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Preparation and Characterization of Novel Poly(imidoaryl ether ketone)s and Poly(imidoaryl ether sulfone)s Derived from Phenolphthalein

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ABSTRACT: Seven novel aromatic imidoaryl biphenols **5d–j** with various groups on the pendant phenyl ring have been synthesized from phenolphthalein. These monomers were polymerized in dipolar aprotic solvents with 4,4′-difluorodiphenyl sulfone, 4,4′-difluorobenzophenone, and 1,3-bis(4-fluorobenzoyl)benzene to furnish a series of high molecular weight polymers. Glass transition temperatures for the polymers are in the range 245–310 °C, and they exhibit 10% weight loss at 532–578 °C by thermogravimetric analysis. Solution casting of the polymers from chloroform or *sym*-tetrachloroethane yields tough, clear, creasable films. Young's moduli obtained from thermal mechanical analysis/stress–strain measurements are in the range 1.4–3.4 GPa at temperatures close to T_g. Many of the polymers are soluble in chloroform at room temperature.

Introduction

Thermoplastics with high glass transition temperatures and high thermooxidative stabilities are making inroads as matrices for advanced composites due to their outstanding interlaminar fracture toughness and acceptable compression values after impact.[1] A disadvantage of thermoplastics as matrix resins is generally their poor solvent resistance. In addition, thermoplastic prepregs can be stored for extended periods at ambient temperatures without any deleterious effects, and long cure cycles are not required.

We recently reported the synthesis of three novel imidoaryl biphenols **5a–c** (R = methyl, dodecyl, and phenyl) derived from phenolphthalein[2] (Scheme I). These monomers can be readily polymerized with activated aromatic dihalides in dipolar aprotic solvents to give high molecular weight poly(imidoaryl ether ketone)s and poly(imidoaryl ether sulfone)s that exhibit glass transition temperatures (T_g) as high as 314 °C (R = methyl) and 10% weight loss at 550 °C (R = phenyl) by thermogravimetric analysis (TGA). Since many of the polymers are also soluble in common organic solvents such as chloroform, which allows for facile solution processing, these materials show potential for application as advanced composite matrices.

Herein we report the synthesis of seven additional imidoaryl biphenols **5d–j** with substituents attached to the pendant phenyl at various positions and the corresponding poly(imidoaryl ether ketone)s and poly(imidoaryl ether sulfone)s.

This work was undertaken to determine the effect of changing the substituent attached to the pendant phenyl ring on the T_g, thermooxidative stability, and solubilities of the resulting poly(imidoaryl ether ketone)s and poly(imdoaryl ether sulfone)s. The 23 polymers presented here and the 9 synthesized previously (R = methyl, dodecyl, and phenyl), have now been fully characterized by differential scanning calorimetry (DSC), TGA, isothermal aging experiments (at 400 °C in flowing air), and thermal mechanical analysis/stress–strain (TMA/SS) measurements. In addition, the effect of molecular weight and end-capper on T_g, thermooxidative stability, and solubility of the ketone and sulfone polymers where R is phenyl is examined.

Experimental Section

Materials. Pyridine (A&C) and triethylamine (A&C) were dried by refluxing over calcium hydride and distilled immediately prior to use. *N*-Methylpyrrolidinone (NMP; Aldrich) was distilled from calcium hydride and stored over 4-Å molecular sieves. Dimethylacetamide (DMAc; Aldrich) and dimethylformamide (DMF; Anachemia) were dried over 3-Å molecular sieves for at least 48 h prior to use. Sodium acetate (Aldrich) was fused under vacuum. 4-Phenylphenol (Eastman Kodak) was recrystallized once from ethanol, and isophthaloyl chloride (Aldrich) was distilled under reduced pressure. Zinc dust (Aldrich) was activated by washing with 18% aqueous HCl, water, and ethanol according to Fieser.[3] Sulfolane, *sym*-tetrachloroethane (*sym*-TCE), *N*-methylmaleimide (**6a**), *N*-phenylmaleimide (**6c**), 4,4′-difluorobenzophenone, 4,4′-difluorodiphenyl sulfone, phenolphthalein (**1**), *n*-dodecylamine, and poly(ether sulfone)s **17–19** were used as obtained from Aldrich. $Ni(OAc)_2{\cdot}4H_2O$ (Fisher), maleic anhydride (Baker), toluene (A&C), methyl ethyl ketone (MEK; ACP), ethanol, sulfuric acid (A&C), acetic anhydride (A&C), and anhydrous potassium carbonate (Baker) were used without purification.

Characterization. The T_g's of the polymers and melting points of the monomers and maleimides were obtained using a Seiko 220 DSC instrument at a heating rate of 10 °C/min in N_2 (50 mL/min). When recording T_g values, samples were never heated above 340 °C to prevent cross-linking, and the values were recorded from the second scan. The T_g was taken from the midpoint of the change in slope of the baseline, while melting temperatures were taken from the onset of the change in slope to the minimum of the endotherm peak. The weight loss data were obtained from a Seiko 220 TG/DTA instrument at a heating rate of 10 °C/min in N_2 and air (200 mL/min). TGA data were collected from samples which had just been analyzed using DSC, so that the thermal history of each sample was known and to ensure that there was no residual solvent embedded in the polymer. For all DSC and TGA measurements, polymer pellets were pressed under 5 tons of pressure with a small-scale version of a KBr die. Inherent viscosity data were obtained with a calibrated Ubbelohde viscometer. The measurements were done in *sym*-TCE at 25 °C with a 1B(205) viscometer or in NMP at 60 °C with a 1(165) viscometer. A water bath with a Julabo (Model Type PC) heater was employed to control the temperature. $\bar{M}_w$ and $\bar{M}_n$ were obtained relative to polystyrene standards in chloroform solution using a Waters 510 HPLC equipped with μStyragel columns (500, 10^3, 10^4, and 100 Å) arranged in series with a UV detector. ^{1}H-NMR spectra were recorded at 200 or 270 MHz using a Varian XL-200 or a JEOL 270 CPF spectrometer, respectively, in $CDCl_3$ or DMSO-d_6 with $(CH_3)_4Si$ as the internal standard. Microanalyses were obtained from Galbraith Laboratories Inc., Knoxville, TN. High-resolution mass spectroscopy

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(HRMS) data were recorded on a ZAB 2F HS spectrometer, ion source 240 °C and 70-eV electron impact, direct inlet: *m/e* (assignment).

Film Casting. Polymer films were cast from chloroform or *sym*-TCE. A typical procedure is as follows: 130 mg of polymer was dissolved in 2–5 mL of chloroform. This solution was filtered and transferred into a glass ring (diameter = 3.5 cm, height = 2 cm, thickness = 0.4 cm) located on a glass plate. The glass ring was covered with a glass plate, and the solvent was slowly evaporated at room temperature (12–24 h) to yield tough and flexible films (thickness = 0.070–0.120 mm) which were fingernail creasable. For *sym*-TCE, films were cast in a forced-air oven at 110–120 °C (12–24 h). If the films could not be removed from the glass plate, they were placed into a beaker of water (25–90 °C) for 1–10 h, followed by drying at 118–120 °C for 2–5 h. Typical film thickness was in the range 0.080–0.120 mm.

