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Polyimides Containing Quinoxaline and Benzimidazole Units

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ABSTRACT: Two new aromatic dianhydrides containing 2,3-quinoxaline and 5,5′-bis(benzimidazole) units were synthesized and used to prepare polyimides. The aromatic nucleophilic substitution reaction of either *N*-phenyl-4-fluorophthalimide or *N*-phenyl-4-nitrophthalimide with the disodium salts of 2,3-bis(4-hydroxyphenyl)quinoxaline or 5,5′-bis[2-(4-hydroxyphenyl)benzimidazole], respectively, in DMSO at 80 °C provided the intermediate 4-substituted *N*-phenylphthalimides. The *N*-phenylphthalimides were hydrolyzed with aqueous sodium hydroxide and subsequently acidified to yield the bis(1,2-dicarboxylic acid)s. Reaction of these compounds with acetic anhydride provided the dianhydrides. Polyimides prepared from these new dianhydrides with various diamines exhibited relatively high glass transition temperatures and good thermal stability. Some of the polyimides formed tough, creasible films with good mechanical properties. Several of the polyimides containing the 5,5′-bis(benzimidazole) group were soluble in DMAc and NMP.

Introduction

Recent reviews on the chemistry of polyimides have revealed a variety of new polyimides with unique properties.[1,2] Many new monomers were synthesized to provide specific properties, such as solubility, improved processability, low dielectric constant and moisture absorption, and high optical transparency, in addition to the good thermal stability expected of polyimides. Usually, novel aromatic diamines were synthesized and reacted with a variety of commercially available dianhydrides. Some of the new diamines contained heterocyclic groups. Heterocycles such as 2,6-pyridine,[3] 2,5- and 2,6-pyrazine,[4] 5,5′-(2,2′-bipyridine),[5] 1,4-piperazine,[6] 2,5-thiophene,[7] 2,3-quinoxaline,[8] 2,5-benzimidazole,[9] and 1,3,4-oxadiazole[10] have been incorporated into diamines which were used to synthesize polyimides. Older literature similarly cites the incorporation of 2,2′-(6,6′-bibenzothiazole),[11] 2,5-benzoxazole,[11,12] 2,2′-(6,6′-biquinoxaline),[13] 2,6-quinoxaline,[14] 2,5-(1,3,4-thiadiazole),[15] 2,5-(1,3,4-oxadiazole),[16] and 2,2′-(5,5′-bibenzimidazole)[16] into the diamine segment of a polyimide. The effect of the heterocyclic unit on the glass transition temperature of the polyimide was variable. However, groups which increased the rigidity of the polyimide backbone or provided strong intermolecular association generally resulted in increased glass transition temperatures.

The list of dianhydrides containing heterocyclic units is smaller, no doubt resulting from their more difficult synthesis as compared with diamines. Dianhydrides containing heterocyclic units such as thianthrene,[17] xanthene,[18,19] phenylquinoxaline,[20] and dibenzo[*b*,*e*][1,4]dioxin[21] have recently been used in the preparation of a variety of polyimides. The older literature reports the use of heterocyclic dianhydrides such as 2,3,5,6-pyrazinetetracarboxylic dianhydride[15] in polyimide formation.

One approach of incorporating a heterocyclic group into a dianhydride uses bis(hydroxyphenyl) heterocyclic compounds which were used to synthesize poly(arylene ether)s.[22–26] These bisphenols were used to prepare bis(ether anhydrides) by aromatic nucleophilic substitution reaction with appropriate substrates. The displacement of the nitro group from *N*-phenyl-3- or 4-nitrophthalimide by a bisphenoxide was of particular interest.[27] In this scheme the resulting *N*-phenylarylenebis(phthalimido) ethers were hydrolyzed to the tetracarboxylic acids which were then converted to the dianhydrides. A more direct route involved the reaction of the arylenebisphenol with 4-fluorophthalic anhydride using potassium fluoride.[28] In this paper we report the use of the former method in conjunction with bis(hydroxyphenyl) heterocyclic compounds to prepare two new dianhydrides. These new dianhydrides were then reacted with a variety of diamines to prepare polyimides.

