
		IH IH SH	CH <sub>2</sub> Cl <sub>2</sub> DMAC m-cresol

S Soluble at 25°C

SH Soluble at bp. of the solvent

IH Insoluble at the bp. of the solvent

Table II. Solubility of isomeric ODPA polyimide films.

\*Cured to 300°C in air



# Report Documentation Page

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16. Abstract Much of the polyimide research at Langley Research Center has focused on isomeric modification of the diamine component; polyimides having considerably improved processability and adhesion have resulted. The present structure-property study was designed to investigate how isomeric attachment of the three oxydiphthalic anhydride (ODPA) polyimides affects their properties. Each dianhydride, 3,4,3',4'-oxydiphthalic anhydride (4,4'-ODPA, I), 2,3,2',3'-oxydiphthalic anhydride (3,3'-ODPA, II), and 2,3,3',4'-oxydiphthalic anhydride (3,4'-ODPA, III), was reacted with p-phenylenediamine, 4,4'-oxydianiline, 3,3'-diaminodiphenylsulfone, 3,3'-diaminobenzophenone, and 4,4'-bis(3-aminophenoxy)benzophenone in DMAc. The inherent viscosities of the resulting poly(amic acids) were determined. Thermally imidized films were studied for their creasability and solubility, as well as by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and wide angle x-ray scattering (WAXS). A comparison of these properties will be made.					
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