Measurement of Mechanical Properties. Mechanical properties were measured on the cast films. A typical procedure to obtain Young's Modulus at 25 °C and to determine how it varies with temperature was performed as follows: a stamp was used to cut out a film strip (length = 5–10 mm, width = 2 mm, thickness = 0.09 mm) which was mounted between two chucks in a Seiko TMA/SS 120 instrument. For Young's modulus at 25 °C, the parameters were set as follows: offset = 20–30 g, amplitude = 5–10 g, and cycling frequency = 0.05–0.1 Hz. After there data were collected, the same film was used without changing the parameters to measure Young's modulus variation with temperature by heating to 380 °C at a ramp rate of 3 °C/min in static air. To obtain an accurate tan δ value, the film was also heated in the same manner as above; however, the offset and amplitude values were reduced to 2 and 1 g, respectively. This load reduction was necessary to obtain a symmetrical curve at δ. If a higher load was employed (offset = 20–30 g, amplitude = 5–10 g), these thin films distorted too much when the temperature approached T_g (δ maximum).

Monomer Synthesis. Synthesis of Biphenols. Phenolphthalin (2) was synthesized in 95–98% yield from phenolphthalein (1) as described in the literature.[4]

Isobenzofuran (3). Typical Procedure.[2-5] **Procedure 1.** A dry 250-mL round-bottom flask equipped with a Caframo mechanical stirrer and 20 g (62.4 mmol) of finely powdered dry phenophthalin (2) was immersed in an ice water bath for 5 min. Concentrated sulfuric acid (25 mL, also cooled to 0 °C) was poured into the flask, and the mixture was stirred at a rate which was sufficient to dissolve all of the solids within 2–3 min. The yellowish-green slurry was quickly poured into a 1-L beaker containing 600 mL of ice water, and the remaining solids in the flask were removed with a spatula, while washing with small aliquots of cold water (~20–30 mL × 4). The green solids were combined, filtered, washed with 1–2 L of cold water, and dried on the filter for 15–20 min before being used in the Diels–Alder reaction.

Procedure 2. To an Eberach blender containing 20 g (62.4 mmol) of phenolphthalin (2) was added 25 mL of concentrated sulfuric acid. The contents were mixed for 2–3 min, generating a green solution, 200 mL of ice was added, and mixing was continued for 30 s. The reaction mixture was poured into 600 mL of ice water, stirred for 30 s, and filtered. The filtrate was washed with 1–2 L of cold water, and dried for 15–20 min, and used immediately in the Diels–Alder reaction (the isobenzofuran is unstable, and even if washed with 5% sodium bicarbonate solution it decomposes).

The highest yields are obtained from procedure 1, since it is very difficult to filter the fine dispersion of solids obtained in procedure 2 after mixing with the Eberach blender.

Diels–Alder Adducts (4a–j): Typical Procedure. To a 500-mL round-bottom flask containing 11.9 g (68.7 mmol) of *N*-phenylmaleimide (**6c**) in 200 mL of absolute ethanol was added the isobenzofuran **3** synthesized above. The mixture was quickly heated to 60 °C. After 15–20 min the Diels–Alder reaction was complete as indicated by thin-layer chromatography (TLC) and a change in color from red and clear to light brown and clear. This product was not isolated, since some of the Diels–Alder adduct undergoes dehydration to form **5a**, due to the presence of residual sulfuric acid from the acid-catalyzed rearrangement above.

4,4′-Imidoaryl Biphenols (5a–j): Typical Procedure. To the reaction flask containing a mixture of products from the Diels–Alder reaction was added HCl(g), while the temperature was maintained between 70 and 90 °C. Complete dehydration usually occurred in about 60 min. The precipitated product was filtered by suction and dried to afford to 14.2 g (52%) of a yellow solid. **5b**, **5c**, **5e**, and **5i–j** were recrystallized from glacial acetic acid, while for **5d** and **5f**, 95% ethanol and absolute ethanol were used, respectively. **5a** and **5g** could not be purified as the biphenol and were converted to the bisacetate and purified as described below. In addition, small amounts of **5b**, **5c**, **5i**, and **5j** were also converted to bisacetates. For **5b** and **5c** we wanted to compare the melting points to those of the respective biphenols, and for **5i** and **5j**, bisacetates were required to obtain accurate results from microanalysis, presumably due to small amounts of solvent inclusion in the biphenols. Table I shows the yields and properties of the biphenols.

Bisacetates of 4,4′-Imidoaryl Biphenols (5a–c,g,i,j): Typical Procedure. To 7.95 g (20.1 mmol) of **5a** in 100 mL of pyridine at 0 °C was added 30 mL of acetic anhydride dropwise. The ice bath was removed and the temperature increased to 23 °C over 1–1.5 h. The contents were poured into a beaker containing 200 mL of 10–15% aqueous HCl at 0 °C. The precipitate was filtered by suction and dried to give 8.61 g (89%[5]) of a white solid. **5a–c** were recrystallized from glacial acetic acid, and **5g**, **5i**, and **5j** were recrystallized from absolute ethanol.

Hydrolysis of 4,4′-Imidoaryl Biphenol Bisacetates (5a,c,g): Typical Procedure. To 6.7 g (14.0 mmol) of the bisacetate of **5c** was added 300 mL of methanol and 0.200 g of anhydrous potassium carbonate. This was stirred at 60 °C overnight. The mixture was cooled to room temperature and acidified slowly to pH 2–4 using 10% aqueous HCl. Water (100 mL) was added and the precipitate was filtered, dried by suction for 5 h, and dried at 60 °C under reduced pressure to afford 5.3 g (96%) of a yellow powder, which was pure enough to be used in the polymerization reactions.

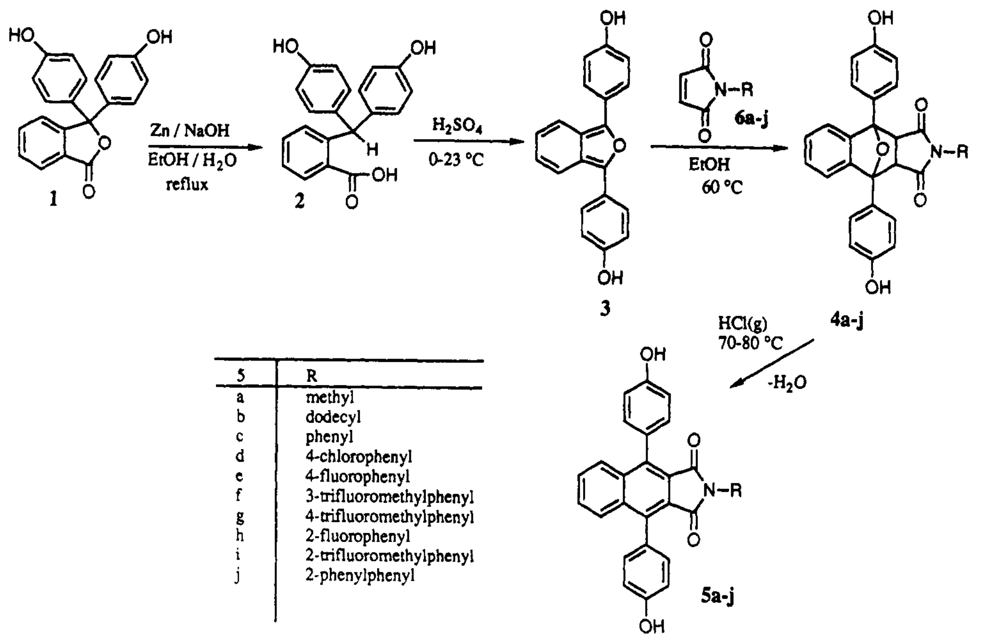
Synthesis of 1,3-Bis(4-fluorobenzoyl)benzene. To a dry 500-mL round-bottom flask containing 15 g (0.74 mol) of isophthaloyl chloride were added 200 mL of carbon disulfide and 23.8 g (0.163 mol) of aluminum chloride. To this was added 15.6 g (0.163 mol) of fluorobenzene slowly in a dropwise manner. The solution became gray. It was left stirring for 4 days at 23 °C, another 15.6 g of fluorobenzene was added, and the mixture was refluxed for 2 h. After cooling to 23 °C, 800 mL of water was added. The precipitate was filtered, washed with water (100 mL × 5), and dried. Recrystallization from ethanol yielded 18 g (85%) of a silver solid: mp 179–180 °C (lit.[6] mp 178–179 °C).

