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Synthesis of Soluble Poly(ether imide)s from Bis(ether anhydride)s Containing Bulky Substituents

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ABSTRACT: New bis(ether phthalic anhydride)s were synthesized from hindered biphenylols, such as 2,2′,3,3′,5,5′-hexaphenyl-1,1′-biphenyl-4,4′-diol or 3,3′,5,5′-teraphenyl-1,1′-biphenyl-4,4′-diol, and poly(ether imide)s have been prepared from them by solution condensation polymerization in *N*-methylpyrrolidinone with *o*- or *p*-phenylenediamines. The glass transition temperatures of the poly(ether imide)s are increased by introduction of the rigid biphenyl moieties and they are soluble in common organic solvents, methylene chloride, chloroform, and DMSO at room temperature.

Introduction

Uses for aromatic polyimides have developed rapidly in recent years due to their outstanding properties.[1,2] However, their applications have been limited in many fields because aromatic polyimides are normally insoluble in common organic solvents. The excellent mechanical properties at high temperatures are due to the rigid structures which result in high glass transition temperatures or melting points. However the inter/intramolecular properties which lead to high glass transition temperatures and melt points often result in poor solubility which limits their uses. Modified structures with flexible linkages between aromatic rings in the diamine and dianhydride have been synthesized which provide improved solubility. Several soluble polyimide systems have been described. The stability of the polymers obtained are correspondingly reduced. Kurita[3] demonstrated that the introduction of bipyridyl units into the polymer chain enhanced the solubility of the polymer. Takekoshi *et al.*[4,5] have synthesized bis(ether dianhydride)s by the condensation of 4,4′-isopropylidenediphenol (BPA) and 4-nitro-*N*-methylphthalimide followed by conversion to the dianhydride. The dianhydride is polymerized with *m*-phenylenediamine to give ULTEM resin which has excellent processability. Harris[6] reported soluble polyimides through the introduction of trifluoromethyl substituents in the 2,2′-positions of 4,4′-diaminobiphenyl which forces the aromatic rings into a noncoplanar conformation.

In this paper we describe the synthesis of dianhydride monomers which incorporate both flexible ether linkages and rigid biphenyl units containing bulky phenyl substituents. We describe the successful synthesis of a series of novel soluble aromatic poly(ether imide)s prepared by the condensation of these monomers with *o*- and *p*-phenylenediamines by a two step polymerization. These aromatic poly(ether imide)s are all amorphous and are readily soluble in organic solvents at room temperature. They have excellent thermo-oxidative stabilities with high glass transition temperatures.

Experimental Section

General Methods. ^{1}H NMR spectra were taken in CDCl$_3$ solution on a Varian XL-200 instrument. Chemical shifts are given in parts per million downfield from tetramethylsilane. Mass spectra were recorded on a VG ZAB-HS spectrometer, ion source at 240 °C and with 70-eV electron impact, direct inlet: *m/z* (assignment). Melting points were determined on a Fisher-Johns melting point apparatus. Elemental analyses were performed by Galbraith Laboratories Inc. IR spectra were performed on a Analet AQS-60 FTIR spectrophotometer. In experiments requiring dry solvent, DMAc and NMP were dried by shaking with 3-Å molecular sieves and were dried over calcium hydride and then distilled under vacuum. Phenylenediamines were purified by distillation or sublimation. Pure 4-nitro-*N*-methylphthalimide and BPA–dianhydride were supplied from the General Electric Co. Common reagents, e.g. potassium carbonate, potassium hydroxide (50%), and acetic anhydride, were used without further purification.

Polymer Characterization. Inherent viscosities were measured in a calibrated Ubbelohde viscometer at a concentration of 0.5 g/dL in CHCl$_3$ at 25 °C. Polymer molecular weights were determined relative to polystyrene by gel permeation chromatography (GPC) in CHCl$_3$ as solvent on a Waters 510 HPLC with a set of four microstyragel columns (500, 10^4, 10^5, and 100 Å) in series and a UV detector. Differential scanning calorimetry (DSC) and thermogravimetric analyses (TG) were performed with a

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Seiko 220 DSC at a heating rate of 20 °C/min with 50 mL/min gas flow and a Seiko 220 TG/DTA instrument, respectively, at a heating rate of 10 °C/min with 200 mL/min gas flow rate under nitrogen and air. Mechanical properties were measured on a Seiko TMA/SS 120 instrument from 25 to 350 °C with a heating rate of 3 °C/min in static air. The polymer films for the mechanical analyzer were cast from chloroform solution (100 mg/5 mL) on a glass plate (3-cm diameter) by evaporation of solvent at room temperature for 48 h and dried at 100 °C for 24 h. Film thickness was measured with a micrometer.

