Synthesis and Characterization of New Aromatic Poly(Ether Ketone)s

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SYNOPSIS

A general method for the preparation of aromatic poly(ether ketone)s containing amide, amide-imide, cyano, oxadiazole, and pyridazine moieties has been developed. Polymerization is based on a ketone-activated halide displacement from amide-, amide-imide-, cyano-, oxadiazole-, or pyridazine-containing bis(4-fluorobenzoyl) moieties by bisphenoxides in a polar aprotic solvent. The bis(4-fluorobenzoyl) moieties were prepared by reaction of 4-fluorobenzoyl chloride with diphenoxy monomers containing amide, amide-imide, cyano, oxadiazole, or pyridazine groups under modified Friedel–Crafts conditions in methylene chloride. All of the polyether ketones prepared were amorphous and exhibited T_gs ranging from 134 to 218°C. In addition, films of the aromatic polyether ketones displayed good thermal stability and flexibility. The dielectric constants of the films were characterized as a function of relative humidity (RH). © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Linear aromatic polymers have long been known for their usefulness in meeting the high-performance requirements for structural resins, polymer films, and coating materials needed by the aerospace and electronics industry. Aromatic polyimides[1-4] and polyetherketones[5,6] are the polymers of choice for these applications because of their unique combination of chemical, physical, and mechanical properties. Poly(ether ketone)s are especially desirable because they are economically accesible by both nucleophilic and electrophilic routes and are more easily processed than polyimides, because of the flexibilizing ether and ketone groups present in the polymer backbone.

Recently, another class of polymers that has been investigated for high-performance applications are the poly(aryl ether)s containing heteroatom substitutents. These poly(aryl ether)s can be prepared by the nucleophilic displacement of activated aromatic dihalides by alkali metal bisphenoxides in a polar aprotic medium. Heterocycles such as benzox-

azoles,[7,8] imidazoles,[9] phenylquinoxalines,[10,11] 1,2,4-triazoles,[12] and oxadiazoles[12-14] have been incorporated within poly(arylene ethers) utilizing this synthetic procedure.

The synthesis of aromatic poly(ether amide)s[15,16] by nucleophilic displacement of activated aryl fluorides has been reported. Recently, work has also appeared describing the synthesis of poly(ether ketone amide)s and poly(ether ketone imide)s using Friedel–Crafts syntheses.[17]

Aromatic polyethers containing pendent cyano groups [poly(ether nitrile)s] have also been studied. For example, Kricheldorf described the preparation of aromatic polyethers containing pendent cyano groups by the condensation of silylated diphenols with difluorobenzonitriles.[18] Several new, high molecular weight, soluble polyarylether alternating copolymers containing pendent cyano groups have also been prepared by sequential reaction of 2-chloro-6-fluorobenzonitrile with the potassium salts of two different diphenols. In this case, reaction of 2 mol of 2-chloro-6-fluorobenzonitrile with 1 mol of a diphenoxide yields a bis(3-chloro-2-cyanophenyl)ether (bis-CCPE) as the only product. Subsequent reaction of a second bisphenoxide with the bis-CCPEs
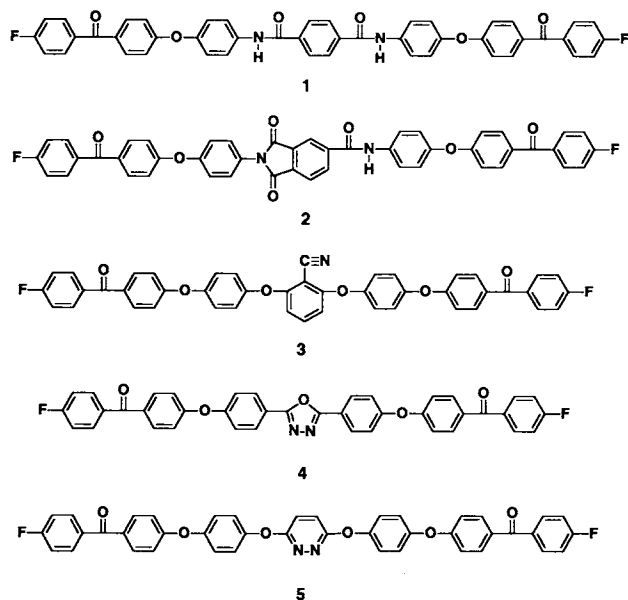
Figure 1 Difluoro-containing monomers used to prepare poly(Aryl ether ketone)s.

causes displacement of the activated chloro groups and formation of alternating copolymers containing pendent cyano groups.[19]

Aromatic poly(oxadiazoles) (POXs) are a class of high temperature-resistant heterocyclic polymers that show excellent thermal stability. POXs can be prepared by the cyclodehydration of polyhydrazides containing the —CONHNHCO— group. This can be done thermally near the glass transition temperature of the polyhydrazide or in solution by using dehydrating agents such as polyphosphoric acid, sulfuric acid, or phosphorous oxychloride.[20–23] Until recently, the use of POXs has been limited, because most POXs were described as being soluble only in strong acids and could not be processed from organic solvents.

The synthesis of poly(arylene ether oxadiazole)s from bis(hydroxyphenyl oxadiazoles) and commercially available activated aromatic dihalides has recently been reported.[12] Alternatively, we reported a series of poly(arylene ether-1,3,4-oxadiazoles) prepared by the reaction of bisphenols with the 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazoles using potassium carbonate in N,N-dimethylacetamide.[13]

Aromatic poly(ether pyridazine)s (PEPs) are a class of high temperature-resistant heterocyclic polymers that have received only limited study. PEPs can be prepared by the condensation of a dialkali metal salt of a diphenol with 3,6-dichloropyridazine in an anhydrous dipolar aprotic solvent. For example, preparation of a PEP from bisphenol A

and 3,6-dichloropyridazine was described by Johnson.[24] Alternatively, we recently described two poly(ether imide pyridazine)s prepared by the reaction of 3,6-bis(4-aminophenoxy)pyridazine and 3,6-bis(3-aminophenoxy)pyridazine with 2,2-bis(3,4-dicarboxyphenyl)hexafluoroisopropane dianhydride (6FDA).[25]

As part of an effort to develop high-performance, high temperature-resistant polymers for microelectronic applications, we have prepared a series of poly(aryl ether ketone)s containing amide, amide-imide, cyano, oxadiazole, or pyridazine groups and characterized their thermal and electrical properties. The poly(arylene ether ketone)s reported herein were prepared by the reaction of a bisphenol with 1, 2, 3, 4, or 5 using potassium carbonate in N,N-dimethylacetamide. All of the resulting poly(arylene ether ketone)s were amorphous and soluble in polar aprotic solvents.

EXPERIMENTAL

Starting Materials

N,N-Dimethylacetamide (DMAc), N-methyl-2-pyrrolidinone (NMP), 4-fluorobenzoyl chloride, 4-phenoxyaniline, terephthaloyl chloride, trimellitic anhydride chloride, hydrazine hydrate, phosphorus oxychloride, 2,6-difluorobenzonitrile, 3,6-dichloropyridazine, 4,4-(hexafluoroisopropylidene)diphenol (6F-BPA), phenol, resorcinol, 4-phenoxyphenol, 2,7-dihydroxynaphthalene (NE), and potassium carbonate were obtained from Aldrich and used without purification. 9,9-bis(4-Hydroxyphenyl)fluorene (HPF) and 1,1-bis(4-hydroxyphenyl)-1-phenylethane (bisphenol AP) were obtained from Kennedy and Klim and used without purification.

Monomers

N,N-Bis(4-phenoxyphenyl)terephthalamide (NPT) was prepared by reaction of terephthaloyl chloride with 4-phenoxyaniline in DMAc at room temperature in a manner similiar to that previously described.[26] Aqueous workup followed by drying and recrystallization (xylene/DMAc) yielded N,N-bis(4-phenoxyphenyl)-terephthalamide as a white powder (78% yield).

4-(4-Phenoxyphenycarbamoyl)-N-(4-phenoxyphenyl)phthalimide (PPP) was prepared in a manner similiar to that previously described.[26] The synthesis of PPP was carried out by reaction of trimellitic anhydride chloride with 4-phenoxyaniline

in DMAc at 5°C for 2 h. The intermediate amic acid was dehydrated to PPP by refluxing in DMAc for 4 h. After cooling to room temperature, aqueous workup, followed by drying and recystallization (xylene), yielded PPP as a light yellow powder (81% yield).