Synthesis of Maleimides. Procedure 1. Synthesis of 6b. *N*-Dodecylmaleamic Acid. To a 1-L beaker containing 37.8 g (0.204 mol) of dodecylamine in 150 mL of cyclohexane was added 20 g (0.204 mol) of maleic anhydride. This was warmed to 60 °C to dissolve all of the solids, and 2 drops of concentrated sulfuric acid was added. After 2 h the mixture contained a fine white precipitate. This was filtered, washed with petroleum ether (50 mL × 5), and dried to give 55.5 g (96%) of a white solid: mp 92–94 °C.

***N*-Dodecylmaleimide 6b.** To a dry 1-L round-bottom flask containing 600 mL of methyl ethyl ketone (MEK) and 70.8 g (0.25 mol) of the amic acid was added 52.2 mL (0.375 mol) of dry triethylamine in a dropwise manner over 5 min (most of the amic acid dissolves when the amine is added). Acetic anhydride (35.4 mL, 0.375 mol) was then added slowly while the temperature was increased to 60 °C. After 22 h the temperature was reduced to 23 °C, and the contents were poured into 2 L of water. This was stirred overnight, filtered by suction, and dried to give 66.8 g (96%[7]) of a tan solid: mp 47–51 °C. This was used without further purification.

Procedure 2. Synthesis of 6d–j. The remaining maleimides were synthesized in a one-pot reaction by mixing the appropriate amine with maleic anhydride in NMP or DMAc to form the amic acid, which was then dehydrated at room temperature using a catalytic amount of $Ni(OAc)_2\cdot H_2O$ and 4 equiv of acetic anhydride.[8] For the syntheses of *N*-(4-chlorophenyl)maleimide (**6d**),[9] *N*-[3-(trifluoromethyl)phenyl]maleimide (**6f**),[10] and *N*-[4-(trifluoromethyl)phenyl]maleimide (**6g**), reactions were run at 50–60 °C for 24–48 h after in situ formation of the amic

Scheme I



5	R
a	methyl
b	dodecyl
c	phenyl
d	4-chlorophenyl
e	4-fluorophenyl
f	3-trifluoromethylphenyl
g	4-trifluoromethylphenyl
h	2-fluorophenyl
i	2-trifluoromethylphenyl
j	2-phenylphenyl

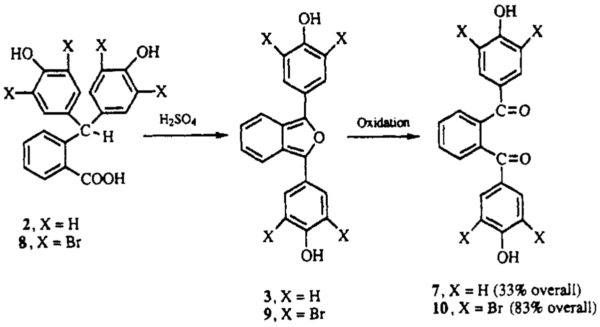
acid. For *N*-(4-fluorophenyl)maleimide (**6e**), *N*-(2-fluorophenyl)maleimide (**6h**), *N*-[2-(trifluoromethyl)phenyl]maleimide (**6i**), and (2-phenylphenyl)maleimide (**6j**), the reactions were run for 24–60 h at 23 °C. In the workup of **6f**, **6i**, and **6j** the solids did not precipitate when poured into water; therefore the organics were extracted with a solvent (250 mL × 4) (**6f**, $CHCl_3$; **6i**, EtOEt; **6j**, EtOAc). The combined extracts were washed with 5–10% $NaHCO_3$ (150 mL × 2), brine (300 mL × 3), and H_2O (300 mL × 3) and dried over $MgSO_4$, and solvent was removed under reduced pressure. Maleimides **6d** and **6e** were purified by recrystallization, while **6f–j** were purified by flash column chromatography.

Table II shows the yields and properties of the maleimides along with the reaction conditions and purification procedures employed.

Polymer Synthesis: Typical Procedure. To a dry 50-mL three-neck flask equiped with a Dean–Stark trap, cold water condenser, thermometer, and nitrogen inlet were added 0.860 g (1.88 mmol) of imidoaryl biphenol **5c** and 0.605 g (1.88 mmol) of 1,3-bis(4-fluorobenzoyl)benzene. Toluene (3.7 mL) was used to wash any remaining solids stuck to the mouth of the flask. NMP (7.3 mL) was added, and the contents were warmed to 40 °C. Anhydrous potassium carbonate (0.346 g, 2.632 mmol; 40% excess) was added all at once, the temperature was increased to 140 °C, and the mixture was refluxed for 4–5 h. The temperature was then increased to 150 °C for 2 h (a significant increase in viscosity was apparent), 160 °C for 2 h, 170 °C for 1 h, and 180 °C for 30 min. The reaction mixture was diluted with 15–20 mL of NMP, filtered hot through a bed of Celite to remove the inorganic salts, and precipitated dropwise into 400 mL of methanol with stirring. After suction filtration and drying, the polymer was redissolved in 40 mL of chloroform and precipitated again into 400 mL of methanol to yield a white fibrous polymer after filtration. This was dried at 80 °C under vacuum for 24 h. Yield = 70%. The yields for the other polymers ranged from 60 to 85%. The reason these yields were not quantitative was due to some adsorption of polymer by the Celite.

Polymerization with End-Capping: Typical Procedure. To a dry 100-ml three-neck flask equipped with a cold water condenser, Dean–Stark trap, Caframo mechanical stirrer, and thermometer were added 4 g (8.74 mmol) of imidoaryl biphenol **5c**, 2.256 g (8.871 mmol, 1.5% excess relative to biphenol of 4,4′-difluorodiphenyl sulfone, 0.054 g (0.262 mmol) of 3,5-di-*tert*-butylphenol, 29.5 mL of NMP, 15 mL of toluene, and 1.69 g (12.24 mmol, 40% excess) of anhydrous potassium carbonate. The mixture was heated to reflux (130 °C). The temperature was maintained between 130 and 140 °C for 3–5 h to ensure complete dehydration and was then increased to 143 °C for 1 h, 150 °C for 1 h, 165 °C for 30 min, and 170 °C for 30 min. From 143 to 170 °C the color changed from dark red to light brown to dark brown. The reaction mixture was diluted with 25 mL of NMP, filtered hot through a thin bed of Celite, and added dropwise to a beaker containing 800 mL of methanol which was rapidly stirred. The fibrous polymer was filtered, washed with H_2O and then methanol, and dried by suction overnight; weight = 5.9 g, yield = 99%. The polymer was redissolved in 50–60 mL of chloroform to give a clear gold viscous solution and added dropwise to a stirred solution of 800 mL of methanol:400 mL of H_2O. The fibrous polymer was filtered and dried.

Scheme II



2, X = H
8, X = Br

3, X = H
9, X = Br

7, X = H (33% overall)
10, X = Br (83% overall)

End-capping reactions for poly(imidoaryl ether ketone)s **12e** and **12i** were run in the same manner using 1% excess 4,4′-difluorobenzophenone without 3,5-*tert*-butylphenol or 4-phenylphenol.

All of the reactions, except the synthesis of phenolphthalin (**2**) were run under an atmosphere of nitrogen.