Experimental Section

Starting Materials. *N*-Phenyl-4-fluorophthalimide (mp 182.5–184 °C) and *N*-phenyl-4-nitrophthalimide (mp 192–193.5 °C) were prepared as described in the literature.[29] 4-Fluorophthalic anhydride (mp 75–76 °C) was used as received from Occidental Chemical Corp. 2,3-Bis(4-hydroxyphenyl)quinoxaline[22] (mp 354 °C), 2,5-(4-hydroxyphenyl)-1,3,4-oxadiazole[25] (mp 349 °C), 2-phenyl-4,5-bis(4-hydroxyphenyl)imidazole[26] (mp 327 °C), 5,5′-bis[2-(4-hydroxyphenyl)benzimidazole][23] (mp 383 °C), and 6,6′-bis[2-(4-hydroxyphenyl)benzoxazole][24] (mp 375 °C) were prepared as previously described. Melting points of these compounds were taken as the onset of the melting endotherm as determined by differential scanning calorimetry (heating rate, 10 °C/min). 1,4-Phenylenediamine (1,4-PDA; mp 139–141 °C) and 1,3-phenylenediamine (1,3-PDA; mp 62.5–64.5 °C) were purified by sublimation. 4,4′-Methylenedianiline (4,4′-MDA; mp 90.5–91.5 °C) was recrystallized from toluene. 4,4′-Oxydianiline (4,4′-ODA; mp 189–190.5 °C) and 1,3-bis(4-aminophenoxy-4′-benzoyl)benzene (1,3-BABB; mp 154–155.5 °C) were used as obtained from Wakayama Seika Kogyo Co., Ltd., and Daychem Laboratories, Inc., respectively. Anhydrous grades of solvents such as *N*,*N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), *N*-methylpyrrolidinone (NMP), and *m*-cresol were purchased and used without further purification.

2,3-Quinoxalinediylbis[*N*-phenyl-4-(4-phenoxy)phthalimide]. Aqueous sodium hydroxide (8.3 mL of a 48.12% w/v solution, 0.10 mol) was added to a solution of 2,3-bis(4-hydroxyphenyl)quinoxaline (15.72 g, 0.050 mol) dissolved in 200 mL of DMSO contained in a three-neck flask equipped with a Dean–Stark trap. Toluene (60 mL) was added and water removed by azeotropic distillation. The mixture was allowed to cool to room temperature (disodium salt precipitated), and *N*-phenyl-4-fluorophthalimide (24.12 g, 0.10 mol) was added. The mechanically stirred mixture was maintained overnight (∼16 h) at 80 °C under a nitrogen atmosphere. Solid began to precipitate after several hours. The reaction mixture was allowed to cool.

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Table 1. Yields of Heterocyclic Containing *N*-Phenylphthalimides

leaving group	reaction temp, °C	crude yield (recryst.), %			
		2,3-quinoxaline	2,5-(1,3,4-oxadiazole)	5,5′-bis(benzimidazole)	6,6′-bis(benzoxazole)
F	80	77 (67)	73 (62)	63	96 (74)
F	100	57 (52)	35 (32)		
NO_2	80	16 (12)	49 (44)	59	
NO_2	100	45 (39)	68 (55)		

The solid was collected by filtration, washed with DMSO and with methanol, and dried at 200 °C to afford 30.1 g of crude material. Recrystallization from DMAc followed by drying at 200 °C afforded 2,3-quinoxalinediylbis[*N*-phenyl-4-(4-phenoxy)phthalimide] (25.4 g, 67% yield) as a white solid (Table 1); visual mp 287–288 °C. IR (KBr): 1774 (m, sharp), 1722 and 1703 cm^{-1} (vs) (imide carbonyls).