N,N-Bis[4-(4-fluorobenzoyl)-(4-phenoxy-phenyl)]-terephthalamide (**1**) was prepared as depicted in Scheme 1 using modified Friedel–Crafts reaction conditions[27] with the following procedure: to a 250 mL round bottom flask was added 12.31 g (0.0246 mol) of *N,N*-bis(4-phenoxy-phenyl)tere-phthalamide, 8.04 g (0.0507 mol) of 4-fluorobenzoyl chloride, 2.3 g (0.0246 mol) of dimethyl sulfone, and 132 g of dichloromethane. The mixture was stirred under nitrogen, cooled in an ice bath to 5°C, and 14.5 g (0.109 mol) of aluminum chloride was added. The mixture was stirred for 1 h at ice bath temper-ature, 2 h at room temperature, and 1 h at reflux. The mixture was allowed to cool to room tempera-ture and poured into a mixture of methanol and ice. The resulting solid was filtered, washed with meth-anol and water, dried, and recrystallized from DMAc to yield 14.2 g (75% yield). m.p. = 339–341°C. Cal-culated for $C_{46}H_{28}N_2O_6F_2$: C, 74.39; H, 3.77; N 3.77; F, 5.12. Found: C, 74.64; H, 3.46; N, 3.62; F, 5.44.

4-[(4-Fluorobenzoyl)-(4-phenoxyphenylcarba-moyl)]-*N*-[(4-fluorob enzoyl)-(4-phenoxyphenyl)] phthalimide (**2**) was prepared as depicted in Scheme 2 in a similar manner to **1**, except that PPP was used in place of NPT. The resulting solid was fil-tered, washed with methanol and water, dried, and recrystallized from NMP (87% yield). m.p. = 292–294°C. Calculated for $C_{47}H_{26}N_2O_7F_2$: C, 73.44; H, 3.41; N 3.64; F, 4.94. Found: C, 73.81; H, 3.46; N, 3.60; F, 4.84.

2,6-Bis(4-phenoxyphenyl)benzonitrile (BPB) was prepared as follows: To a 100 mL round bottom flask was added 2.5 g (0.0179 mol) of 2,6-difluorobezo-
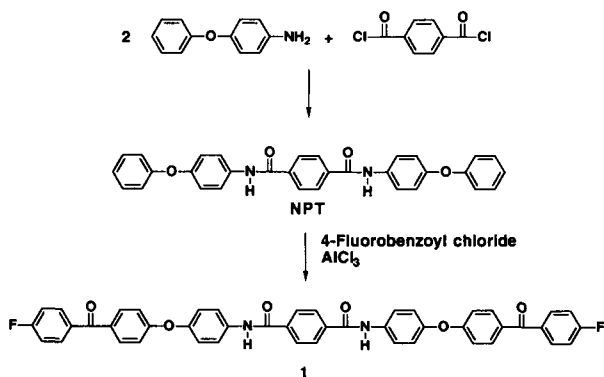
Scheme 1 Synthesis of **1**.
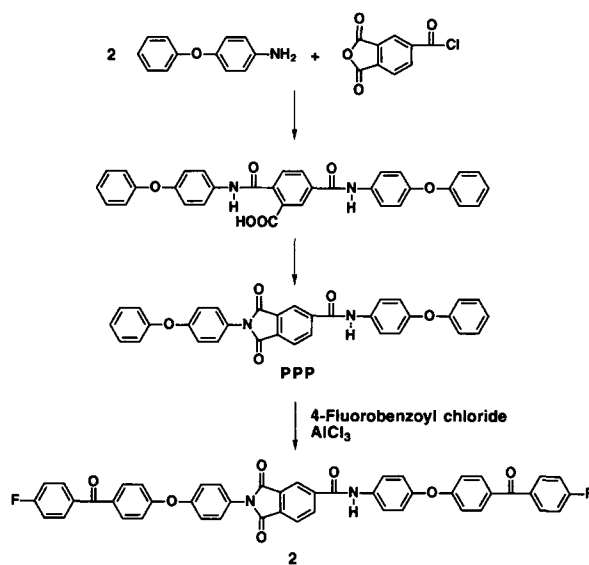
Scheme 2 Synthesis of **2**.

nitrile, 6.69 g (0.0358 mol) of 4-phenoxyphenol, 5.5 g (0.040 mol) of potassium carbonate, and 55 g of DMAc. The mixture was heated to 160°C, with stir-ring under nitrogen for 18 h. Isolation by aqueous workup followed by recrystallization (toluene/hex-ane) afforded 6.9 g (84% yield) of 2,6-bis(4-phen-oxyphenyl)benzonitrile as a white crystalline solid. m.p. = 150–151°C. M^+/e = 471. Calculated for $C_{31}H_{21}NO_4$: C, 78.97; H, 4.49; N, 2.97. Found: C, 78.64; H, 4.26; N, 2.92.

2,5-Bis(4-(4-fluorobenzoyl)-(4-phenoxy-phenyl))benzonitrile (**3**) was prepared as depicted in Scheme 5 using the following procedure: To a 250 mL round bottom flask was added 5.00 g (0.0106 mol) of 2,6-bis(4-phenoxyphenyl)benzonitrile, 3.38 g (0.0212 mol) of 4-fluorobenzoyl chloride, 1.3 g (0.0139 mol) of dimethyl sulfone, and 102 g of di-chloromethane. The mixture was stirred under ni-trogen until the solids dissolved, cooled in an ice bath, and 14.5 g (0.109 mol) of aluminum chloride was added. The mixture was stirred for 1 h at ice bath temperature, 3 h at room temperature, and 1 h at reflux. The mixture was allowed to cool to room temperature and poured into methanol. The result-ing solid was filtered, washed with methanol and water, dried, and recrystallized from DMAc to yield 6.2 g (81%) of **3** as a white powder. m.p. = 201–202°C. Calculated for $C_{45}H_{247}NO_6F_2$: C, 75.52; H, 3.80; N, 1.96; F, 5.31. Found: C, 75.73; H, 3.66; N, 1.92; F, 5.34.

2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole (BFO) was prepared as previously described.[30] Methyl 4-fluorobenzoate was purified by distillation. The in-

termediates, 4-fluorobenzoic hydrazide and 1,4-bis(4-fluorophenyl)hydrazide, were washed with methanol, dried, and used without further purification. Dehydration of 1,4-bis(4-fluorophenyl) hydrazide was carried out in refluxing phosphorous oxychloride overnight. Removal of most of the phosphorous oxychloride by distillation, followed by workup in water yielded 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole as a white powder; m.p. = 201–203°C (lit.[30] m.p. = 200–202°C), gas chromatographic/mass spectral analysis gave $M^+/e = 258$.

2,5-Bis(4-phenoxyphenyl)-1,3,4-oxadiazole (BPO) was prepared as follows: to a 100 mL round bottom flask was added 2.5 g (0.00968 mol) of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole, 2.18 g (0.0232 mol) of phenol, 3.2 g (0.0232 mol) of potassium carbonate, and 40 g of DMAc. The mixture was heated at 150°C with stirring under nitrogen for 16 h. Isolation by aqueous workup followed by recrystallization (toluene/hexane) afforded 3.4 g (86% yield) of 2,5-bis(4-phenoxyphenyl)-1,3,4-oxadiazole as a white crystalline solid. m.p. = 161–163°C. $M^+/e = 406$. Calculated for $C_{26}H_{18}N_2O_3$:C, 76.83; H, 4.46; N, 6.89. Found: C, 76.74; H, 4.36; N, 6.92.

2,5-Bis(4-(4-fluorobenzoyl)-(4-phenoxyphenyl))-1,3,4-oxadiazole (4) was prepared as depicted in Scheme 7 using the following procedure: to a 250 mL round bottom flask was added 10.00 g (0.0246 mol) of 2,5-bis(4-phenoxyphenyl)-1,3,4-oxadiazole, 2.3 g (0.0246 mol) of dimethyl sulfone, and 132 g of dichloromethane. The mixture was stirred under nitrogen until the solids dissolved, cooled in an ice bath, and 14.5 g (0.109 mol) of aluminum chloride was added. The mixture was stirred for 15 min at ice bath temperature then 8.04 g (0.0507 mol) of 4-fluorobenzoyl chloride was added. The mixture was stirred for an additional 1 h at ice bath temperature, 2 h at room temperature, and 1 h at reflux. The mixture was allowed to cool to room temperature and poured into methanol. The resulting solid was filtered, washed with methanol and water, dried, and recrystallized from DMAc affording 14.2 g (89% yield) of 4 as a white crystalline powder. m.p. = 261–263°C. Calculated for $C_{40}H_{24}N_2O_5F_2$: C, 73.84; H, 3.72; N 4.31; F, 5.84. Found: C, 73.74; H, 3.36; N, 4.32; F, 5.74.

3,6-Bis(4-phenoxyphenoxy)pyridazine (BPP) was prepared as follows: to a 100 mL round bottom flask was added 1.50 g (0.010 mol) of 3,6-dichloropyridazine, 4.32 g (0.0232 mol) of 4-phenoxyphenol, 3.2 g (0.0232 mol) of potassium carbonate, and 40 g of DMAc. The mixture was heated at 150°C with stirring under nitrogen for 40 h. Isolation by aqueous workup followed by recrystallization (toluene/hex-

ane) afforded 5.7 g (76% yield) of 3,6-bis(4-phenoxyphenoxy)-pyridazine as a white crystalline solid. m.p. = 144–146°C. Calculated for $C_{28}H_{20}N_2O_4$: C, 74.99; H, 4.50; N, 6.25. Found: C, 74.74; H, 4.36; N, 6.32.