Results and Discussion

Monomer Synthesis. Bisphenols. As was shown earlier for imidoaryl biphenols **5a–c** (R = methyl, dodecyl, and phenyl),[2] the synthesis for the monomers herein is also a four-step reaction sequence, but the last two steps can be done in one pot (Scheme I). Phenolphthalein (**1**) is first reduced to phenolphthalin (**2**) (yield = 95%) employing the procedure of Blicke and Patelski[4] and **2** is then rearranged in concentrated sulfuric acid to furnish isobenzofuran **3**.[11] Blicke and Wienkauff[11] have shown that **3** can be oxidized to 1,2-bis(4-hydroxybenzoyl)benzene (**7**) (overall yield of 33%, Scheme II). The yield of intermediate **3** is not reported. One can assume that the major side reaction contributing to low yields is probably sulfonation while generating the isobenzofuran, since the

Table I
Synthesis and Properties of Biphenols

compd	R	yield (%)	mp (°C)	appearance	elem anal. (%) calcd	elem anal. (%) found
5a	methyl	50–60	410[a] 328[b]	yellow powder white needles	C, 75.94; H, 4.33; N, 3.53	C, 75.81; H, 4.33; N, 3.51
5b	dodecyl	50–60	253–255 173[b]	yellow needles white needles	C, 78.66; H, 7.15; N, 2.55	C, 78.59; H, 7.13; N, 2.57
5c	phenyl	50–60	383[a] 293[b]	yellow needles white needles	C, 78.76; H, 4.19; N, 3.06	C, 78.44; H, 4.44; N, 3.06
5d	4-chlorophenyl	47	157–159	yellow needles	C, 73.25; H, 3.69; N, 2.85; Cl, 7.12	C, 73.25; H, 3.84; N, 2.84; Cl, 6.90
5e	4-fluorophenyl	51	367–370	yellow needles	C, 75.78; H, 3.82; N, 2.95; F, 4	C, 75.70; H, 3.89; N, 2.91; F, 3.73
5f	3-(trifluoromethyl)phenyl	62	362[a]	yellow needles	C, 70.86; H, 3.45; N, 2.76; F, 10.85	C, 71.24; H, 3.43; N, 2.71; F, 10.53
5g	4-(trifluoromethyl)phenyl	43	>385[a] 216[b]	yellow needles white needles	C, 70.86; H, 3.45; N, 2.76; F, 10.85	C, 71.17; H, 3.42; N, 2.74; F, 10.80
5h	2-fluorophenyl	46	374–376	yellow needles	C, 75.78; H, 3.82; N, 2.95; F, 4	C, 75.48; H, 3.81; N, 2.59; F, 3.89
5i	2-(trifluoromethyl)phenyl	41	358[a] 270–272[b]	yellow needles white needles	C, 68.97; H, 3.64; N, 2.3; F, 9.35	C, 69.51; H, 3.73; N, 2.02; F, 9.36
5j	2-phenylphenyl	40	329–331 246–249[b]	light green needles white crystals	C, 77.78; H, 4.41; N, 2.27	C, 77.52; H, 4.39; N, 1.97

[a] Decomposes at melting point. [b] Bisacetate of biphenol.

Table II
Synthesis and Properties of Maleimides

compd	R	yield (%)	mp (°C)	appearance	procedure	solvent	temp (°C)	purification procedure
6b	dodecyl	96	47–51[a,b]	light brown powder	1	MEK	60	
6d	4-chlorophenyl	82	115–117[c]	yellow needles	2	DMAc	60 (48 h)	recrystallization (Cx/MeOH)
6e	4-fluorophenyl	81	153–155[a]	yellow needles	2	DMAc	23 (24 h)	recrystallization (MeOH)
6f	3-(trifluoromethyl)phenyl	41	oil[d]	orange	2	DMAc	50 (24 h)	flash column chromatography (petroleum ether:EtOAc, 8:1)
6g	4-(trifluoromethyl)phenyl	61	151–153[a]	white powder	2	DMAc	60 (24–48 h)	flash column chromatography (petroleum ether:EtOAc, 3:1)
6h	2-fluorophenyl	64	70[a]	yellow needles	2	DMAc	23 (24 h)	flash column chromatography (petroleum ether:EtOEt, 3:1)
6i	2-(trifluoromethyl)phenyl	67	89–90[a]	white needles	2	DMAc	23 (60 h)	flash column chromatography (petroleum ether:EtOEt, 4:1)
6j	2-phenylphenyl	43	141–142[a]	yellow powder	2	DMAc	23 (24 h)	flash column chromatography (petroleum ether:EtOAc, 3:1)

[a] Satisfactory HRMS obtained $m/z \pm 0.0001$. [b] Small amount purified by flash column chromatography (petroleum ether:EtOAc, 7:3). [c] Reference 9. [d] Reference 10.

same reaction sequence employing the tetrabromo derivative **8**, which would not undergo sulfonation, furnishes the bisketone **10** in 83% overall yield.[12] To minimize sulfonation of **3**, we cooled the sulfuric acid and **2** to 0 °C, before mixing, and also minimized the ratio of sulfuric acid to **2** (1.25:1 volume to mass, respectively). The isobenzofuran is unstable; therefore it is important to react it with a maleimide within a short time (e.g., 15 min) after isolation, and as a result the isobenzofuran is added to the maleimide before it has been completely dried. Adams[13,14] has shown that the Diels–Alder adduct of isobenzofuran (without hydroxyl groups at the para position of the phenyl) and maleic anhydride can be dehydrated to provide a fully aromatized product by using HCl(g) in refluxing methanol. We found that these Diels–Alder adducts **4d–j** (Scheme I) can also be dehydrated in this manner to provide biphenols **5d–j**. However, if the isobenzofuran is not throughly washed, then there is enough residual acid remaining for aromatization to occur, and HCl(g) is not required.

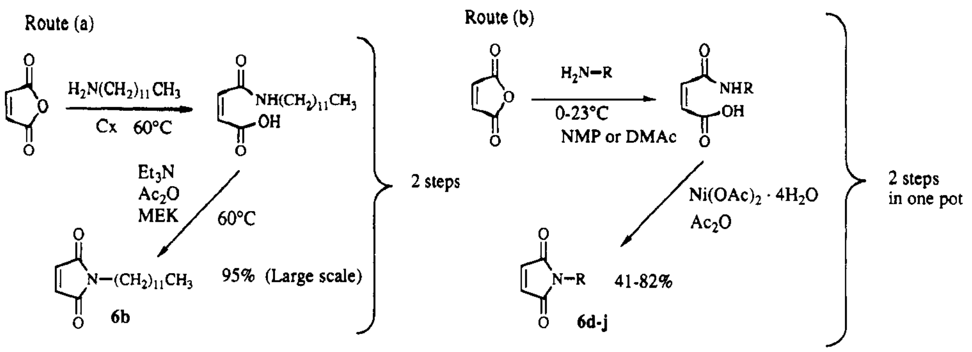
Table I shows the yields (41–62% overall) and properties of the biphenols. They are all yellow except **5j** and the bisacetates of the biphenols are white. Except for monomers **5b** and **5d**, all have high melting points. It was previously reported that **5a** (R = methyl) and **5c** (R = phenyl) were only soluble (20% w/v solids) in NMP:toluene (2:1) at 80 and 60 °C, respectively,[2] whereas all of the biphenols reported here with substituents on the pendant phenyl **5d–j** are readily soluble at room temperature to give homogeneous solutions.