Anal. Calcd for $C_{48}H_{28}N_4O_6$: C, 76.18; H, 3.73; N, 7.40. Found: C, 76.49; H, 3.68; N, 7.44.

2,5-(1,3,4-Oxadiazolediyl)bis[*N*-phenyl-4-(4-phenoxy)phthalimide]. 2,5-(1,3,4-Oxadiazolediyl)bis[*N*-phenyl-4-(4-phenoxy)phthalimide] was similarly prepared using 2,5-bis(4-hydroxyphenyl)-1,3,4-oxadiazole at a reaction temperature of 80 °C. Recrystallization from DMAc followed by drying at 200 °C provided a 62% yield of white solid; mp 337 °C (onset of sharp DSC endotherm). IR (KBr): 1780 (m, sharp), 1717 cm^{-1} (vs, sharp) (imide carbonyls).

Anal. Calcd for $C_{42}H_{24}N_4O_7$: C, 72.41; H, 3.47; N, 8.04. Found: C, 72.72; H, 3.84; N, 8.02.

5,5′-Bis[4-(2-benzimidazolyl-4′-phenoxy)phthalimide]. 5,5′-Bis[*N*-phenyl-4-(2-benzimidazolyl-4′-phenoxy)phthalimide] was similarly prepared using 5,5′-bis[2-(4-hydroxyphenyl)benzimidazole] and *N*-phenyl-4-fluorophthalimide at a reaction temperature of 80 °C. This compound was obtained as a pale yellow solid at a crude yield of 63% and used without further purification; mp 379 °C (onset of sharp DSC endotherm). IR (KBr): 3390 (w, br, NH), 1775 (m, sharp), 1722 cm^{-1} (vs, sharp) (imide carbonyls).

Anal. Calcd for $C_{54}H_{32}N_6O_6$: C, 75.34; H, 3.75; N, 9.76. Found: C, 75.26; H, 4.15; N, 10.04.

6,6′-Bis[*N*-phenyl-4-(2-benzoxazolyl-4′-phenoxy)phthalimide)]. 6,6′-Bis[*N*-phenyl-4-(2-benzoxazolyl-4′-phenoxy)phthalimide] was similarly prepared using 6,6′-bis[2-(4-hydroxyphenyl)benzoxazole] and *N*-phenyl-4-fluorophthalimide at 80 °C. This compound precipitated from the DMSO reaction mixture to give a crude yield of 96%. Recrystallization from NMP provided a 74% yield of white solid; mp 386 °C (onset of sharp DSC endotherm). IR (KBr): 1769 (m, sharp), 1726 (vs, sharp) (imide carbonyls).

Anal. Calcd for $C_{54}H_{30}N_4O_8$: C, 75.17; H, 3.50; N, 6.49. Found: C, 74.98; H, 3.58; N, 6.54.

2,3-Quinoxalinediylbis[4-(4-phenoxy)phthalic acid]. 2,3-Quinoxalinediylbis[*N*-phenyl-4-(4-phenoxy)phthalimide] (26.49 g, 0.035 mol) was added to a stirred solution of sodium hydroxide (11.20 g, 0.28 mol) dissolved in 80 mL of water. The suspension was heated at a reflux under an atmosphere of flowing nitrogen until the collection of aniline in a Dean–Stark trap ceased. The solution was allowed to cool, then filtered, and slowly added to 90 mL of concentrated hydrochloric acid to precipitate a solid. The solid was collected by fitration, washed with water, and dried at 100 °C to provide 2,3-quinoxalinediylbis[4-(4-phenoxy)phthalic acid] (22.3 g, 99% yield) as a yellow solid; visual mp 219–222 °C. IR (KBr): 2900 (m, br, OH), 1724 and 1691 cm^{-1} (C═O).

Anal. Calcd for $C_{36}H_{22}N_2O_{10}$: C, 67.29; H, 3.45; N, 4.36. Found: C, 67.20; H, 3.64; N, 4.40.