3,6-Bis[4-(4-fluorobenzoyl)-(4-phenoxyphenoxy)]pyridazine (5) was prepared as depicted in Scheme 9, using the following procedure: to a 250 mL round bottom flask was added 11.02 g (0.0246 mol) of 3,6-bis(4-phenoxyphenoxy)pyridazine, 14.5 g (0.109 mol) of aluminum chloride, 2.3 g (0.0246 mol) of dimethyl sulfone, and 132 g of dichloromethane. The mixture was stirred under nitrogen until the solids dissolved, cooled in an ice bath, and 8.04 g (0.0507 mol) of 4-fluorobenzoyl chloride was added. The mixture was stirred for 1 h at ice bath temperature, 2 h at room temperature, and 2 h at reflux. The mixture was allowed to cool to room temperature and poured into a methanol/ice mixture. The resulting solid was filtered, washed with methanol and water, dried, and recrystallized from DMAc affording 15.1 g (88.5% yield) of 5 as a white powder. m.p. = 192–194°C. Calculated for $C_{42}H_{26}N_2O_6F_2$: C, 72.83; H, 3.78; N 4.04; F, 5.49. Found: C, 72.74; H, 3.46; N, 4.02; F, 5.54.

Polymerizations

Aromatic poly(ether ketone)s were prepared by the reaction of a bisphenol and 1, 2, 3, 4, or 5 in the presence of potassium carbonate in DMAc at 160°C. Below are listed general synthetic procedures for the preparation of the poly(aryl ether ketone)s.

Aromatic Poly(ether ketone amide)s and Poly(ether ketone amide-imide)s Synthesis

To a 100 mL round bottom flask was added 7.68 g (0.010 mol) of 2, 3.36 g (0.010 mol) of 4,4'-(hexafluoroisopropylidene) diphenol, 40.0 g of DMAc, and 3.6 g (0.027 mol) of potassium carbonate. The mixture was heated at 160°C with stirring under nitrogen for 17 h. The mixture was allowed to cool to room temperature. The polymer was precipitated by pouring the reaction mixture into a blender containing about 200 mL of water, filtered, washed three times with water, and dried to yield 9.1 g (92% yield) of a white powder. The synthesis of poly(arylene ether ketone amide)s and poly(arylene ether ketone amide-imide)s are depicted in Schemes 3 and 4, respectively.

Aromatic Poly(ether ketone nitrile)s Synthesis

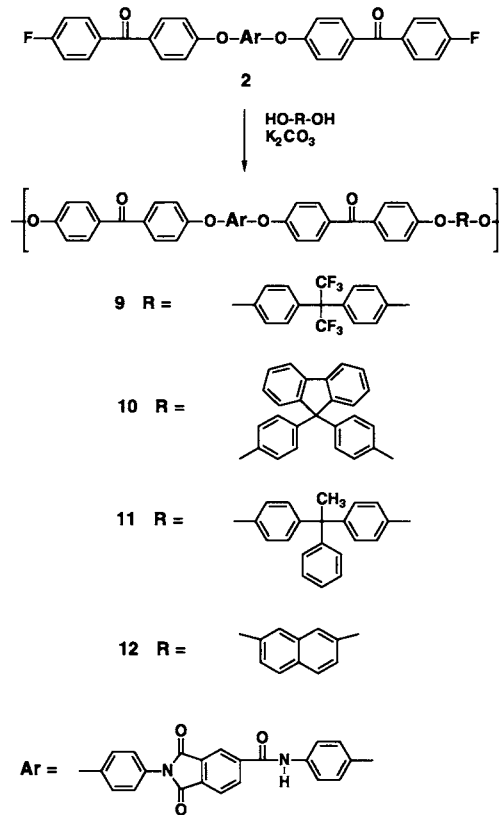To a 100 mL round bottom flask was added 7.16 g (0.010 mol) of 3, 3.36 g (0.010 mol) of 4,4'-(hexa-
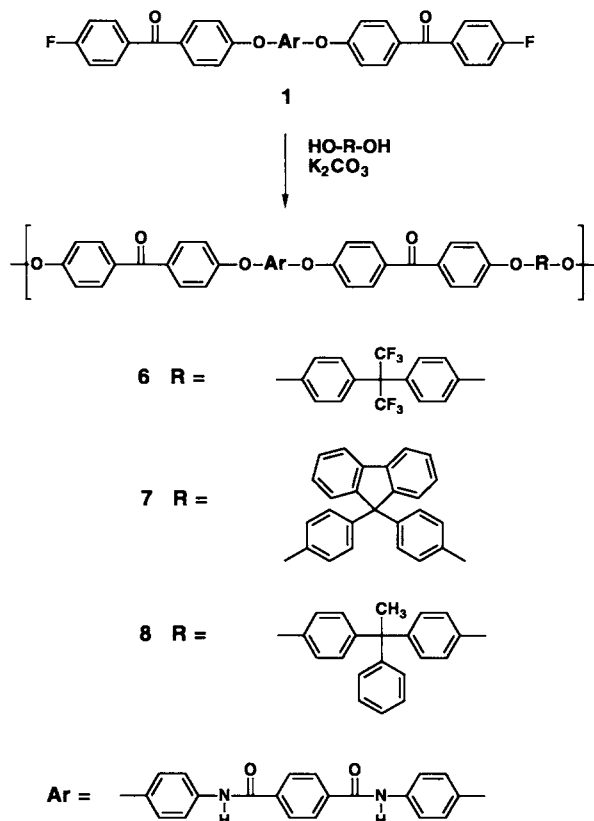
Scheme 3 Synthesis of poly(ether ketone amide)s from **1**.

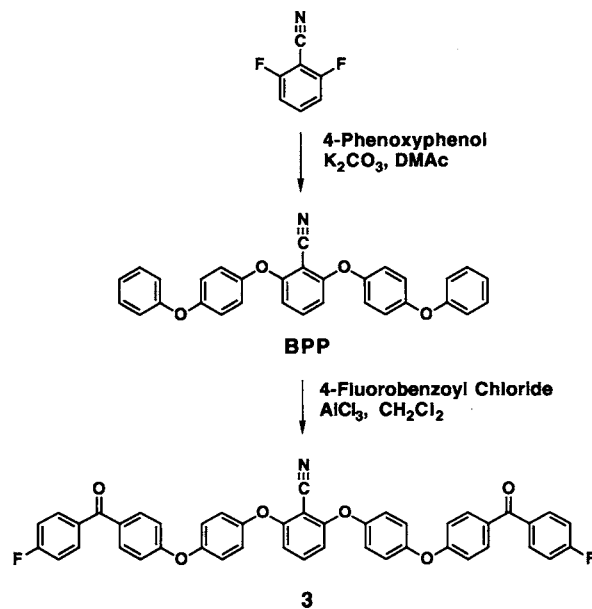**Scheme 4** Synthesis of poly(ether ketone amide-imide)s from **2**.

fluoroisopropylidiene) diphenol, 42 g of DMAc, and 3.1 g (0.022 mol) of potassium carbonate. The mixture was heated at 160°C with stirring under nitrogen for 17 h. The mixture was allowed to cool to room temperature. The polymer was precipitated by pouring the reaction mixture into a blender containing about 200 mL of water, filtered, washed three times with water, and dried to yield 8.9 g (91% yield) of a white powder. The synthesis of poly(arylene ether ketone nitrile)s is depicted in Scheme 6.

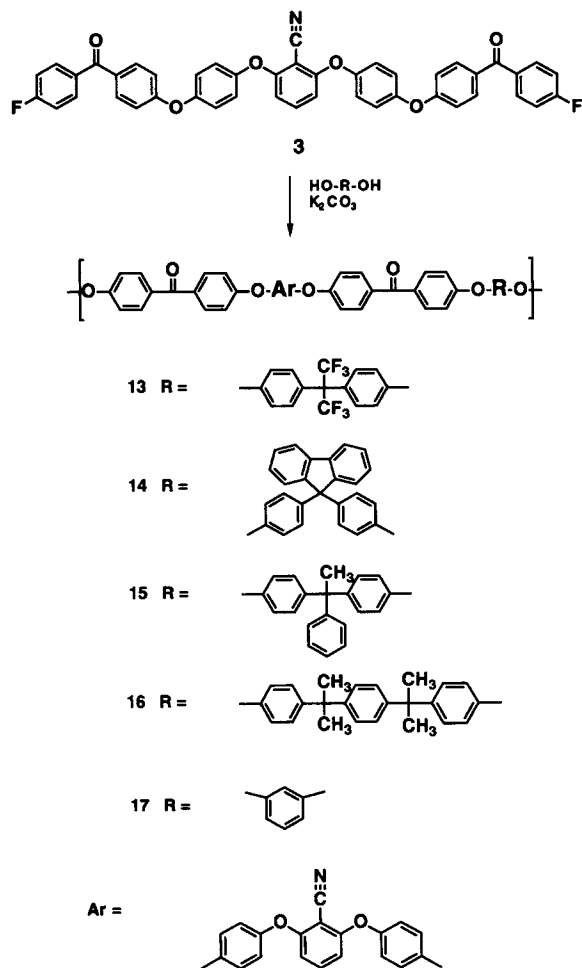### Aromatic Poly(ether ketone oxadiazole)s Synthesis