Maleimides Synthesis. Scheme III shows the methods used to synthesize the maleimides, and Table II gives the properties, purification procedures, and yields. *N*-Dodecylmaleimide (**6b**) was synthesized by ring closure of the amic acid produced from maleic anhydride and dodecylamine (route a, Scheme III). Cyclodehydration using the procedure of Wang (Et_3N/Ac_2O)[15] gave an excellent yield (95%) of the resulting maleimide, while other methods ($NaOAc/Ac_2O$[16] and $Ni(OAc)_2{\cdot}4H_2O$[8]) provided yields which were below 40%.

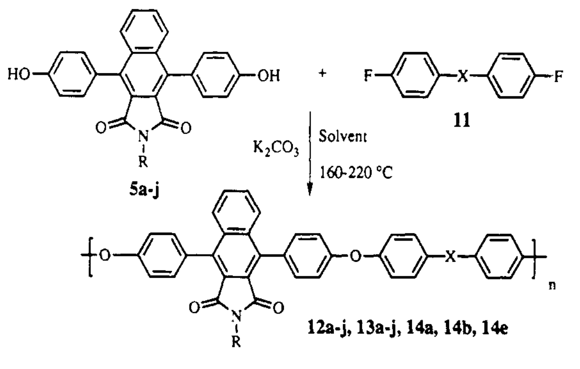
For the phenyl-substituted maleimides we found the procedure of Hergenrother et al.[8] ($Ni(OAc)_2{\cdot}4H_2O$) to be the most effective and convenient, since the yields were reasonable and the reaction could be done in one pot, and in most cases at ambient temperatures (route b, Scheme III). Lower yields were obtained employing other methods (Et_3N/Ac_2O[15] and $NaOAc/Ac_2O$[16]), particularly when the substituents on the phenyl were fluoro and trifluoromethyl.

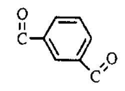
Polymer Synthesis. Imidoaryl biphenols **5c–j** were polymerized with 4,4′-difluorobenzophenone, 4,4′-difluorodiphenyl sulfone, and 1,3-bis(4-fluorobenzoyl)benzene (Scheme IV) to give polymers **12c–j**, **13c–j**, and **14e**[17] employing standard conditions in NMP or DMSO as solvent (depending on the polymer solubility) in the presence of excess anhydrous potassium carbonate.[18–20] Table III lists the inherent viscosities, T_g's, and solubilities of the polymers. With the exception of the ketone and sulfone polymers **12c** and **13c** (R = phenyl),[2] the remaining

Scheme III



Scheme IV



Polymer	X
12a-j	CO
13a-j	SO2
14a, b, e	

Polymers 12-14	R
a	methyl
b	dodecyl
c	phenyl
d	4-chlorophenyl
e	4-fluorophenyl
f	3-trifluoromethylphenyl
g	4-trifluoromethylphenyl
h	2-fluorophenyl
i	2-trifluoromethylphenyl
j	2-phenylphenyl

materials all contain substituents on the pendant phenyl (**12d–j**, **13c–j**, and **14e**).

Polymer Solubilities. All of the polymers in Table III are high molecular weight (η_{inh} = 0.45–1.07 dL/g) and yield tough, clear, flexible films which are fingernail creasable when cast from a solution of chloroform or *sym*-TCE. Except for the ketone and sulfone polymers of **12d** and **13d** (R = 4-chlorophenyl), all of these materials are less soluble than **13c** (R = phenyl) when the viscosities are similar. Polymers **12h–j** and **13h–j**, which have a substituent at the ortho position of the pendant phenyl ring, are also surprisingly less soluble. The ketones are, in general, less soluble than the sulfones, and all of the polymers appear to be amorphous, as was described previously for **12a–c**, **13a–c**, and **14a–c**.[2]

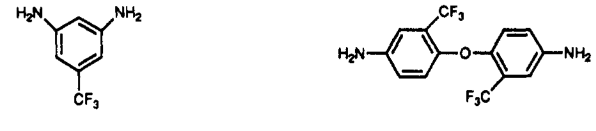
Glass Transition Temperatures. The T_g's of the polymers synthesized herein are all below that of poly(imidoaryl ether sulfone) **13c** (T_g = 310 °C). Thus, it is not possible to increase the T_g by incorporating a halide, trifluoromethyl, or phenyl at the ortho, meta, or para position on the pendant phenyl ring. The addition of substituents on the pendant phenyl group serves only to increase the asymmetry of the molecule, and hence lower the T_g, and does not affect the rigidity of the backbone of the polymer.

Thermooxidative Stability. The temperatures at which 10% weight loss occurs in air and nitrogen by TGA of the ketones and sulfones **12c–j**, **13c–j**, and **14e** are compiled in Table III. The addition of substituents has little effect on the thermooxidative stabilities, even when a strong electron-withdrawing group is attached to the pendant phenyl group. This observation is similar to the preliminary results obtained by Gerber et al.[21] and Buchanan et al.,[22] who found no differences between polyimides which were synthesized using 3,5-diaminobenzotrifluoride (**15**) and 4,4'-oxybis[(3-(trifluoromethyl)benzenamine] (**16**) (Figure 1), respectively, and polyimides synthesized from diamines without trifluoromethyl groups. We also ran isothermal experiments at 400 °C in flowing air (200 mL/min), because such an experiment would be more sensitive to subtle differences in thermooxidative stability. Since isothermal experiments are normally reported for a variety of conditions in the literature, we also measured the known commercial poly(ether sulfone)s **17–19** (Figure 2), which would serve as a useful comparison to the poly(imidoaryl ether ketone)s and poly(imidoaryl ether sulfone)s.

Table III
Thermal Properties and Solubilities of Polymers 12c–j, 13c–j, and 14e

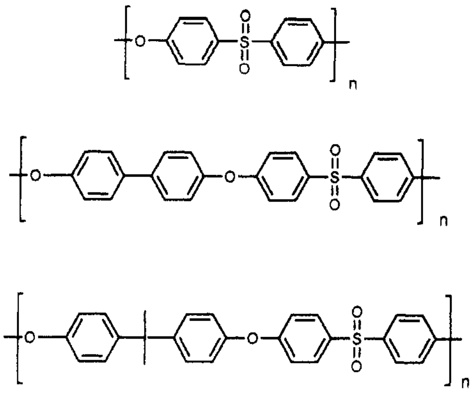
			TGA (°C)		
polymer[a]	η_{inh}[b] (dL/g)	T_g (°C)	air (–10%)	N_2 (–10%)	solubility
12c[c]	0.52	272	551	561	$CHCl_3/CH_2Cl_2$
13c[c]	0.52	310	555	547	$CHCl_3$
12d	0.71	272	550	564	$CHCl_3$
13d	0.45[e]	280	539	552	$CHCl_3$
12e	1.07	290	561	577	NMP
12e[d]	0.62	290	560	578	TCE
13e	0.69[e]	300	558	555	$CHCl_3$
14e	0.71[e]	243	572	569	$CHCl_3$
12f	0.65	252	561	569	TCE
13f	0.63[e]	282	550	550	$CHCl_3/CH_2Cl_2$
13f	0.76	279	558	550	TCE (hot)/NMP
12g	0.84	260	552	573	TCE
13g	0.56[e]	290	540	542	$CHCl_3$
12h	0.61	282	560	565	TCE
13h	0.53	ND[g]	549	540	TCE
12i[d]	0.59	260	552	573	TCE
13i	0.60	290[f]	551	550	TCE (hot)
12j	0.61	245	558	550	TCE
13j	0.74	278	547	539	TCE

[a] Except for polymer **12c**, which was run in DMSO, all of the polymerizations were done in NMP. [b] 0.5 g/dL in NMP at 60 °C. [c] 1.5% excess difluorobenzophenone or difluorodiphenyl sulfone and end-capped with 4-phenylphenol. [d] 1% excess difluorobenzophenone. [e] 0.5 g/dL in TCE at 23 °C. [f] Weak transition. [g] ND = not detectable.