5,5′-Bis[4-(2-benzimidazolyl-4′-phenoxy)phthalic acid]. 5,5′-Bis[*N*-phenyl-4-(2-benzimidazolyl-4′-phenoxy)phthalimide] (8.61 g, 0.010 mol) was added to a stirred solution of sodium hydroxide (6.40 g, 0.16 mol) dissolved in 100 mL of water. DMSO (25 mL) was added and the mixture heated at reflux for approximately 16 h, and the condensate collected in a Dean–Stark trap. The cool solution was filtered and the filtrate slowly added to excess hydrochloric acid solution. The precipitated solid was collected by filtration, washed with water, and redissolved in aqueous sodium hydroxide (2.4 g, 0.060 mol). The solution was filtered, reprecipitated into an excess of a hydrochloric acid solution, collected by filtration, washed with water, and dried at 125 °C to provide 5,5′-bis[4-(2-benzimidazolyl-4′-phenoxy)phthalic acid] (7.1 g, 95% yield) as a yellow solid; mp 263 °C (onset of broad DSC endotherm). IR (KBr): 3425 (m, NH), 2900 (m, br, OH), 1713 and 1700 cm^{-1} (C═O).

Anal. Calcd for $C_{42}H_{26}H_4O_{10}$: C, 67.56; H, 3.51; N, 7.50. Found: C, 66.53; H, 3.65; N, 7.43.

2,3-Quinoxalinediylbis[4-(4-phenoxy)phthalic anhydride]. A magnetically stirred mixture of 2,3-quinoxalinediylbis[4-(4-phenoxy)phthalic acid] (12.85 g, 0.020 mol), glacial acetic acid (40 mL), and acetic anhydride (20 mL, 0.21 mol) was heated at reflux for 4 h. The solution was filtered hot and allowed to cool. The crystallized solid was collected by filtration and recrystallized from 3:1 glacial acetic acid/acetic anhydride to provide 2,3-quinoxalinediylbis[4-(4-phenoxy)phthalic anhydride] (9.6 g, 79% yield) as a pale yellow solid; visual mp 184.5–185.5 °C, after drying under vacuum at 165 °C. IR (KBr): 1851 and 1769 cm^{-1} (s and vs, sharp, C═O).

Anal. Calcd for $C_{36}H_{18}N_2O_8$: C, 71.29; H, 2.99; N, 4.62. Found: C, 71.69; H, 3.35; N, 4.57.

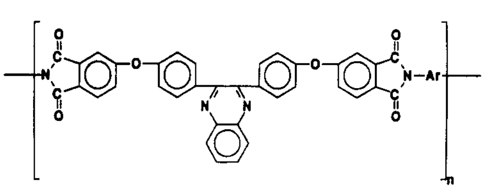
5,5′-Bis[4-(2-benzimidazolyl-4′-phenoxy)phthalic anhydride]. A magnetically stirred mixture of 5,5′-bis[4-(2-benzimidazolyl-4′-phenoxy)phthalic acid] (9.33 g, 0.0125 mol), DMAc (95 mL), and acetic anhydride (75 mL, 0.97 mol) was heated at reflux for 3 h. The solid dissolved after sufficient distillate (~40 mL) was removed using a Dean–Stark trap. The solution was filtered hot and most of the solvent removed under vacuum. Acetic anhydride (~50 mL) was added to the residue, and the mixture was heated to form a crystalline precipitate. The mixture was cooled, and the solid was collected by filtration and dried under vacuum at 200 °C to yield 5,5′-bis[4-(2-benzimidazolyl-4′-phenoxy)phthalic anhydride] (6.9 g, 77% yield) as a yellow solid; mp 359 °C (onset of DSC endotherm). IR (KBr): 3442 (s, NH), 1845 and 1773 cm^{-1} (m and vs, sharp, C═O).