To a 100 mL round bottom flask was added 6.51 g (0.010 mol) of **4**, 3.36 g (0.010 mol) of 4,4'-(hexafluoroisopropylidiene) diphenol, 40 g of DMAc, and 3.1 g (0.022 mol) of potassium carbonate. The mixture was heated at 160°C with stirring under nitrogen for 17 h. The mixture was allowed to cool to room temperature. The polymer was precipitated by pouring the reaction mixture into a blender containing about 200 mL of water, filtered, washed three times with water, and dried to yield 5.1 g (92% yield)
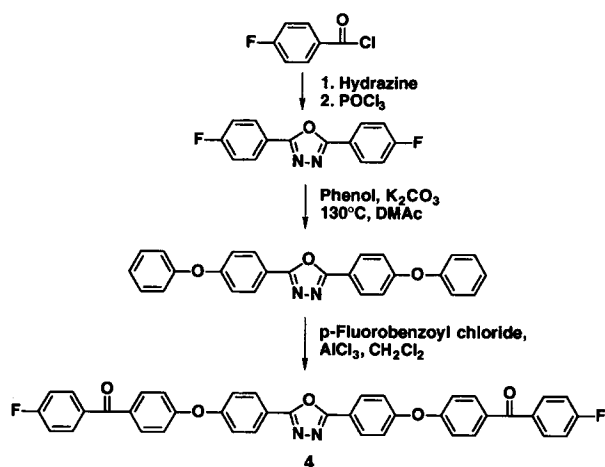

Scheme 5 Synthesis of **3**.

Scheme 6 Synthesis of poly(ether ketone nitrile)s from **3**.

of a white powder. The synthesis of poly(arylene ether ketone-1,3,4-oxadiazole)s is depicted in Scheme 8.

Aromatic Poly(ether ketone pyridazine)s Synthesis

To a 100 mL round bottom flask was added 3.46 g (0.005 mol) of **5**, 1.68 g (0.005 mol) of 4,4'-(hexafluoroisopropylidene) diphenol, 25.2 g of DMAc, and 2.1 g (0.016 mol) of potassium carbonate. The mixture was heated at 160°C with stirring under nitrogen for 17 h. The mixture was allowed to cool to room temperature. The polymer was precipitated by pouring the reaction mixture into a blender containing about 100 mL of water, filtered, washed three times with water, and dried to yield 4.55 g (92% yield) of a white powder. The synthesis of poly(arylene ether ketone pyridazine)s is depicted in Scheme 10.
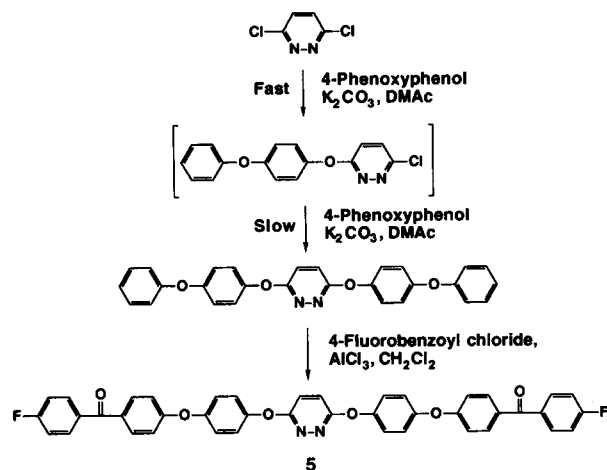

Scheme 7 Synthesis of **4**.

Polymer Films

Solutions of the polymers (15–20 wt % solids) in NMP were spin coated onto glass substrates. The coatings were dried 1 h at 100°C and 45 min at 200°C. The films, about 10 μm in thickness, were released from the glass substrates by placing the
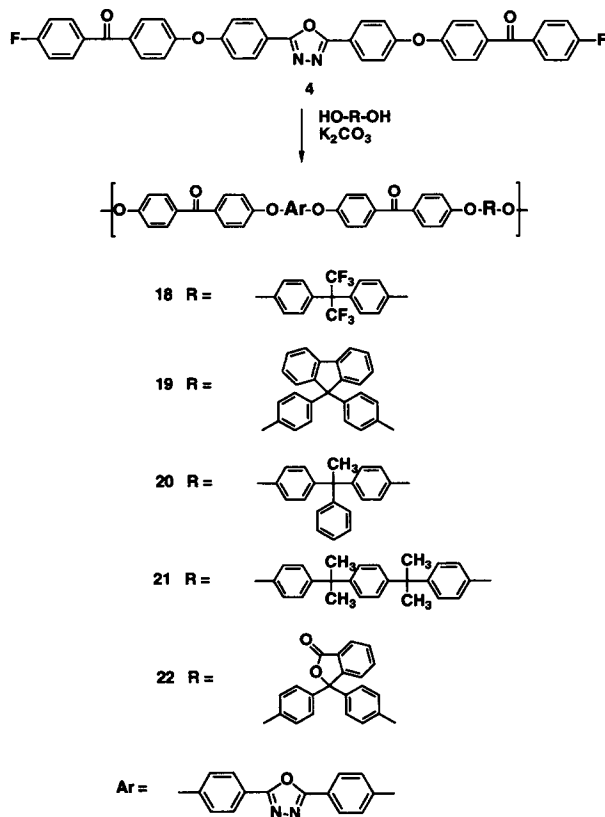
Scheme 8 Synthesis of poly(ether ketone oxadiazole)s from **4**.

Scheme 9 Synthesis of 5.

substrate in deionized water after cooling to room temperature. All seven poly(ether ketone amides)s yielded tough, flexible, creasable films.

Measurements

Dielectric constants were measured using the previously described fluid displacement method.[29] The capacitance of the films was measured using circular gold electrodes (1 inch diameter) mounted in a brass dielectric cell held a constant 25°C and a GenRad Precision LC Digibridge (Model 1688) at 10 kHz. Percent relative humidity was measured using a General Eastern dew point hygrometer (System 1100DP). Dielectric constants were measured at 0%, 26%, and 54% RH. Glass transition temperatures (T_g), taken as the midpoint of the change in slope of the baseline, were determined using differential scanning calorimetry (DSC) using a heating rate of 10°C/min. Thermal gravimetric analyses (TGA) were determined in air using a heating rate of 20°C/min. Both DSC and TGA were performed on a Seiko SSC 5200 System DSC 220C TGA/DTA 320. Infrared spectral analysis was performed on a Bio-Rad FTS-60A FTIR. The molecular weight distributions were measured using a Waters GPC in the dual-detection mode (DRI and UV). The UV detector was operated at 254 nm. The samples were prepared by dissolving 2 mg of polymer in 10 mL THF. The injection volume was 200 μ liters. Separations were affected using 2 Polymer Labs 10 microns PL mixed-B columns. THF was used as the mobile phase. The molecular weight distributions were calculated relative to narrow polystyrene standards ranging from 10^2 to 4×10^6 M_W. Proton-decoupled ^{13}C NMR

spectra were recorded on a Varian XL-300 operating at 75.4 MHz.

RESULTS AND DISCUSSION

Polyether Ketone Amides and Polyether Ketone Imide-Amides

The syntheses of the diketones 1 and 2 involve a number of different synthetic procedures, and their syntheses are depicted in Schemes 1 and 2, respectively. Reaction of 4-phenoxyaniline with terephthaloyl chloride and trimellitic anhydride chloride afforded NPT and PPP, respectively. Both reactions proceeded in high yield, and no purification of the intermediate compounds, NPT and PPP, was required during the reaction sequences. Acylation of NPT and PPP with 4-fluorobenzoyl chloride to prepare 1 and 2, respectively, was carried out under modified Friedel–Crafts reaction conditions[17,27] in methylene chloride using aluminum chloride catalyst and dimethylsulfone as catalyst moderator. Both 1 and 2 were easily recrystallized from DMAc or NMP to yield high purity monomers suitable for polymerizations.