1-((-*N*-Methylphthalimid-4-yl)oxy)-2,3,6-triphenylbenzene (1). 2,3,6-Triphenylphenol (1 g, 3.10 mmol) and 4-nitro-*N*-methylphthalimide (0.83 g, 4.03 mmol) were dissolved in NMP (10 mL) and toluene (7 mL) under nitrogen atmosphere in a flask equipped with a Dean-Stark trap. After a homogeneous solution was obtained, potassium carbonate (0.56g, 4.03 mmol) was added. The mixture was heated to reflux until no further water appeared. The toluene was then removed by distillation. The reaction was maintained for 10 h at 170 °C. The mixture was extracted with $CHCl_3$ and water. The organic layer was evaporated, and the recovered solid was recrystallized from $CHCl_3$ and methanol; mp 198–201 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.08 (s, 3 H, CH_3), 6.96–7.94 (m, ArH). Anal. Calcd for $C_{33}H_{232}O_3N$: C, 82.30; H, 4.82; N, 2.91. Found: C, 81.75; H, 5.10; N, 2.73.

4,4′-Bis(*N*-methylphthalimid-4-yl)oxy)-3,3′,5,5′-tetraphenyl-1,1′-biphenyl (3a). A mixture of 3,3′,5,5′-tetraphenyl-1,1′-biphenyl-4,4′-diol (**2a**) (7.5 g, 15.2 mmol), 4-nitro-*N*-methylphthalimide (9.4 g, 45.6 mmol), potassium carbonate (6.7 g, 48.48 mmol), DMAc (50 mL), and toluene (25 mL) was stirred under a nitrogen atmosphere at reflux in a three necked flask equipped with a Dean-Stark trap for 3 h. Toluene was then removed, and the reaction was maintained at 165 °C for 10 h. The solution was precipitated in a mixture of water (50 mL) and methanol (150 mL). A crude product (10.6 g, 86% yield) was isolated by filtration and washed with hot methanol and recrystallized from ethyl acetate and then dried in vacuum (98% purity by HPLC); mp 254–255 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.05 (s, 6 H, CH_3), 6.85–7.77 (m, ArH). MS (EI): calcd *m/z* 808.90, found *m/z* 808.5 (M$^+$). Anal. Calcd for $C_{54}H_{36}O_6N_2$: C, 80.18; H, 4.49; N, 3.46. Found: C, 79.76; H, 4.50; N, 3.55.

4,4′-Bis(3,4-dicarboxyphenoxy)-3,3′,5,5′-tetraphenyl-1,1′-biphenyl (4a). A mixture 4,4′-bis((*N*-methylphthalimid-4-yl)-oxy)-3,3′,5,5′-tetraphenyl-1,1′-biphenyl (**3a**) (7.5 g, 9.3 mmol), methanol (100 mL), water (50 mL), and 50% sodium hydroxide (20 g) was stirred at reflux for 7 h. Acidification of the solution with concentrated hydrochloric acid gave 7.5 g (98% yield) of product; mp 173–176 °C. ^{1}H NMR (200 MHz, CD_3OD): δ 6.81–8.08 (m, ArH). IR: 3300 cm^{-1} (OH stretch of –COOH).

4,4′-Bis(3,4-dicarboxyphenoxy)-3,3′,5,5′-tetraphenyl-1,1′-biphenyl Dianhydride (5a). A mixture of 4,4′-bis(3,4-dicarboxyphenoxy)-3,3′,4,4′-tetraphenyl-1,1′-biphenyl (**4a**) (7.0 g, 8.5 mmol), acetic acid (60 mL), and acetic anhydride (6 mL) was stirred at reflux for 5 h. The solution was cooled, and the solid was removed by filtration and dried (5.7 g, 85%); mp 276–279 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.05–7.79 (m, ArH). MS (EI): calcd for $C_{52}H_{30}O_8$ *m/z* 782.81, found *m/z* 782.3 (M$^+$).

4,4′-Bis((*N*-methylphthalimid-4-yl)oxy)-2,2′-dimethyl-3,3′,5,5′-tetraphenyl-1,1′-biphenyl (3b). To a 50-mL three necked round-bottomed flask equipped with a Dean-Stark trap and condenser were added 2,2′-dimethyl-3,3′,5,5′-tetraphenyl-1,1′-biphenyl-4,4′-diol (**2b**) (8 g, 15.4 mmol), 4-nitro-*N*-methylphthalimide (7.9 g, 38.3 mmol), DMAc (45 mL), and toluene (20 mL) under nitrogen atmosphere. The reaction mixture was stirred, and potassium carbonate (6.8 g, 49.2 mmol) was added. The reaction mixture was heated to reflux (150 °C) for 3 h until the water of reaction was removed. Toluene was removed from the Dean-Stark trap until the temperature rose to about 160 °C, and the reaction was maintained at this temperature for 10 h. The reaction mixture was precipitated in a mixture of methanol (150 mL) and water (50 mL) and the product was isolated by filtration and dried. The crude product (9.8 g, 87% purity in HPLC, 85% yield) was recrystallized from isopropyl alcohol to give fine white crystals (98% purity by HPLC, 82% yield), mp 234–236 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.00 (s, 6 H, CH_3), 3.08 (s, 6 H, N–CH_3), 6.75–7.65 (m, 28 H). MS (EI): calcd *m/z* 836.95, found *m/z* 836.4 (M$^+$). Anal. Calcd for $C_{18}H_{40}O_6N_2$: C, 80.37; H, 4.82; N, 3.46. Found: C, 80.71; H, 4.94; N, 3.54.