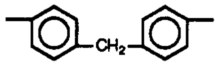
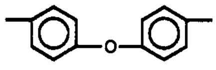
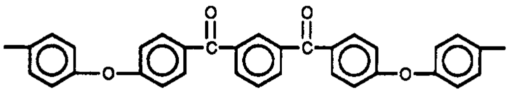
Anal. Calcd for $C_{42}H_{22}N_4O_8$: C, 70.99; H, 3.12; N, 7.88. Found: C, 69.71; H, 3.66; N, 7.60.

Polymer Synthesis. Polyamide acids containing the 2,3-quinoxaline unit were prepared at a concentration of 15% solid (w/w) by the addition of a stoichiometric amount of 2,3-quinoxalinediylbis[4-(4-phenoxy)phthalic anhydride] to a mechanically stirred solution of the diamine in DMAc under a nitrogen atmosphere at room temperature. Polymerization solutions were stirred overnight, and inherent viscosities (η_{inh}) at 0.5% (w/v) concentration were subsequently determined at 25 °C (Table 2). The polyamide acids were centrifuged, the decantate was cast onto plate glass using a blade set at 0.76 mm (30 mil), and the films were allowed to dry to a tack-free state in a dust-free, low-humidity chamber. The films on the glass plates were then thermally converted to the polyimide by heating in air at 100, 200, and 300 °C for 1 h at each temperature, followed by slow cooling to room temperature. Removal of the cured films from the plates was aided by immersion in hot water. Mechanical properties of the 0.050–0.064 mm (2.0–2.5 mil) thick films were determined according to ASTM D882 using four to five specimens per test condition.

Polyimides containing the 5,5′-bis(benzimidazole) unit were prepared by the reaction of stoichiometric quantities of 5,5′-bis[4-(2-benzimidazolyl-4′-phenoxy)phthalic anhydride] with the various diamines in *m*-cresol at 7% concentration (w/w). Toluene and a catalytic amount of isoquinoline were added, and the mechanically stirred mixture was heated at reflux for several hours under nitrogen, while water was removed using a Dean–Stark trap. Toluene was removed and the mixture maintained at 190–200 °C for 4 h. After cooling, the reaction mixture was filtered and the filtrate added to methanol in a blender to precipitate the polyimide. The polyimide was collected by filtration, stirred in hot methanol, recollected, washed with methanol, and dried under vacuum at 200 °C. Inherent viscosities (η_{inh}) of the soluble polyimides were determined at 0.5% (w/v)

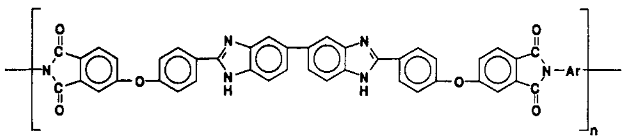
Table 2. Properties of Polyamide Acids and Polyimides Containing the 2,3-Quinoxaline Unit

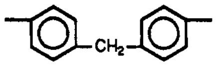
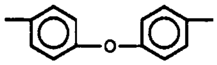
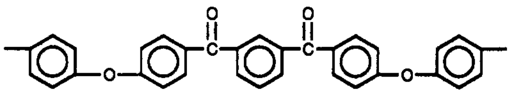


Ar	η_{inh}, dL/g	polyimide		
		T_g, °C	T_m,[a] °C	film quality
	1.22	281	395	brittle
	0.73	267	ND	slightly flexible
	0.82	254	ND	brittle
	1.02	252	ND	slightly flexible
	1.34	218	ND	tough, flexible

[a] ND = not detected.

Table 3. Properties of Polyimides Containing the 5,5′-Bis(Benzimidazole) Unit



Ar	polyimide		
	η_{inh}, dL/g	T_g, °C	film quality
	[a]	380	
	0.40	370	tough, flexible
	0.99	346	tough, flexible
	1.10	353	tough, flexible
	1.32	290	tough, flexible

[a] Precipitated during polymerization.

concentration in DMAc at 25 °C (Table 3). Films were cast from 10% (w/w) DMAc solutions and cured under vacuum by slowly heating to a maximum temperature of 300 °C, holding at 300 °C for 1 h, and slowly cooling under vacuum. Mechanical and thermal properties of the films were determined as previously described.