The reactions of 1 and 2 with diphenols to yield polyetherketones 6–12 were carried out in DMAc
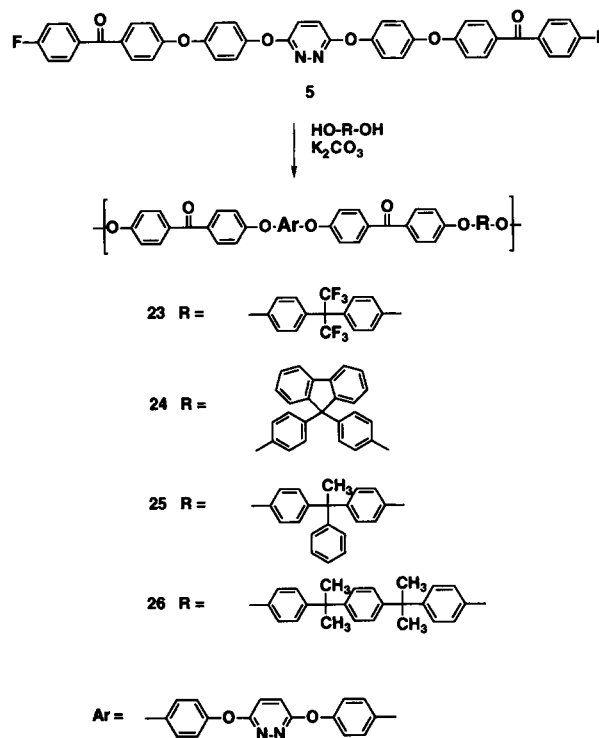
Scheme 10 Synthesis of poly(ether ketone pyridazine)s from 5.

using an excess of potassium carbonate to yield viscous solutions. Subsequent workup in water yielded the polymers as white powders. Judging by the viscosity increase, the polymerization reactions were near completion after only about 6 h at 160°C. The syntheses of polyetherketones 6–12 are depicted in Schemes 3 and 4.

Poly(ether ketone amide)s 6, 7, 9, and 10, were soluble in DMAc and NMP but were insoluble in cyclohexanone, tetrahydrofuran, and xylene. Polymers 6 and 9 swell in cyclohexanone and tetrahydrofuran and 7 swells in cyclohexanone.

The T_gs for the poly(ether ketone amide)s prepared from 1 and 6F-BPA, HPF, and Bisphenol AP were 185, 186, and 165°C, respectively. Thermal gravimetric analysis of 6, 7, and 8 reveals that the polymers exhibit initial weight loss in air at about 460°C (scan rate = 20°C/min.). The T_gs for the poly(ether ketone amide)s prepared from 2 and 6F-BPA, HPF, and Bisphenol AP were 146, 146, and 134°C, respectively. The T_g for the polyether prepared from 2 and 2,6-dihydroxynaphthalene was not detected by DSC. Thermal gravimetric analysis of 9, 10, 11, and 12, reveals that these polymers are less thermally stable than polyethers 6, 7, and 8. Polyethers 9, 10, 11, and 12 exhibit initial weight loss in air at 400 to 425°C, whereas polyethers 5, 6, and 7 exhibit initial weight loss in air at about 460°C. Table I presents the characterization data of the poly(ether ketone amide)s.

The key structural features of polymers 6 through 12 can be identified by FT-IR spectroscopy. Key features in the FTIR spectrum of 6 include the following absorptions: amide N—H, 3312 cm^{-1}, aromatic C—H, 3049 cm^{-1}, ketone C=O, 1653 cm^{-1}, amide C O, 1596 cm^{-1}; aromatic C=C, 1502 cm^{-1}; and aromatic ether Ar-O-Ar, 1253 cm^{-1}.

At 0% relative humidity (RH), 6, 7, and 8 have dielectric constants (measured at 10 kHz) of 3.51,

3.70, and 3.69, respectively. At 54% RH, the dielectric constants of 6, 7, and 8 increase to 4.54, 4.68, and 4.14, respectively. At 0% RH, 9, 10, 11, and 12 have dielectric constants of 3.11, 3.35, 3.27, and 3.47, respectively. At 54% RH, the dielectric constants of 9, 10, 11, and 12 increased to 4.73, 3.63, 5.13, and 3.89, respectively. The relationship between dielectric constant and relative humidity for polymers 6–12 is depicted graphically in Figures 2 and 3. For comparison, one of the most common polyimides used as a dielectric in microelectronics applications is the polyimide PMDA-ODA,[30] made by reaction of pyromelletic dianhydride (PMDA) and 4,4'-diaminodiphenylether (ODA). For PMDA-ODA, the dielectric constant is 3.10 at 0% RH and 3.71 at 58% RH.[29]

Polyether Ketones Nitriles

The synthesis of 2,6-bis(4-phenoxyphenoxy)benzonitrile, as depicted in Scheme 5, proceeds in high yield. Displacement of the two fluoro groups in the 2,6-difluorobenzonitrile proceeds readily to yield 2,6-bis(4-phenoxyphenoxy)benzonitrile and is near completion in about 8 h, as shown by GC/Mass. Spec. The cyano group can accept a negative charge and lower the activation energy for the displacement of the chloro-substituent through a Meisenheimer complex, analogous to more common activating groups such as ketone or sulfone. Friedel–Crafts acylation of 2,6-bis(4-phenoxyphenoxy)benzonitrile with 4-fluorobenzoyl chloride was carried out under modified Friedel–Crafts reaction conditions[16,17] using dimethylsulfone as a catalyst moderator to yield 2,6-bis[4-(4-fluorobenzoyl)(4-phenoxyphenyl)]benzonitrile (3) in high yield.

The reactions of 3 with 6F-BPA, HPF, Bisphenol AP, Bisphenol P, and resorcinol were carried out in DMAc at 160°C using an excess of potassium car-

Table I Properties of Poly(Ether Ketone Amide)s and Poly(Ether Ketone Amide-Imide)s

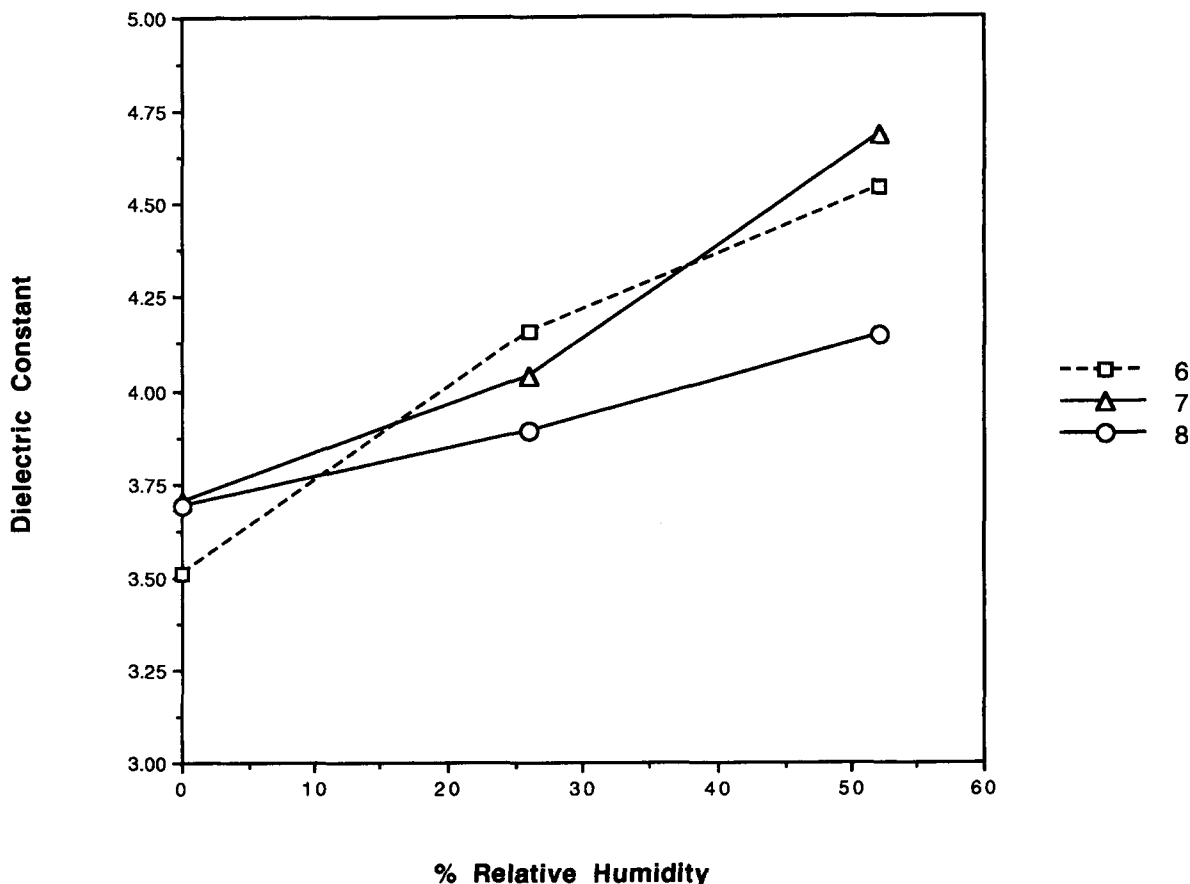| Polymer	Diphenol	T_g (°C) (DSC)	TGA (°C) Onset	Dielectric Constant	
				0% RH	54% RH
6	6F-BPA	185	458	3.51	4.54
7	HPF	186	466	3.70	4.68
8	Bisphenol AP	168	468	3.69	4.14
9	6F-BPA	146	409	3.11	4.73
10	HPF	146	425	3.35	3.63
11	Bisphenol AP	134	403	3.27	5.13
12	NE	ND[a]	400	3.47	3.76

[a] ND = not detected.