4,4′-Bis(3,4-dicarboxyphenoxy)-2,2′-dimethyl-3,3′,5,5′-tetraphenyl-1,1′-biphenyl (4b). A mixture of 4,4′-bis((*N*-methylphthalimid-4-yl)oxy)-2,2′-dimethyl-3,3′,5,5′-tetraphenyl-1,1′-biphenyl (**3b**) (9.0 g, 10.8 mmol), isopropyl alcohol (60 mL), water (20 mL), and 50% sodium hydroxide (20 g) was stirred at reflux for 5 h, and then water (20 mL) was added. Acidification of the hot solution with hydrochloric acid was carried out over 2 h, and the reaction was then cooled down. The product was isolated by filtration and washed with hot water and dried. The product was obtained as a white solid (8.9 g, 97% yield), mp 167–169 °C. ^{1}H NMR (200 mHz, CD_3OD): δ 6.60–7.67 (m, ArH). IR: 3300 cm^{-1} (OH stretch of –COOH).

4,4′-Bis(3,4-dicarboxyphenoxy)-2,2′-dimethyl-3,3′,5,5′-tetraphenyl-1,1′-biphenyl Dianhydride (5b). A mixture of 4,4′-bis(3,4-dicarboxyphenoxy)-2,2′-dimethyl-3,3′,5,5′-tetraphenyl-1,1′-biphenyl (**4b**) (9.0 g, 10.6 mmol), glacial acetic acid (60 mL), and acetic anhydride (6 mL) were stirred at reflux for 5 h until a white solid precipitated. The product (7.8 g, 90%) was purified by recrystallization from toluene/acetic acid; mp 275–278 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.01 (s, 6 H, CH_3), 6.90–7.63 (m, 28 H, ArH). MS (EI): calcd *m/z* 810.87, found *m/z* 810.1 (M$^+$). Anal. Calcd for $C_{54}H_{34}O_8$: C, 79.99; H, 4.23. Found: C, 80.17; H, 4.17.

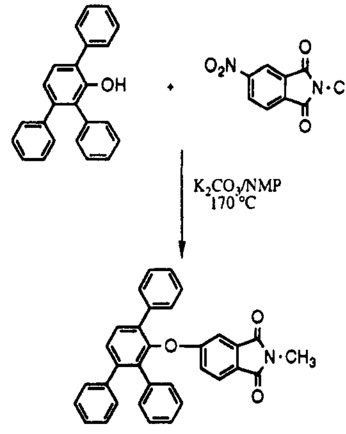
4,4′-Bis((*N*-methylphthalimid-4-yl)oxy)-2,2′,3,3′,5,5′-hexaphenyl-1,1′-biphenyl (3c). A mixture 2,2′,3,3′,5,5′-hexaphenyl-1,1′-biphenyl-4,4′-diol (**2c**) (8 g, 12.4 mmol) and 4-nitro-*N*-methylphthalimide (6.2 g, 30.1 mmol) was placed in a 100-mL three necked flask equipped with a Dean-Stark trap and a stirrer. The mixture was stirred and heated under nitrogen for 3 h during which time the water was azeotropically removed, and then the reaction was maintained at 160 °C for 10 h. After cooling, the solution was poured into a mixture of water (50 mL)/methanol (150 mL) and then the crude white precipitate was collected by filtration. The product was thoroughly washed with water and hot methanol and dried under vacuum. The product was recrystallized from acetonitrile and chloroform (10.5 g, 88%), mp 268–270 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.06 (s, 6 H, CH_3), 6.60–7.45 (m, 38 H, ArH). MS (EI): calcd *m/z* 961.10, found *m/z* 960.6 (M$^+$). Anal. Calcd for $C_{66}H_{44}O_6N_2$: C, 82.48; H, 4.61; N, 2.91. Found: C, 82.44; H, 4.74; N, 2.73.

4,4′-Bis(3,4-dicarboxyphenoxy)-2,2′,3,3′,5,5′-hexaphenyl-1,1′-biphenyl (4c). A mixture of 4,4′-bis((*N*-methylphthalimid-4-yl)oxy)-2,2′,3,3′,5,5′-hexaphenyl-1,1′-biphenyl (**3c**) (9.0 g, 9.4 mmol), isopropyl alcohol (40 mL), methanol (20 mL), water (15 mL), and 50% sodium hydroxide (15 g) was stirred at reflux for 3 h. Water (50 mL) was added, and the resulting mixture was acidified with hydrochloric acid. The white precipitate was filtered out and washed with hot water and then dried under vacuum (8.8 g, 96%), mp 169–172 °C. ^{1}H NMR (200 MHz, CD_3OD): δ 6.78–8.03 (m, ArH). IR: 3300 cm^{-1} (OH stretch of –COOH).