15 **16**

Figure 1. Diamines containing trifluoromethyl substituents.



17

18

19

Figure 2. Poly(ether sulfone)s.

Table IV
Isothermal Thermooxidative Stability of Polymers 17–19, 12e, and 13c–g at 400 °C in Air[a]

			weight remaining (%)		
entry	polymer	η_{inh}[b] (dL/g)	10 h	20 h	23 h
1	**17**	1.37[e]	95	90	88
2	**18**		92	79	74
3	**19**	1.24[e]	85	62	57
4	**13c**[c]	0.52	95	75	67
5	**13c**[d]	0.91	96	87	79–82
6	**13d**	0.45[f]	94	38	<10
7	**12e**	1.07	94	75	56
8	**13e**	0.69[f]	96	89	82
9	**13f**	0.63[f]	95	88	85
10	**13g**	0.56[f]	94	83	71

[a] Flowing air at 200 mL/min. [b] 0.5 g/dL in NMP at 60 °C. [c] 1.5% excess 4,4′-difluorodiphenyl sulfone and end-capped with 4-phenylphenol. See Table V, entry 4. [d] Table V, entry 1. [e] Reported by Aldrich Chemical Co. [f] 0.5 g/dL in TCE at 23 °C.

Table IV shows the results for isothermal aging of the poly(ether sulfone)s **17**, **18**, and **19** (entries 1–3). As expected, **17** (Figure 2) is the most stable, with 88% mass remaining after 23 h at 400 °C, and **19** is the least stable with 57% mass remaining. This is reasonable, since the former has one SO_2 group for every aryl ether linkage, while the latter has only one SO_2 for every two aryl ether linkages and an isopropylidene group.

When electron-withdrawing group are attached to the pendant phenyl group, polymers **13d–j** are not more thermooxidatively stable at 400 °C. Thus, these groups must be too far from the aryl ether linkage which is the least thermooxidatively stable part of the molecule to exert a noticeable effect. The naphthylimido group is sufficiently electron withdrawing to make poly(imidoaryl ether sulfone) polymers **13c** (uncapped) and **13e** (entry 8) and **13f** (entry 9) more stable than poly(ether sulfone)s **18** and **19** (Figure 2). The high molecular weight polymer **13c** (η_{inh} = 0.91 dL/g, entry 5) is considerably more stable than the lower molecular weight polymer **13c** (η_{inh} = 0.52 dL/g, entry 4), even though the latter is end-capped with 4-phenylphenol. The deleterious effect of a shorter chain is also apparent for sulfone polymer **13g** (R = 4-trifluoromethyl, entry 10), where only 71% mass of the original mass remains after 23 h. Thus, it appears a minimum inherent viscosity of about 0.60 dL/g is required to yield poly(imidoaryl ether sulfone)s which exhibit good stability. Surprisingly, when R is 4-chlorophenyl, poly(imidoaryl ether sulfone) **13d** (entry 6) degrades rapidly after 10 h. As expected, the poly(imidoaryl ether ketone) **12e** (entry 7) exhibits much lower thermooxidative stability, even though it is very high molecular weight (η_{inh} = 1.07 dL/g), presumably because of the lower stability of the carbonyl group in the backbone.

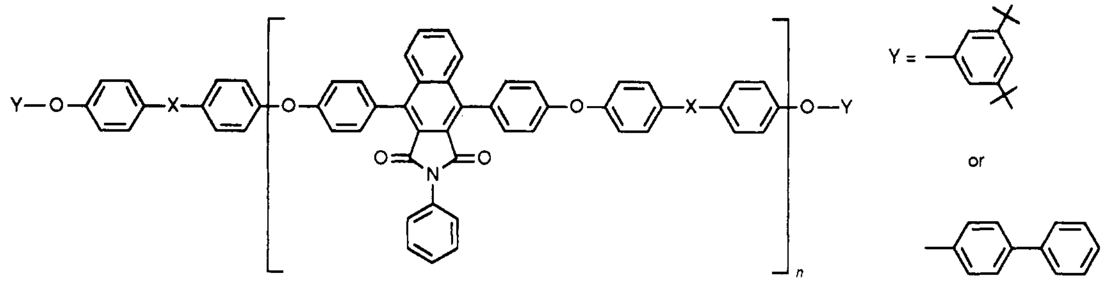
End-Capping Study. We reported previously that poly(imidoaryl ether sulfone) **13c** and poly(imidoaryl ether ketone) **12c** are soluble in chloroform.[2] However, the former can only be fully dissolved at reflux (Table V, entry 1), while the latter exhibits a broad molecular weight distribution (Table V, entry 5) when a 1:1 stoichiometric ratio of biphenol **5c**:difluoride **11** (Scheme V) is employed. We wanted to determine if polymerization by end-capping could improve the molecular weight distribution of **12c** by reducing the chain length and by how much the chain length of both **13c** and **12c** could be reduced, without sacrificing the high T_g and thermooxidative stability. Scheme V outlines the approach which was taken to control the molecular weight by using an appropriate excess of dihalide **11** (difluorobenzophenone and difluorodiphenyl sulfone) to control the molecular weight and then adding enough of either 3,5-di-*tert*-butylphenol or 4-phenylphenol to react with the dihalide at the chains ends.

Table V illustrates that using 2% excess of 4,4′-difluorodiphenyl sulfone (entry 2) significantly decreases the molecular weight and improves the solubility of poly(imidoaryl ether sulfone) **13c** (R = phenyl), so that now it dissolves rapidly at 23 °C in chloroform. However, the polymer films, while flexible, breaks along the crease line, the T_g decreases from 310 to 290 °C, and the inherent viscosity has dropped to 0.31 dL/g. Thus, the polymer is of insufficient molecular weight to demonstrate good polymeric film properties. If the amount of excess 4,4′-difluorodiphenyl sulfone is decreased to 1.5% (entries 3 and 4), then the polymer properties improve significantly. A cast film is now tough and creasable, the T_g is 310 °C (same as uncapped polymer, entry 1), and the polymer is still soluble in chloroform at 23 °C. Similarly, when a 1.5% excess of 4,4-difluorobenzophenone was employed under these conditions with 4-phenylphenol as the end-capper, a lower molecular weight poly(imidoaryl ether ketone) **12c** was obtained with the same inherent viscosity (0.52 dL/g, entry 6) as poly(imdoaryl ether sulfone) **13c** (entry 4), and the polydispersity was significantly improved relative to uncapped polymer **12c** (entry 5). End-capped **12c** is also soluble in chloroform at 23 °C. In addition, for poly(imidoaryl ether ketone)s **12e** (R = 4-fluorophenyl) and **12i** (R = 2-(trifluoromethyl)phenyl), a 1% excess of 4,4′-difluorobenzophenone was necessary to provide polymers which were soluble.

Table V also shows the importance of end groups in determining polymer thermooxidative (air) and thermal (N_2) stability. When samples of long chain (entries 1 and 5) and shorter chain length end-capped polymers (entries 2–4 and 6) were heated from 25 to 600 °C in the TGA, those with 3,5-di-*tert*-butylphenol end groups (entries 2 and 3) had noticeably lower thermooxidative stability due to degradation of the *tert*-butyl groups, while those with 4-phenylphenol had the same stability as the long-chain polymers.