Figure 2   Relationship of dielectric constant to % relative humidity for poly(ether ketone amide)s 6-8.

bonate to yield viscous solutions of polymers **13**, **14**, **15**, **16**, and **17**, respectively. Subsequent workup in water yields the polymers depicted in Scheme 6 as white powders. Judging by the viscosity increase of the reaction media, the polymerization reaction was near completion after only about 7 h at 160°C.

The T_gs for the poly(ether ketone nitrile)s **13**, **14**, **15**, **16**, and **17**, prepared from **3** and 6F-BPA, HPF, Bisphenol AP, Bisphenol P, and resorcinol, respectively, range from 142 to 200°C. Thermal gravimetric analysis of **13**, **14**, **15**, **16**, and **17** reveals that the polymers exhibit initial weight loss in air at about 500°C (scan rate = 20°C/min.).

At 0% relative humidity (RH), **13**, **14**, **15**, **16**, and **17** have dielectric constants (measured at 10 kHz) of 3.02, 3.44, 3.43, 2.88, and 3.32, respectively. At about 70% RH, the dielectric constants of **12**, **13**, **14**, **15**, and **16** increased to 3.51, 4.36, 4.08, 3.17, and 4.31, respectively. The relationships between dielectric constant and relative humidity for polymers **12–16** are depicted graphically in Figure

4. Table II presents the characterization data of the poly(ether ketone nitrile)s.

The key structural features of the monomers and polymers can be identified by FT-IR spectroscopy. Key features in the FT-IR spectrum of 2,6-bis[4-(4-fluorobenzoyl)(4-phenoxyphenyl)]benzonitrile (**3**) include the following absorptions: aromatic C—H, 3062 cm^{-1}, cyano CN, 2202 cm^{-1}; Ketone C=O, 1653 cm^{-1}; aromatic C=C, 1594 and 1491 cm^{-1}; and aromatic ether Ar-O-Ar, 1247 cm^{-1}. The key features in the FT-IR spectrum of **16** include the following absorptions: aliphatic C—H, 3971 cm^{-1}; aromatic C—H, 3069 cm^{-1}, ketone C=O, 1659 cm^{-1}; cyano CN, 2202 cm^{-1}; aromatic C=C, 1592 and 1491 cm^{-1}, and aromatic ether Ar-O-Ar, 1245 cm^{-1}.

Hergenrother[31] and Haddad[32] have previously reported that aromatic polymers containing pendent cyano groups undergo crosslinking upon heating to elevated temperatures. The crosslinking reaction was described as the thermally induced trimerization of the cyano groups to the sym-triazines. Although
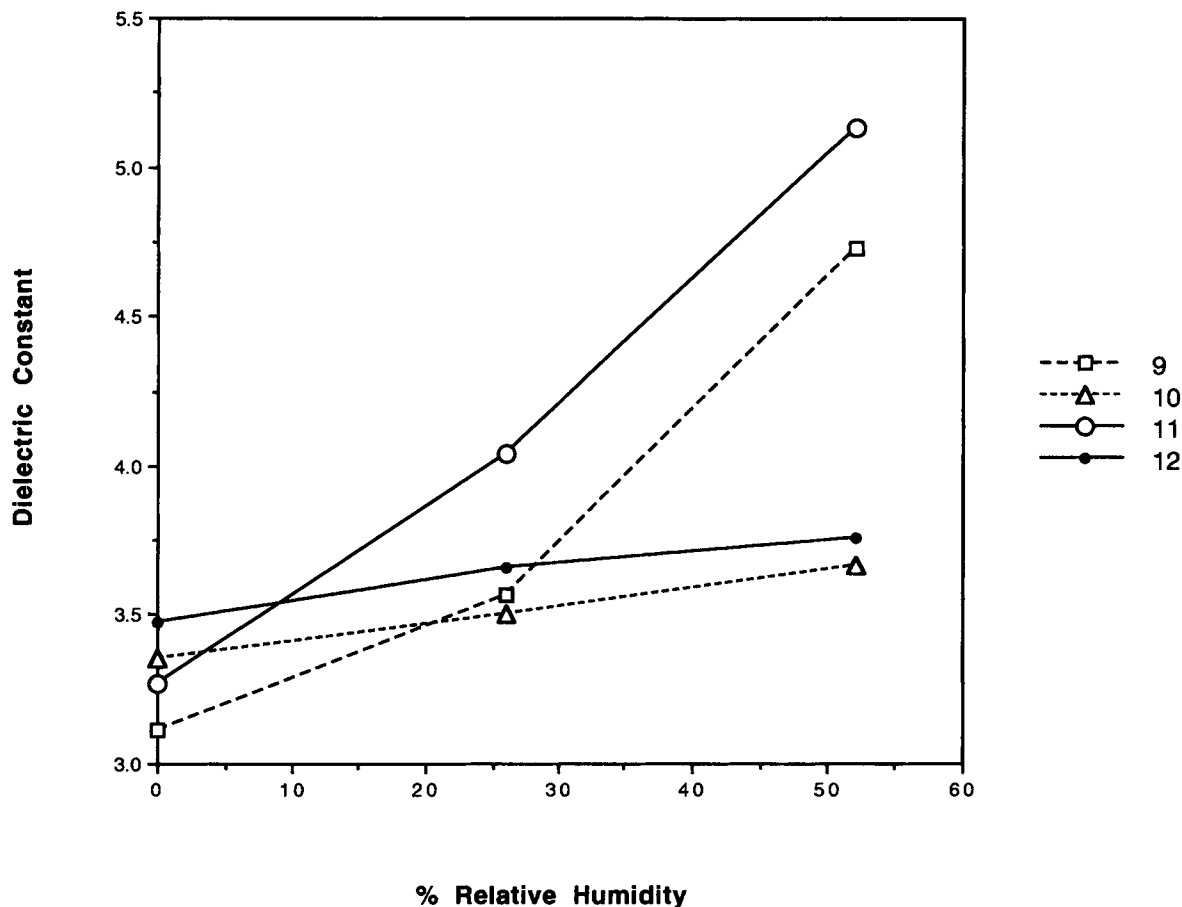
Figure 3   Relationship of dielectric constant to % relative humidity for poly(ether ketone amide-imide)s 9-12.

no exotherm peaks are detected in the DSC thermograms, we found that thermal treatment of films of polymers **12**, **13**, **14**, and **15** at 350°C for 2 h yielded insoluble, crosslinked products. The failure to detect an exotherm in the DSC thermograms would be expected if the thermal crosslinking reactions of the cyano groups are slow and/or the heat of reaction is small. The crosslinking reactions of the cyano groups may be sterically inhibited by the two ether linkages, both of which are meta to the cyano group. This steric interference would cause slow crosslinking reactions and could explain the high temperatures needed for the crosslinking reactions to proceed.

Polyether Ketone Oxadiazoles

The synthesis of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole, as depicted in Scheme 7, proceeds in high yield, and no purification of intermediate compounds was required during the reaction sequence. Nucleo-

philic displacement of the activated aromatic aryl fluorides in 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole with potassium phenoxide in DMAc yields 2,5-bis(4-phenoxyphenyl)-1,3,4-oxadiazole. The oxadiazole moiety can accept a negative charge and thereby lower the activation energy for the displacement of the para-substituted fluoro-substituent through a Meisenhimer complex, analogous to conventional activating groups such as ketone or sulfone. Friedel–Crafts acylation of 2,5-bis(4-phenoxyphenyl)-1,3,4-oxadiazole with 4-fluorobenzoyl chloride yields **4** in high yield.

The reactions of **4** with 6F-BPA, HPF, Bisphenol AP, Bisphenol P, and phenolphthalein (PPH), as depicted in Scheme 8, were carried out in DMAc at 160°C using an excess of potassium carbonate to yield viscous solutions of polymers **18**, **19**, **20**, **21**, and **22**, respectively. Subsequent workup in water yields the polymers as white powders.