4,4′-Bis(3,4-dicarboxyphenoxy)-2,2′,3,3′,5,5′-hexaphenyl-1,1′-biphenyl Dianhydride (5c). A mixture of 4,4′-bis(3,4-dicarboxyphenoxy)-2,2′,3,3′,5,5′-hexaphenyl-1,1′-biphenyl (**4c**) (12 g), glacial acetic acid (50 mL), and acetic anhydride (5 mL) was stirred at reflux, during which time a white solid precipitated. The solid was removed by filtration. It was washed twice with acetic acid and water and then dried under vacuum (7.1 g, 93% yield), mp 305–307 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.77–7.55 (m, ArH). MS (EI): calcd *m/z* 935.01, found *m/z* 934.4 (M$^+$). Anal. Calcd for $C_{64}H_{38}O_8$: C, 82.21; H, 4.10. Found: C, 82.28; H, 4.15.

4,4′-Bis((*N*-methylphthalimid-4-yl)oxy)-2-chloro-3,3′,5,5′-tetraphenyl-1,1′-biphenyl (3d). A 100-mL three necked flask equipped with a condenser, Dean-Stark trap, and thermometer inlet was charged with 2-chloro-3,3′,5,5′-tetraphenyl-1,1′-biphenyl-4,4-diol (**2d**) (8 g, 16.34 mmol), 4-nitro-*N*-methylphthalimide (10.12 g, 49.02 mmol), potassium carbonate (2.93 g, 21.24 mmol), DMAc (60 mL), and toluene (30 mL) under nitrogen atmosphere. The reaction mixture was heated to reflux until no water appeared at azeotropic temperature and then maintained at 170 °C for 15 h after toluene was removed. The mixture was cooled and precipitated in mixture of water (200 mL)/methanol (50 mL). The resulting product was recrystallized in ethanol and chlo-

Scheme I. Model Reaction



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roform (68%), mp 215–217 °C. ^{1}H NMR (200 MHz, CDCl$_3$): δ 3.11 (s, 6 H, CH$_3$), 6.88–7.87 (m, ArH). MS (EI): calcd *m/z* 842.34, found *m/z* 843.2 (M$^+$). Anal. Calcd for $C_{54}H_{35}O_8N_2Cl$: C, 76.91; H, 4.18; N, 3.32; Cl, 4.20. Found: C, 77.18; H, 4.06; N, 3.22; Cl, 4.76.

4,4′-Bis(3,4-dicarboxyphenoxy)-2-chloro-3,3′,5,5′-tetraphenyl-1,1′-biphenyl (4d). A mixture of 4,4′-bis((*N*-methylphthalimid-4-yl)oxy)-2-chloro-3,3′,5,5′-tetraphenylbiphenyl (**3d**) (9.0 g, 10.67 mmol), isopropyl alcohol (60 mL), methanol (20 mL), water (15 mL), and 50% sodium hydroxide (17 g) was stirred at reflux for 7 h. Water (50 mL) was added, and the resulting mixture was acidified with hydrochloric acid. The white solid was filtered and washed with hot water and then dried under vacuum (8.5 g, 95%), mp 175–177 °C. ^{1}H NMR (200 MHz, CD$_3$OD): δ 6.78–8.03 (m, ArH). IR: 3300 cm^{-1} (OH stretch of –COOH).

4,4′-Bis(3,4-dicarboxyphenoxy)-2-chloro-3,3′,5,5′-tetraphenyl-1,1′-biphenyl Dianhydride (5d). A mixture of 4,4′-bis(3,4-dicarboxyphenoxy)-2-chloro-3,3′,5,5′-tetraphenyl-1,1′-biphenyl (**4d**) (8 g), glacial acetic acid (50 mL), and acetic anhydride (5 mL) was stirred at reflux for 10 h. The solvent was evaporated and the recovered product recrystallized from acetic acid and chloroform (7.4 g, 95% yield), mp 232–236 °C. ^{1}H NMR (200 MHz, CDCl$_3$): δ 6.77–7.55 (m, ArH). MS (EI) calcd *m/z* 817.26, found *m/z* 817.2 (M$^+$). Anal. Calcd for $C_{52}H_{29}O_8Cl$: C, 76.42; H, 3.58; Cl, 4.34. Found: C, 75.90; H, 3.61; Cl, 4.08.