Characterization. Visual melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN. Infrared spectra were obtained using a Perkin-Elmer Model 1600 FTIR. Differential scanning calorimetry (dsc) was performed on a Shimadzu DSC-50. DSC analysis of monomers and precursors was performed at a heating rate of 10 °C/min. The melting point was taken as the onset of the melting endotherm. DSC of the polyimides was performed at a heating rate of 20 °C/min. Amorphous polyimides were heated 50–100 °C above the glass transition temperature (T_g), quenched, and rerun. Glass transition temperatures were taken at the inflection point of the ΔT versus temperature curve and the crystalline melt temperature (T_m) taken at the peak of the endotherm. Thermogravimetric analysis (TGA) was performed on film specimens using a Seiko TG/DTA at a heating rate of 2.5 °C/min under an atmosphere of flowing air or nitrogen at 40 mL/min.

Results and Discussion

N-Phenylphthalimides were prepared by the aromatic nucleophilic substitution reaction of either *N*-phenyl-4-fluorophthalimide or *N*-phenyl-4-nitrophthalimide with the disodium salts of the bis(4-hydroxyphenyl) heterocyclic compounds in DMSO (Figure 1). The bis(4-hydroxyphenyl) heterocyclic compounds included 2-phenyl-4,5-bis(4-hydroxyphenyl)imidazole, 2,5-bis(4-hydroxyphenyl)-1,3,4-oxadiazole, 5,5′-bis[2-(4-hydroxyphenyl)benzimidazole, and 6,6′-bis[2-(4-hydroxyphenyl)benzoxazole]. Isolation of the heterocyclic containing *N*-phenylphthalimides was greatly facilitated by their precipitation from the reaction mixture. However, no imidazole containing *N*-phen-

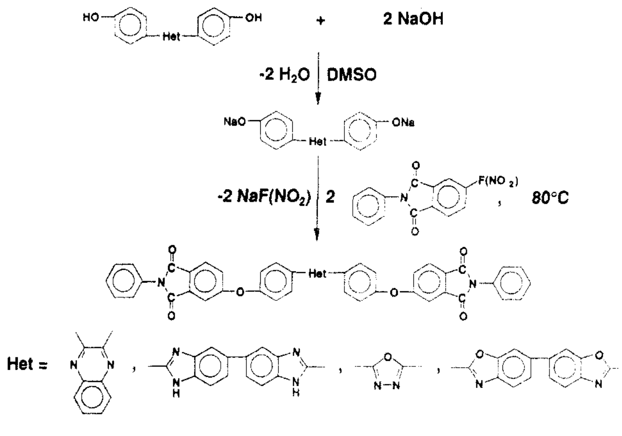


Figure 1. Synthesis of bis(*N*-phenylphthalimido) heterocyclic ethers.

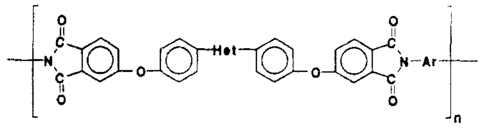
ylphthalimide precipitated from the reaction of *N*-phenyl-4-fluorophthalimide with the disodium salt of 2-phenyl-4,5-bis(4-hydroxyphenyl)imidazole, nor could it be isolated in reasonably pure form from the reaction mixture. Crude yields of the other *N*-phenylphthalimides varied from 16 to 77%, depending upon the leaving group (F or NO_2) and reaction temperature (Table 1). Generally, the use of *N*-phenyl-4-fluorophthalimide provided higher yield at the lower temperature. The use of *N*-phenyl-4-nitrophthalimide required higher temperatures (100 °C), while 80 °C appeared to be optimal when *N*-phenyl-4-fluorophthalimide was used.