Figure 3 shows that when 3,5-di-*tert*-butylphenol locates at the chain ends, it can be used to determine the molecular weight using ^1H NMR, by simply comparing the integration signal from the *tert*-butyl hydrogens to the integration of the aromatic hydrogens. In addition, Table V shows that this is a useful technique, since the molecular weights obtained from GPC relative to polystyrene standards are misleading since the poly(imidoaryl ether ketone)s and poly(imidoaryl ether sulfone)s undoubtedly have different radii of gyration (R_G) than polystyrene samples of similar molecular weight. Entries 2 and 3 illustrate that M_n obtained from ^1H NMR is within experimental error (±5%) to M_n theoretical, when different

Table V
Effect of Molecular Weight and End-Capper on the Properties of 12c and 13c



entry	X	excess of dihalide (%)	amount of end-capper (%)	η_{inh}[a] (dL/g)	T_g (°C)	TGA (°C) (−10%)	^{1}H-NMR M_n	designed[b] M_n	GPC[c] M_w	GPC[c] M_n	solubility
1	SO_2			0.91	310	556			90 000	31 000	$CHCl_3$ (reflux)
2	SO_2	2	4[d]	0.31	290	536	33 540	34 200	19 500	5 950	$CHCl_3$ (23 °C)
3	SO_2	1.5	3[d]	0.56	310	534	49 000	51 000	40 800	10 700	$CHCl_3$ (23 °C)
4	SO_2	1.5	3[e]	0.52	310	555			36 900	12 100	$CHCl_3$ (23 °C)
5	CO			1.07	272	549			47 250	3 900	$CHCl_3$ (23 °C)[f]
6	CO	1.5	3[e]	0.52	275	551			25 600	7 800	$CHCl_3$ (23 °C)

[a] 0.5 g/dL in NMP at 60 °C. [b] Based on stoichiometry. [c] Based on polystyrene standards. [d] 3,5-Di-*tert*-butylphenol. [e] 4-Phenylphenol. [f] This ketone is presumably soluble in $CHCl_3$ at 23 °C because of the cooperative effects from lower molecular weight chains present.

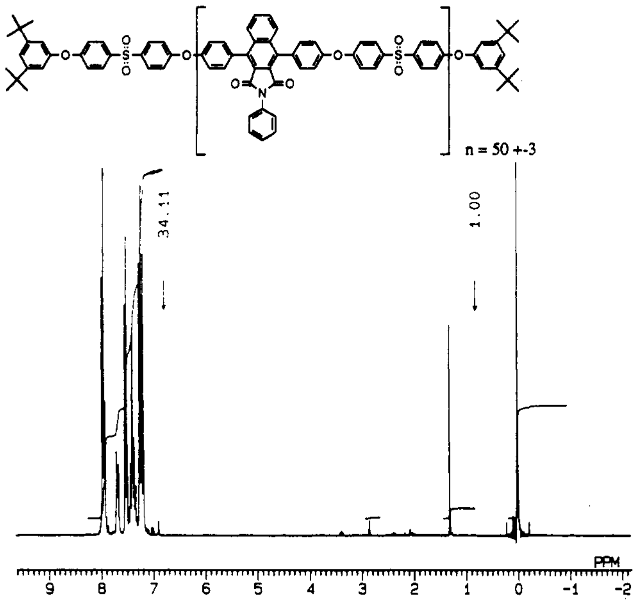


Figure 3. ^{1}H-NMR spectrum of poly(imidoaryl ether sulfone) 13c end-capped with 3,5-di-*tert*-butylphenol.

Scheme V

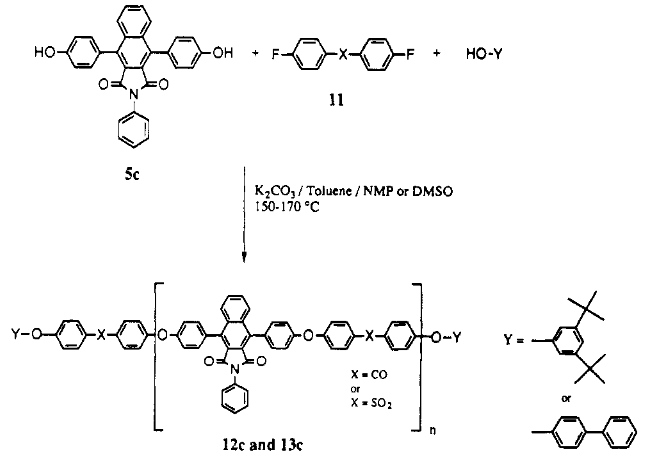


Table VI
Mechanical Properties of Polymers 12a–j, 13a–j, and 14a,b,e

polymer	T_g (°C)[a]	tan δ (TMA/SS)[b]	Young's modulus at 25 °C (GPa)
12a	283		
13a	314	325	2.5 (±0.3)
14a	251	239	2.4
12b	147	113	2.6
13b	167	168	2.6
14b	140	117	2.7
12c[c]	275	277	2.5
13c[c]	310	293	2.6
12d	272	274	2.8
13d	280	312	2.9
12e[d]	290	278	1.9
13e	300	308	2.6
14e	243	245	2.8
12f	252	269[f]	3
13f	282	280	2.3
13f	279[e]	278	2.9
12g	260	274	2
13g	290	311	1.7
12h	282	276	1.4
13h	ND[g]	309	3.4
12i[d]	260	272	2.8
13i	290	284	2.6
12j	245	246	1.7
13j	278	278	2

[a] DSC. [b] Heating rate = 3 °C/min. [c] 1.5% excess difluorobenzophenone or difluorodiphenyl sulfone and end-capped with 4-phenylphenol. [d] 1% excess difluorobenzphenone. [e] Higher molecular weight. [f] Weak transition. [g] ND = not detectable.

amounts of excess sulfone are employed. Thus, as has been shown previously, it is possible to synthesize polymers of desired molecular weight using the appropriate excess of one monomer.[23,24] It should be mentioned that when such measurements are made by NMR, it is vital for the acquisition and delay times to be 3 and 40–60 s, respectively, or else the integration values for the aromatic portion and di-*tert*-butyl groups are incorrect, because the aromatic hydrogens do not have sufficient time to fully relax. We found this to be particularly important for poly(imidoaryl ether sulfone)s with molecular weights above 35 000.

Mechanical Properties. Table VI shows the Young's moduli for polymers **12a–j**, **13a–j**, **14a**, **14b**, and **14e** are all in the range 1.4–3.0 (±0.3) GPa at 25 °C. These values are typical for engineering thermoplastics such as polycarbonate, poly(arylene ether ketone)s, poly(arylene ether sulfone)s, and poly(ether imides). When films of these polymers are heated, they maintain good mechanical properties in the GPa range above 200 °C, except when R is *n*-dodecyl. Figure 4 illustrates a typical example of

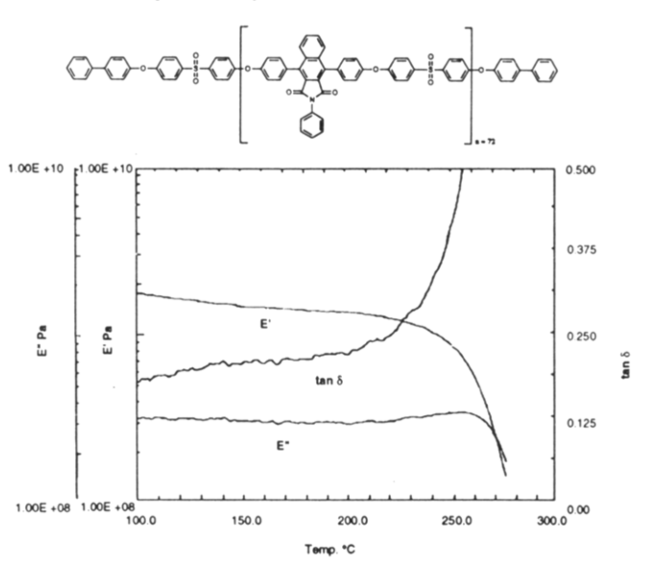
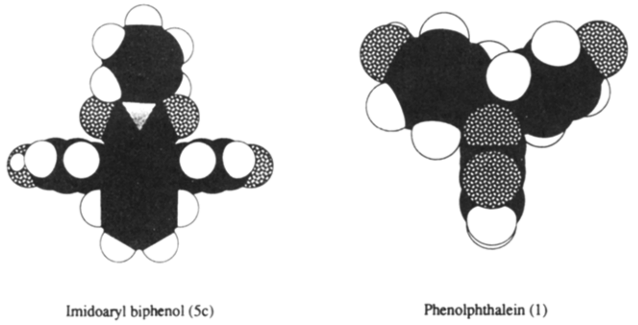


Figure 4. Young's modulus (E'), loss modulus (E''), and tan δ versus temperature for poly(imidoaryl ether sulfone) **13c** end-capped with 4-phenylphenol.