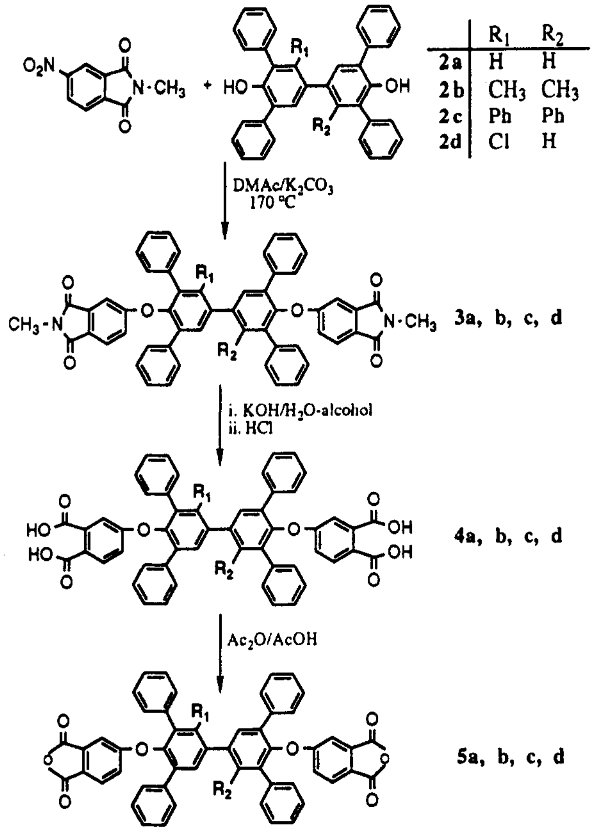
Polymerization. The synthesis of poly(ether imide)s is given below as a general procedure. To a 50-mL round bottom flask was added 4,4′-bis(3,4-dicarboxyphenoxy)-2,2-dimethyl-3,3′,5,5′-tetraphenyl-1,1′-biphenyl dianhydride (**5d**) (1 g, 1.23 mmol), *m*-phenylenediamine (0.133 g, 1.23 mmol), and distilled NMP (8 mL). The flask was purged with nitrogen and the solution was stirred for 3 h under a nitrogen atmosphere at room temperature. The solution became viscous as the poly(amic acid) formed, and 4 mL of chlorobenzene was then added. The reaction system was heated to reflux with stirring for 3 h while chlorobenzene was distilled off and the water removed by azeotropic distillation. The reaction mixture was cooled and precipitated into a large excess of methanol. The polymer was dissolved in chloroform and filtered through Celite. The filtrate was precipitated in methanol. The poly(ether imide)s were separated by filtration and dried in a vacuum oven at 80 °C for 24 h. The TGA curves (Figure 2) are flat until almost 500 °C, indicating complete imidization.

Copolymerization. The same reaction as above was performed for 3 h using 4,4′-bis(3,4-dicarboxyphenoxy)-2,2′-dimethyl-3,3′,5,5′-tetraphenyl-1,1′-biphenyldianhydride (**5b**) (0.5 g, 0.616 mmol), 2,2′-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (**6**) (0.31 g, 0.616 mmol), *p*-phenylenediamine (0.129 g, 1.23 mmol), and NMP (7 mL). The reaction mixture was treated in the same manner as above.

Results and Discussion

Recently, there has been a considerable effort directed at the nitro displacement reaction for the synthesis of poly(ether imide)s by Takekoshi *et al.*[4,5] They found that nitro displacement of *N*-phenyl-3- or *N*-phenyl-4-nitrophthalimide and various biphenylol salts proceeded readily in polar aprotic solvents to form bis(ether imide)s in high yields. The nitroimides are 1 order of magnitude more reactive than the corresponding fluoro derivatives.[7] We