N-Phenylphthalimide rings were hydrolyzed with aqueous sodium hydroxide and acidified to provide bis(1,2-dicarboxylic acid)s. However, the 1,3,4-oxadiazole and 6,6′-bis(benzoxazole) rings of the *N*-phenylphthalimides were also attacked. This should have been expected with the 1,3,4-oxadiazole, since the literature reports ring opening in strong base,[30] but benzoxazoles are known to be stable to alkali attack.[31] The 2,3-quinoxaline and 5,5′-bis(benzimidazole) dianhydrides were prepared by reaction of the carboxylic acids with acetic anhydride. Elemental analyses of various batches of the 5,5′-bis(benzimidazole)dianhydride varied considerably (low carbon content). NMR spectra of the dianhydrides and their precursors were not possible due to insolubility in common solvents such as DMAc at room temperature. Attempts to prepare the dianhydrides directly by reaction of bis(4-hydroxyphenyl) heterocyclic compounds and 4-fluorophthalic anhydride with potassium fluoride were unsuccessful.

High molecular weight polyamide acids were readily prepared by addition of a stoichiometric amount of the dianhydride containing the 2,3-quinoxaline unit to a stirred solution of the diamine in DMAc. Inherent viscosities ($\eta_{\rm inh}$) were as high as 1.34 dL/g (Table 2). Films were cast from the polyamide acid solutions and thermally cyclodehydrated to form the polyimide by heating in air to a maximum temperature of 300 °C. Polyamide acids similarly prepared using the 5,5′-bis(benzimidazole) dianhydride were of low molecular weight as evidenced by low inherent viscosities. Films cast from these solutions and subsequently cured were brittle. However, polyimides prepared by reaction of this dianhydride and the same diamines in *m*-cresol at 190–200 °C in the presence of a catalytic amount of isoquinoline appeared to be of fairly high molecular weight. The polyimide prepared from 1,4-phenylenediamine precipitated during the reaction. The other polyimides remained soluble in *m*-cresol although some gelation was observed. The polyimides were precipitated from the *m*-cresol solution and dried under vacuum at 200 °C. Inherent viscosities of the polyimides were as high as 1.32 dL/g [at a concentration of 0.5% (w/v) in DMAc (Table 3)], and films were cast from 10% (w/w) DMAc solutions. Films dried in air to a maximum temperature of 300 °C were tough, flexible, and insoluble in DMAc or *m*-cresol. Films dried under vacuum at 300 °C were lighter in color and also tough, flexible, and insoluble in DMAc or *m*-cresol. Apparently the polyimides cross-link during the drying process to 300 °C. The exact nature of the cross-linking is unknown.

Glass transition temperatures of the polyimides were determined by DSC and are given in Tables 2 and 3. For polyimides containing the 2,3-quinoxaline unit, glass transition temperatures ranged between 218 and 281 °C.

Table 4. Thermogravimetric Analysis of Polyimides



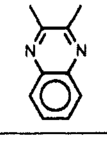
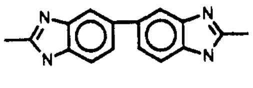
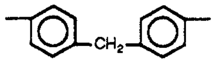
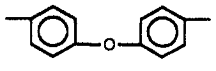
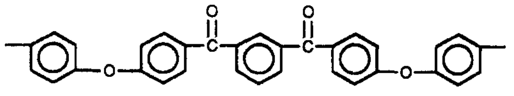
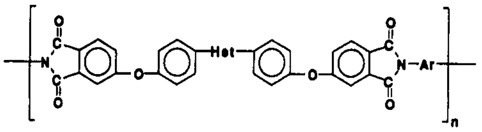
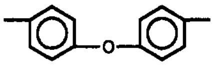
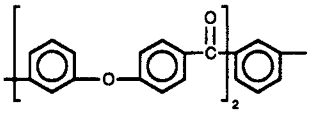
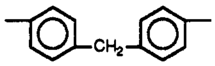
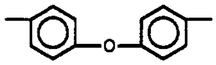
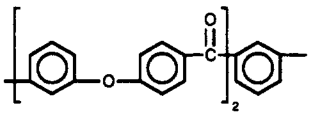
	temp (°C) at 5% wt Loss			
				