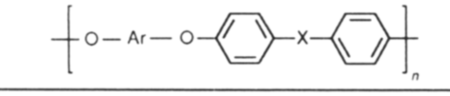


Imidoaryl biphenol (5c)

Phenolphthalein (1)

Figure 5. Comparison of imidoaryl biphenol to phenolphthalein.

Table VII
Polymer Comparison

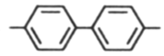


Ar	X	T_g (°C)	T_m (°C)	TGA (°C) (−10%)
20	CO	144^a	335	
21	CO	$200^b/228^c$		
12c–j	CO	245–290		550–561
22	SO_2	230		530
13c–j	SO_2	280–310		539–558

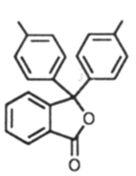
^{a} Reference 25. ^{b} Reference 27. ^{c} Reference 28.

20, Ar =

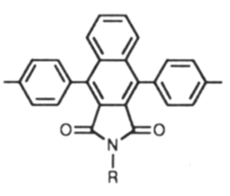
22, Ar =



21, Ar =



12c–j or **13c–j**, Ar =



how the Young's modulus varies with temperature when **13c** (R = phenyl) is heated at 3 °C/min. For all polymers, except the ketone and bisketone of **12b** and **14b**, the T_g values obtained from DSC agree well with tan δ (maximum) obtained from TMA/SS.

Comparison with Other Polymers. Table VII compares known poly(ether ketone)s and poly(ether sulfone)s to the poly(imidoaryl ether ketone)s and poly(imidoaryl ether sulfone)s and illustrates the profound effects of the biphenol on the T_g and thermooxidative stability. In the poly(ether ketone)s, when phenolphthalein (Ar = **21**) is used in place of hydroquinone[25] (Ar = **20**), the polymer becomes completely amorphous[26] and the T_g increases 50–80 °C;[27,28] however, the thermooxidative stability decreases presumably due to the presence of a lactone group in every monomer unit. The imidoaryl group as in **5c–j** further increases the T_g and significantly improves the thermooxidative stability of **12c–j**. The increase in T_g is most likely due to the rigid naphthylimido group, which makes the biphenol (e.g., **5c**) more rigid than phenolphthalein (**1**) (Figure 5), providing sufficient steric bulk to reduce freedom of motion along the backbone. The improved thermooxidative stability may be attributed to the electron-withdrawing ability of the naphthylimido group, which stabilizes the aryl ether linkage toward oxidation. Similar explanations can be used when comparing the poly(imidoaryl ether sulfone)s **13c–j** to poly(ether sulfone)s.

Conclusion

A series of novel poly(imidoaryl ether ketone)s and poly(imidoaryl ether sulfone)s have been synthesized. These materials all appear to be amorphous. When the substituent on the imide group is Ph–Y (where Y = H, Cl, F, Ph, and CF_3) glass transition temperatures are in the range 243–310 °C and the thermooxidative stability is exceptional. The presence of the naphthylimido moiety located between the phenyl rings of the imidoaryl biphenols significantly increases the T_g and also increases the thermooxidative instability of poly(ether ketone)s and poly(ether sulfone)s. These two features can be attributed to the steric bulk and electronegativity of the naphthylimido moiety, respectively. The presence of electron-withdrawing substituents on the pendant phenyl group **12d–j** and **13c–j** does not significantly improve the thermooxidative stability relative to **13c**. Many of these polymers are soluble in common organic solvents such as methylene chloride and chloroform when the inherent viscosity is in the range 0.52 dL/g, which allows for facile solution processing. The mechanical properties are typical of high-performance engineering thermoplastics (modulus = 1.4–3.0 GPa) and the properties are maintained up to temperatures to T_g. These biphenols are readily accessible in four steps from inexpensive starting materials in good yield.

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Registry No. **5a**, 137464-64-3; **5b**, 137464-65-4; **5c**, 137464-66-5; **5d**, 142581-77-9; **5e**, 142581-78-0; **5f**, 142581-79-1; **5g**, 142581-86-0; **5h**, 142581-80-4; **5i**, 142581-81-5; **5j**, 142581-82-6; **6b**, 17616-03-4; **6d**, 1631-29-4; **6e**, 6633-22-3; **6f**, 53629-19-9; **6g**, 54647-09-5; **6h**, 63566-53-0; **6i**, 34520-59-7; **6j**, 65833-05-8; **12a** (copolymer), 137464-68-7; **12a** (SRU), 142581-98-4; **12b** (copolymer), 137464-71-2; **12b** (SRU), 142581-99-5; **12c** (copolymer), 137464-74-5; **12c** (SRU), 142582-00-1; **12d** (copolymer), 142581-83-7; **12d** (SRU), 142582-01-2; **12e** (copolymer), 142581-84-8; **12e** (SRU), 142582-02-3; **12f** (copolymer), 142581-85-9; **12f** (SRU), 142582-03-4; **12g** (copolymer), 142581-87-1; **12g** (SRU), 142582-04-5; **12h** (copolymer), 142581-88-2; **12h** (SRU), 142582-05-6; **12i** (copolymer), 142581-89-3; **12i** (SRU), 142582-06-7; **12j** (copolymer), 142582-07-8; **12j** (SRU), 142611-07-2; **13a** (copolymer), 137464-67-6; **13a** (SRU), 142582-08-9; **13b** (copolymer), 137464-70-1; **13b** (SRU), 142582-09-0; **13c** (copolymer), 137464-73-4; **13c** (SRU), 142582-10-3; **13d** (copolymer), 142581-90-6; **13d** (SRU), 142582-11-4; **13e** (copolymer), 142581-91-7; **13e** (SRU), 142582-12-5; **13f** (copolymer), 142581-92-8; **13f** (SRU), 142582-13-6; **13g** (copolymer), 142581-93-9; **13g** (SRU), 142582-14-7; **13h** (copolymer), 142581-94-0; **13h** (SRU), 142582-15-8; **13i** (copolymer), 142581-95-1; **13i** (SRU), 142582-16-9; **13j** (copolymer), 142581-96-2; **13j** (SRU), 142582-17-0; **14a** (copolymer), 137464-69-8; **14a** (SRU), 142582-18-1; **14b** (copolymer), 137464-72-3; **14b** (SRU), 142582-19-2; **14e** (copolymer), 142581-97-3; **14e** (SRU), 142582-20-5; 1,3-bis(4-fluorobenzoyl)benzene, 108464-88-6; isophthaloyl chloride, 99-63-8; fluorobenzene, 462-06-6; *N*-dodecylmaleamic acid, 52492-69-0; dodecylamine, 124-22-1; maleic anhydride, 108-31-6.