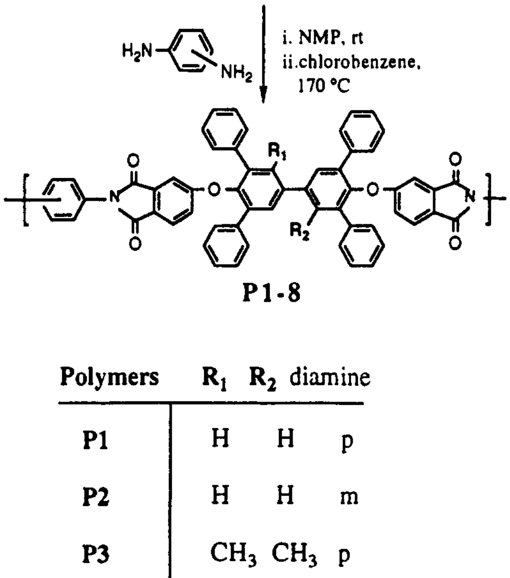
Scheme II. Monomer Synthesis Route



	R$_1$	R$_2$
2a	H	H
2b	CH$_3$	CH$_3$
2c	Ph	Ph
2d	Cl	H

Scheme III. Synthesis of Homopoly(ether imide)s

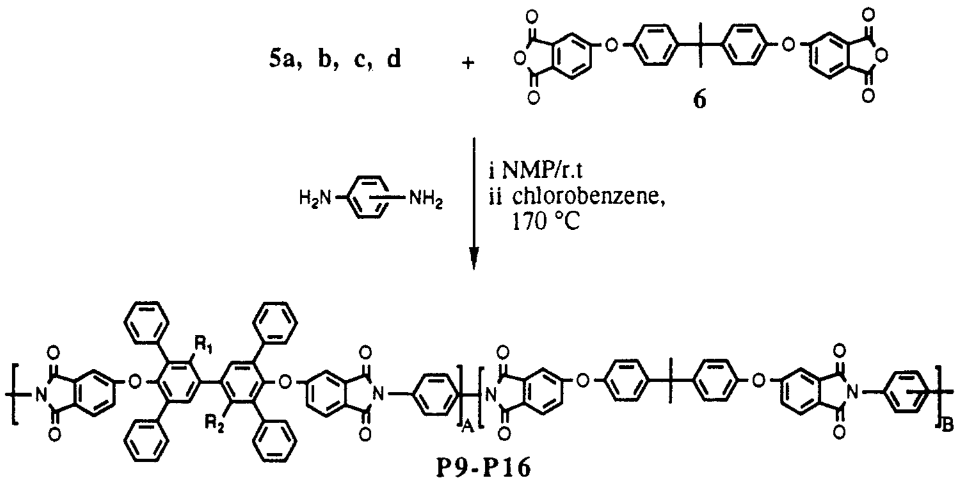
5a, b, c, d



P1-8

Polymers	R$_1$	R$_2$	diamine
P1	H	H	p
P2	H	H	m
P3	CH$_3$	CH$_3$	p
P4	CH$_3$	CH$_3$	m
P5	Ph	Ph	p
P6	Ph	Ph	m
P7	H	Cl	p
P8	H	Cl	m

Scheme IV. Synthesis of Copoly(ether imide)s

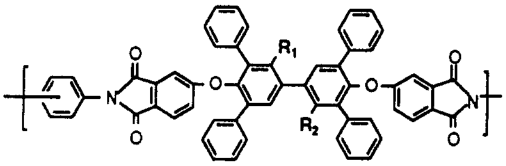


P9-P16

Polymers	R_1	R_2	diamine
P9	H	H	p
P10	H	H	m
P11	CH_3	CH_3	p
P12	CH_3	CH_3	m
P13	Ph	Ph	p
P14	Ph	Ph	m
P15	H	Cl	p
P16	H	Cl	m

have reported[8,9] that hindered biphenylols and hydroquinones react with difluorodiphenyl sulfone and difluorobenzophenone, resulting in high molecular weight poly(ether sulfone)s and poly(ether ketone)s. These polymers showed excellent solubility in organic solvents and have high glass transition temperatures. The 2,2′-phenyl substituents force noncoplanarity between the central phenylene rings, and the addition of further pendant phenyl groups increases the rigidity. We wished to investigate the nitro displacement reaction of *N*-methyl-4-nitrophthalimide with these sterically hindered biphenylols. In a model study (Scheme I) the displacement reaction between *N*-methyl-4-nitrophthalimide and 2,3,6-triphenylphenol was successfully achieved in NMP using potassium carbonate as a base at 170 °C. The displacement reactions had to be carried out under anhydrous conditions because the imide rings of nitrophthalimides are sensitive to a base catalyzed hydrolytic ring opening reaction which produces carboxylic acids. Moreover the displacement reactions with these biphenylols are slower than BPA because of the phenyl substituents in the 2,6-positions which provide steric hindrance. We attempted the nitro displacement reactions with hindered biphenylols (**2a–d**) containing methyl, phenyl, or chloro substituents in the 2-position and *N*-methyl-4-nitrophthalimide in the presence of potassium carbonate and found that these reactions could be successfully performed in yields ranging from 68 to 88%. The displacement reaction with 2-chloro-3,3′,5,5′-tetraphenyl-1,1′-biphenyl-4,4′-diol (**2d**) was considerably slower than the other biphenylols. The first displacement reaction presumably proceeds as rapidly as with the other biphenylols, but the second reaction should be much slower and this effect can be explained in part by the higher acidity influencing the rate.[10] The chlorine in the 2-position would increase the acidity of the phenolic group and hence decrease the nucleophilicity of the anion relative to a hydrogen substituent, which would decrease the rate of