The T_gs for the poly(ether ketone oxadiazole)s prepared from **4** and 6F-BPA, HPF, Bisphenol AP,
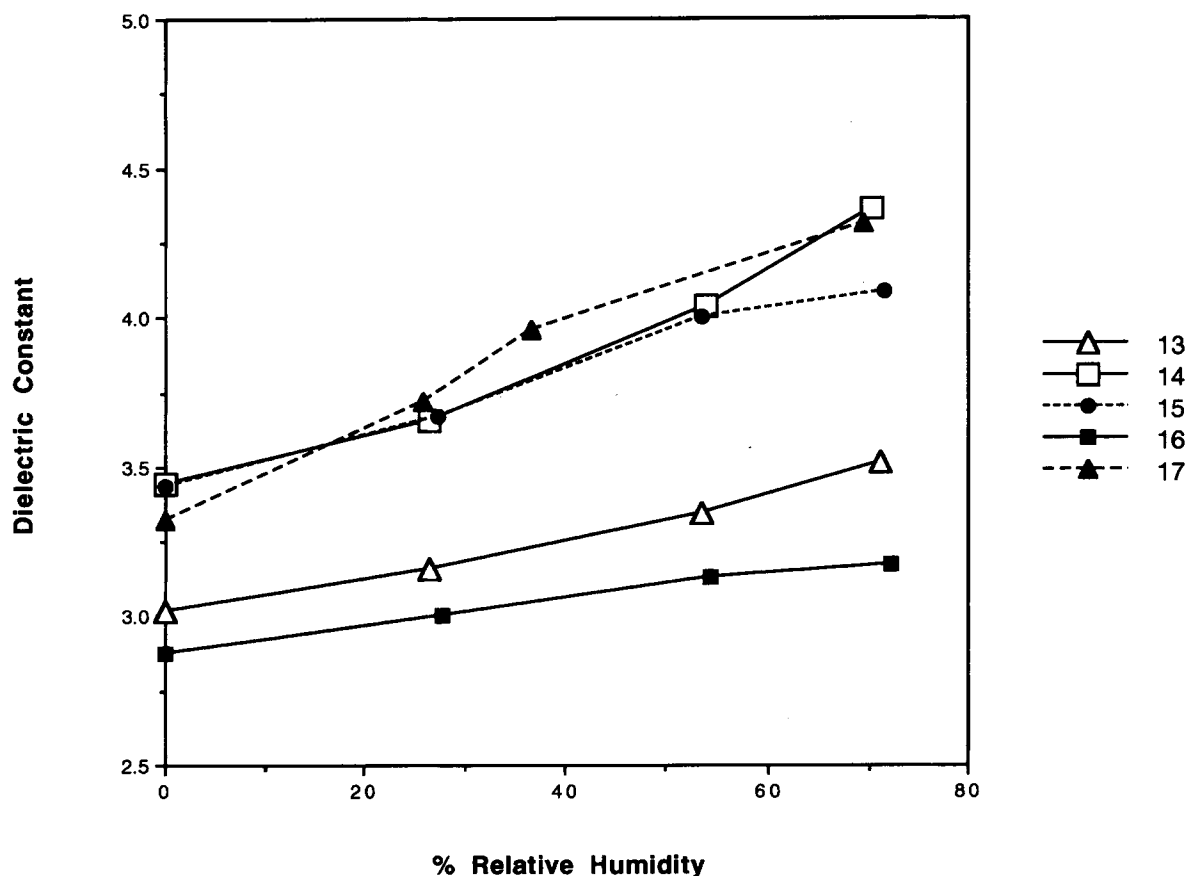
Figure 4   Relationship of dielectric constant to % relative humidity for poly(ether ketone nitrile)s 13–17.

and Bisphenol P were 176, 218, 179, and 172°C, respectively. Thermal gravimetric analysis of **18, 19, 20,** and **21**, reveals that the polymers exhibits initial weight loss in air at about 500°C (scan rate = 20°C/min.). Table III presents the thermal characterization data of the poly(ether imide oxadiazole)s.

At 0% relative humidity (RH), **18, 19, 20, 21,** and **22** have dielectric constants (measured at 10 kHz) of 3.09, 3.36, 3.42, 2.88, and 3.25, respectively.

At about 70% RH, the dielectric constants of **18, 19, 20, 21,** and **22** increased to 3.53, 4.11, 5.88, 3.17, and 4.72, respectively. The relationship between dielectric constant and relative humidity for polymers **18–22** is depicted graphically in Figure 5. Table III presents the characterization data of the poly(ether ketone oxadiazole)s.

The key structural features of the monomers and polymers can be identified by FT-IR and ^{13}C-NMR spectroscopy. Key features in the FT-IR spectrum

Table II   Properties of Poly(Ether Ketone Nitrile)s

| | | | | Dielectric Constant | |
| | | T_g (°C) | TGA (°C) | | |
Polymer	Diphenol	(DSC)	Onset	0% RH	70% RH
13	6F-BPA	162	497	3.02	3.51
14	HPF	200	506	3.44	4.36
15	Bisphenol AP	168	482	3.43	4.08
16	Bisphenol P	163	484	2.88	3.17
17	Resorcinol	142	484	3.22	4.31

Table III Properties of Poly(Ether Ketone Oxadiazole)s

Polymer	Diphenol	T_g (°C) (DSC)	TGA (°C) Onset	Dielectric Constant	
				0% RH	70% RH
18	6F-BPA	176	498	3.09	3.53
19	HPF	218	510	3.36	4.11
20	Bisphenol AP	179	482	3.42	5.88
21	Bisphenol P	172	514	2.88	3.17
22	PPH	—	—	3.25	4.72

of 2,5-bis(4-phenoxyphenyl)-1,3,4-oxadiazole include the following absorptions: aromatic C—H, 3062 cm^{-1}, oxadiazole C=N, 1614 cm^{-1}; aromatic C=C, 1594 and 1491 cm^{-1}; and aromatic ether Ar-O-Ar, 1247 cm^{-1}. The key features in the FT-IR spectrum of 4 include the following absorptions: aromatic C—H, 3074 cm^{-1}, ketone C=O, 1653 cm^{-1}; oxadiazole C=N, 1614 cm^{-1}; aromatic C=C, 1598 and 1499 cm^{-1}; and aromatic ether Ar-O-Ar, 1247 cm^{-1}. The oxadiazole C=N absorption at 1614

cm^{-1} for 3 is reduced to a small shoulder on the peak centered at 1598 cm^{-1}. The key features in the FT-IR spectrum of 21 include the following absorptions: aliphatic C—H, 3971 cm^{-1}; aromatic C—H, 3069 cm^{-1}, ketone C=O, 1659 cm^{-1}; aromatic C=C, 1592 and 1491 cm^{-1}, and aromatic ether Ar-O-Ar, 1245 cm^{-1}.

The 75.4 MHz ^{13}C spectrum for 21 is dominated by signals ranging from 119 to 159 ppm corresponding to the numerous aromatic carbons in the poly-
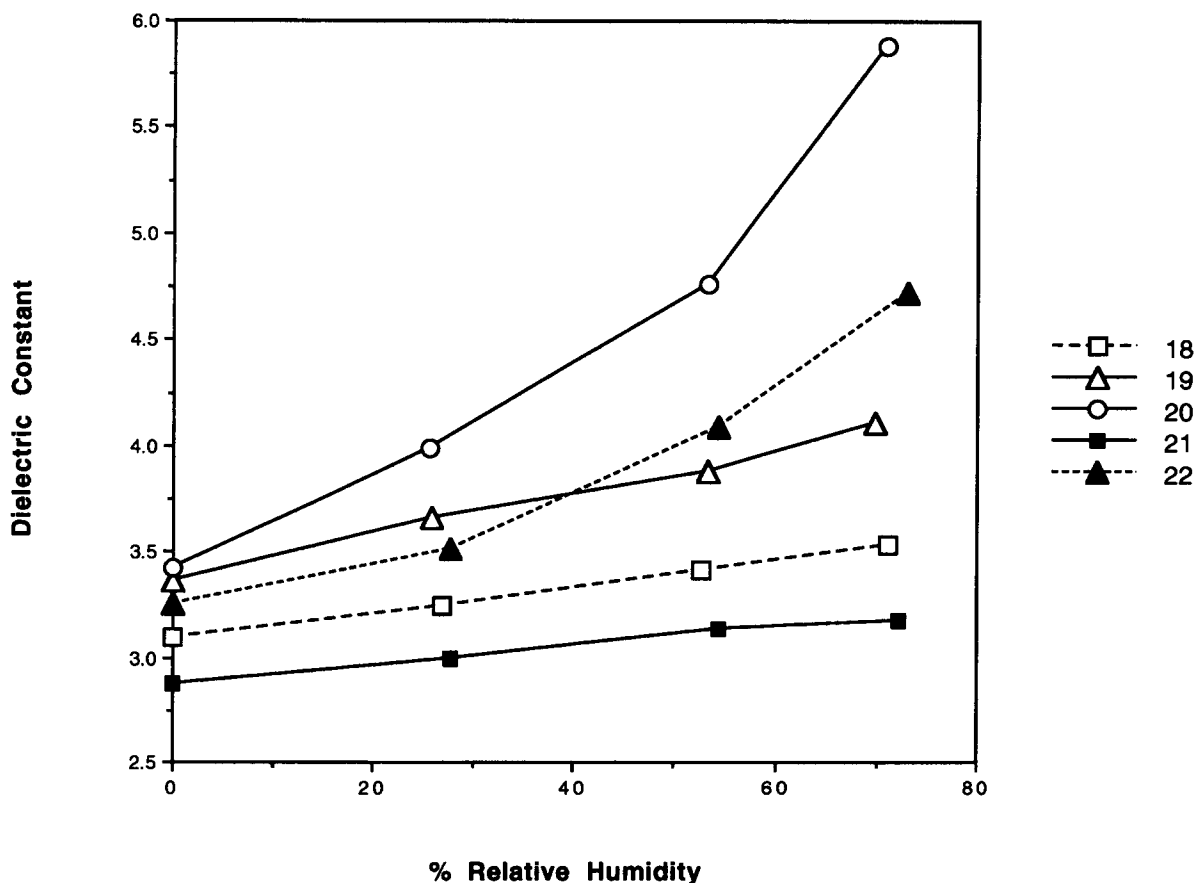

Figure 5 Relationship of dielectric constant to % relative humidity for poly(ether ketone-1,3,4-oxadiazoles)s 18–22.