Ar	nitrogen	air	nitrogen	air
	503	495	525	451
	503	513	457	473
	477	497	483	476
	508	511	497	477
	502	503	492	461

Table 5. Tensile Properties of Polyimide Films



Ar	het	temp, °C	tensile strength at break, MPa (Ksl)	tensile modulus, GPa (Ksl)	elongation at break, %
	2,3-quinoxaline	25	92 (13.4)	2.67 (388)	4
		177	53 (7.7)	1.94 (281)	3
	2,3-quinoxaline	25	101 (14.6)	2.40 (348)	9
		177	49 (7.1)	1.83 (265)	5
	2,3-quinoxaline	25	100 (14.5)	2.55 (370)	8
		177	21 (3.0)	1.74 (252)	27
	5,5′-bis(benzimidazole)	25	165 (24.0)	3.84 (558)	9
		177	70 (10.2)	3.21 (467)	2
	5,5′-bis(benzimidazole)	25	153 (22.2)	3.23 (469)	40
		177	101 (14.7)	2.19 (318)	24
	5,5′-bis(benzimidazole)	25	147 (21.3)	3.54 (514)	15
		177	92 (13.4)	2.25 (326)	19
	5,5′-bis(benzimidazole)	25	114 (16.6)	3.16 (459)	29
		177	71 (10.3)	2.00 (290)	62

The polyimide with 1,4-phenylenediamine exhibited a polymer melt transition at 395 °C. This polyimide was determined to be approximately 17% crystalline by wide-angle X-ray diffraction. The remainder of the polyimides were amorphous. Glass transition temperatures of the polyimides containing the 5,5′-bis(benzimidazole) unit were considerably higher than those containing the 2,3-quinoxaline unit when the same diamine was used because of strong intermolecular association through hydrogen bonding via the benzimidazole NH group. Glass transition temperatures ranged between 290 and 380 °C, but the transitions were poorly defined in the DSC curves. The polyimides were amorphous.

Temperatures at 5% weight loss by dynamic thermogravimetric analysis (TGA) of the various polyimides in both air and nitrogen are reported in Table 4. In air, polyimides containing the 2,3-quinoxaline unit were more stable than similar polyimides containing the 5,5′-bis(benzimidazole) unit. Mechanical properties of the flexible unoriented polyimide films at 25 and 177 °C are given in Table 5. At 25 °C, tensile strengths at break and moduli for polyimides containing the 2,3-quinoxaline unit ranged between 92 and 101 MPa (13.4–14.6 Ksi) and 2.40 and 2.67 GPa (348–388 Ksi), respectively. These are typical values for unoriented amorphous, linear polyimides with a flexible backbone. Polyimides containing the 5,5′-bis(benzimidazole) unit exhibited tensile strengths and moduli that ranged between 114 and 165 MPa (16.6–24.0 Ksi) and 3.16 and 3.84 GPa (459–558 Ksi), respectively. Higher tensile strengths and moduli are indicative of cross-linking or intermolecular association.

Conclusions

New polyimides were synthesized using 2,3-quinoxalinediylbis[4-(4-phenoxy)phthalic anhydride] and 5,5′-bis[4-(2-benzimidazolyl-4′-phenoxy)phthalic anhydride]. These polyimides have relatively high glass transition temperatures and exhibit good thermal stability in air and nitrogen by TGA. Polyimides containing the benzimidazole group cross-linked on heating and exhibited high tensile strengths and moduli at 25 °C and at 177 °C.

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