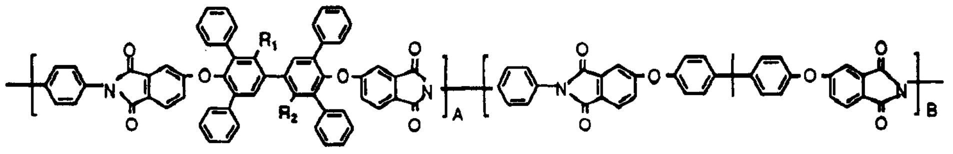
Table I. Physical and Thermal Properties of Homopoly(ether imide)s



poly-mers	R_1	R_2	diamine	T_g[a] (°C)	TGA[b] (°C) air/N_2	η_{inh}[c]	$10^{-3}M_w$[d]	M_w/M_n
P1	H	H	*p*	305	522/568	0.22	22.7	2.56
P2	H	H	*m*	279	520/563	0.13	26.7	2.35
P3	CH_3	CH_3	*p*	312	513/527	0.27	39.4	1.63
P4	CH_3	CH_3	*m*	286	517/521	0.26	37.1	1.57
P5	Ph	Ph	*p*	317	533/558	0.16	25.5	2.00
P6	Ph	Ph	*m*	284	554/566	0.14	25.0	1.85
P7	H	Cl	*p*	300	519/541	0.28	37.5	2.26
P8	H	Cl	*m*	285	526/537	0.20	24.6	1.98

[a] T_g was determined by DSC at heating rate 20 °C/min under nitrogen (50 mL/min). [b] Temperature at which 5% weight loss was determined by TGA at heating rate 10 °C/min under air or nitrogen (flow rate 200 mL/min). [c] Inherent viscosity was measured at a concentration of 0.5 g/dL in chloroform at 25 °C. [d] Molecular weight was determined by GPC in chloroform based on polystyrene standards.

Table II. Physical and Thermal Properties of Copoly(ether imide)s



polymers	R_1	R_2	diamine	T_g[a] (°C)	TGA[b] (°C) air/N_2	η_{inh}[c]	$10^{-3}M_w$[d]	M_w/M_n	YM[e] (GPa)
P9	H	H	*p*	253	512/545	0.21	25.5	2.20	
P10	H	H	*m*	247	527/538	0.19	30.3	1.90	
P11	CH_3	CH_3	*p*	283	508/508	0.31	36.2	2.57	2.46
P12	CH_3	CH_3	*m*	240	501/519	0.18	14.2	2.33	
P13	Ph	Ph	*p*	284	526/535	0.32	37.5	2.48	1.70
P14	Ph	Ph	*m*	246	533/548	0.18	26.5	2.63	
P15	H	Cl	*p*	265	526/531	0.31	41.1	1.98	2.24
P16	H	Cl	*m*	244	518/516	0.20	23.4	2.38	

[a] T_g was determined by DSC at heating rate 20 °C/min under nitrogen (50 mL/min). [b] Temperature at which 5% weight loss was determined by TGA at heating rate 10 °C/min under air or nitrogen (flow rate 200 mL/min). [c] Inherent viscosity was measured at a concentration of 0.5 g/dL in chloroform at 25 °C. [d] Molecular weight was determined by GPC in chloroform based on polystyrene standards. [e] Young's modulus was performed by TMA at room temperature.

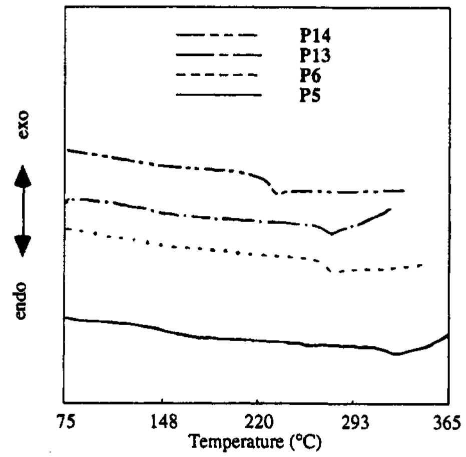


Figure 1. DSC analysis of polymers **P5**, **P6**, **P13**, and **P14** under an atmosphere of nitrogen.

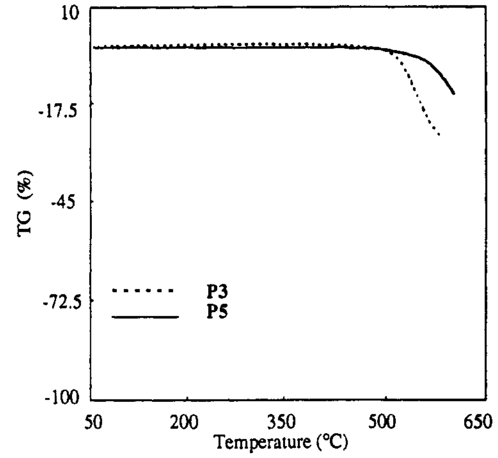


Figure 2. TGA thermogram (weight loss vs temperature) for polymers **P3** and **P5** under an atmosphere of nitrogen.

the displacement reaction. The bis(ether imide)s **3a–d** were hydrolyzed in a conventional manner in an aqueous sodium hydroxide solution containing alcohol for 3–5 h at reflux temperature to the corresponding tetracarboxylic acids **4a–d** in quantitative yield. The anhydrides **5a–d** were formed in high yield via a ring closing reaction of the dicarboxylic acid in the presence of a dehydrating agent such as an acetic anhydride.

Aromatic polyimides are usually insoluble and infusible so that the polymer either precipitates out of solution or solidifies during the reaction. Therefore, most polyimides are preferably formed in two discrete steps, initial formation of the intermediate poly(amic acid), followed by heating to cyclize at high temperature. However modified monomers containing flexible linkages and twisted conformations which give soluble polymers can be polymerized in one step, e.g. thermally in an extruder. We were able to successfully polymerize the bis(ether phthalic anhydride)s obtained with either *m*- or *p*-phenylenediamine in NMP to poly(amic acid)s. The poly(amic acid)s were converted to the corresponding poly(ether imide)s by dehydration. The reactions were maintained at 170 °C for 5 h. The liberated water was removed by azeotropic distillation with chlorobenzene. The polymer properties were evaluated by DSC, TGA/DTA, viscometry, TMA, and GPC. The results are summarized in Tables I and II and described in the following text. The poly(ether imide)s prepared from the bulky dianhydrides that we have synthesized by reaction with *m*- and *p*-phenylenediamines showed no indication of any crystallinity, even after annealing, when examined by DSC. They are soluble in all proportions in common organic solvents such as *N*-methyl-2-pyrrolidinone (NMP), dimethyl sulfoxide, chloroform, and methylene chloride at room temperature. Transparent films can be cast from chloroform at room temperature. The bulky substituents, phenyl groups in the 2,2′-positions, force noncoplanarity between the phenylene rings of the biphenyl moiety to provide a rigid group which with the additional substituents takes up increased spatial volume which hinders packing of the polymer chain and hence increases the solubility. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using polystyrene standards. These polymers had molecular weights in the range 14 200–41 100 and polydispersities (M_w/M_n) of 1.63–2.63. Inherent viscosities (η_{inh} = 0.13–0.32) of polymers were measured at room temperature in chloroform.

The glass transition temperatures (T_g's) of the polymers listed in Tables I and II were determined by differential scanning calorimetry (DSC) at a heating rate of 20 °C/min under air or nitrogen atmosphere. The resulting polymers showed T_g's in the range 240–317 °C (see Figure 1). As we expected the T_g's were increased due to the rigid biphenyl units. The T_g of polymer **P4** (286 °C) derived from dianhydride **5b** and *m*-phenylenediamine was 70 °C higher than the T_g (217 °C) of the commercially available polymer derived from BPA–dianhydride and *m*-phenylenediamine.[11] The T_g's of copolymers prepared from BPA–dianhydride and the hindered dianhydrides appeared at the midpoint between those of the corresponding homopolymers, which is in agreement with calculated values (see Table II).

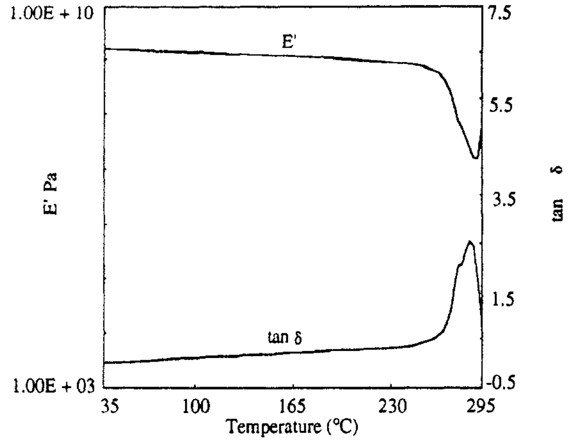


Figure 3. Thermomechanical analysis for polymer **P13**: (a) modulus (E') vs temperature; (b) tan δ vs temperature.

The poly(ether imide)s showed excellent thermo-oxidative stability by thermogravimetric analysis, with 5% weight losses above 500 °C under atmospheres of air and nitrogen (Figure 2). The polymers containing only aromatic substituents demonstrated higher oxidative stability than the corresponding polymer containing aliphatic substituents.[12]

We were able to cast films of the polymers (**P11**, **P13**, **P15**) from chloroform solution (100 mg/5 mL). Young's moduli of thin films (5 mm × 2.05 mm × 0.08 mm) of these polymers ranged from 1.70–2.46 GPa at room temperature. These films maintained good mechanical properties over a wide temperature range from ambient temperature to their glass transition temperatures, as shown by the TMA results (Figure 3). The polymers are a yellow color, presumably resulting from impurities in monomers and small amounts of isoimide that form during cyclodehydration.[13]

Conclusions

We have successfully synthesized a series of modified dianhydrides containing hindered biphenyl units, and poly(ether imide)s were prepared by reaction with *m*- and *p*-phenylenediamine. Because of the pendent phenyl groups on the rigid backbone the polymer chains cannot pack and the resulting polymers show no evidence of any crystallinity. The polymers have high glass transition temperatures along with exceptional solubility. The polymers had 5% weight losses above 500 °C by thermogravimetric analysis, indicating high thermal stability.

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