Table IV   Molecular Weight Distribution of Selected Poly(Ether Ketone Oxadiazole)s

Polymer	M_n	M_w
18	10,855	33,690
19	8,725	28,196
20	7,717	26,409
21	10,077	39,329

mer. Unambiguous spectral assignment of all the aromatic carbons was not possible. However, the ketone and oxadiazole carbons centered at 194.1 and 163.9 ppm, respectively, and the isopropylidene carbons centered at 42.2 and 30.9 ppm are readily identifiable. These assignments were confirmed by examining the ^{13}C spectrum of 2,5-bis(4-fluoro-phenyl)-1,3,4-oxadiazole, 2,5-bis(4-phenoxy-phenyl)1,3,4-oxadiazole, and Bisphenol P.

Results from GPC analysis of polymers **18, 19, 20**, and **21** are listed in Table IV.

Polyether Ketone Pyridazines

The synthesis of 3,6-bis(4-phenoxyphenoxy)pyr-idazine (BPP), as depicted in Scheme 9, proceeds in high yield. Nucleophilic displacement of the activated aromatic chlorides in 3,6-dichloropyridazine with potassium 4-phenoxyphenoxide in DMAc can be followed by GC/Mass. Spec. Displacement of the first chloro group in the 3,6-dichloropyridazine proceeds readily to yield 3-chloro-6-(4-phenoxyphen-oxy)-pyridazine and is near completion in about 8 h. Displacement of the second chlorine atom in the resulting 3-chloro-6-(4-phenoxyphenoxy)pyridazine is much slower and the reaction takes an additional 32 h to reach completion and yield the desired BPP. Friedel–Crafts acylation of 3,6-bis(4-phen-oxyphenyl)pyridazine with 4-fluorobenzoyl chloride was carried out under modified Friedel–Crafts reaction conditions[17,27] using dimethylsulfone as catalyst moderator to yield 3,6-bis[4-(4-fluoroben-zoyl)(4-phenoxyphenyl)]pyridazine (**5**) in high yield.
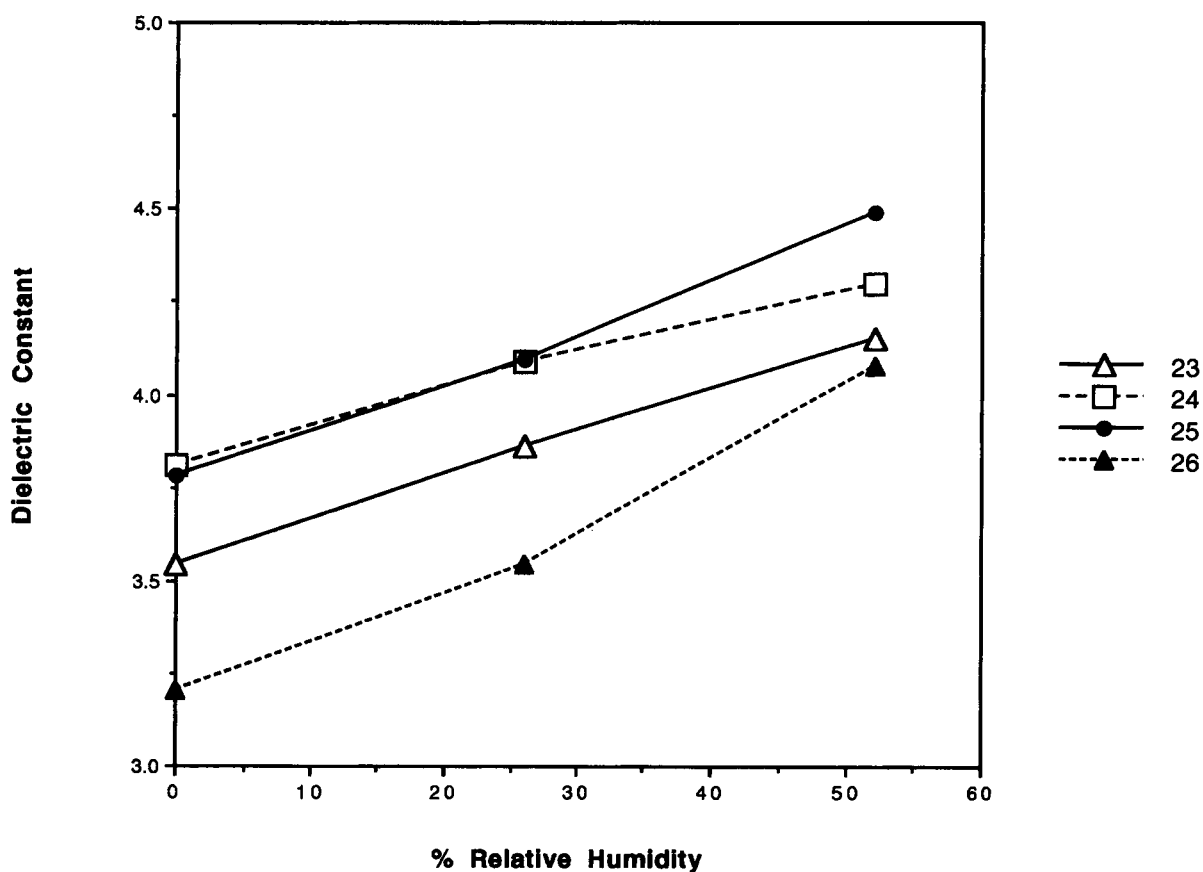

Figure 6   Relationship of dielectric constant to % relative humidity for poly(ether ketone pyridazine)s 23–26.

Table V Properties of Poly(Ether Ketone Pyridazine)s

Polymer	Diphenol	T_g (°C) (DSC)	TGA (°C) Onset	Dielectric Constant	
				0% RH	52% RH
23	6F-BPA	164	366	3.54	4.15
24	HPF	198	450	3.81	4.30
25	Bisphenol AP	168	432	3.78	4.49
26	Bisphenol P	159	419	3.20	4.08

The reactions of **5** with diphenols were carried out in DMAc using an excess of potassium carbonate. Subsequent workup of the viscous solution in water yields the polymers as white powders. Judging by the viscosity increase, the polymerization reaction was near completion after only about 6 h at 160°C. The synthesis of the poly(ether ketone pyridazine)s is depicted in Scheme 10.

The poly(ether ketone pyridazine) powders were soluble in DMAc, NMP, cyclohexanone, and THF. Solutions of the polymers (15–25 wt % solids) in a 1:1 mixture of DMAc and cyclohexanone were spin coated onto glass substrates and dried to yield transparent, flexible films. The poly(ether ketone pyridazine) powders could also be compression molded at 200 to 270°C to yield transparent, flexible films.

The T_gs for the poly(ether ketone pyridazine)s prepared from **5** and 6F-BPA, HPF, bisphenol AP, and bisphenol P, to yield polymers 23, **24, 25**, and **26**, were 164, 198, 168, and 159°C, respectively. Thermal gravimetric analysis of **23, 24, 25**, and **26** reveals that the polymers exhibits initial weight loss in air (scan rate = 20°C/min.) at 366, 450, 432, and 419°C, respectively.

At 0% relative humidity (RH), **23, 24, 25**, and **26** have dielectric constants (measured at 10 kHz) of 3.54, 3.81, 3.78, and 3.20, respectively. At 52% RH, the dielectric constants of **23, 24, 25**, and **26** increased to 4.15, 4.30, 4.49, and 4.08, respectively. The relationship between dielectric constant and relative humidity for polymers **23–26** is depicted graphically in Figure 6.

Table VI Molecular Weight Distribution of Selected Poly(Ether Ketone Pyridazines)s

Polymer	M_n	M_w	M_z
23	8,821	220,900	2,214,400
24	5,218	108,500	1,388,400
25	5,717	116,300	2,221,900

The previously reported[33] fluorinated poly(ether ketone) **27** has dielectric constants at 0% RH and 57% RH of 2.94 and 3.25, respectively. All of the poly(ether ketone pyridazine)s described in this article have dielectric constants significantly greater than that of **27**. Pyridazine containing fluorinated poly(ether imide pyridazine)s were also found to display dielectric constants higher than that of aromatic fluorinated poly(ether imide)s, which do not contain pyridazine moieties.[25] Because the dielectric constant of a polymer is a function the polymer's total polarizability, α_T, polymers displaying higher dielectric constants have higher polarizability.[34,35] The high dielectric constants of the poly(ether ketone pyridazine)s **23–26**, compared to that of **27**, are attributed to high polarizability of the pyridazine moieties in those polymers.

27
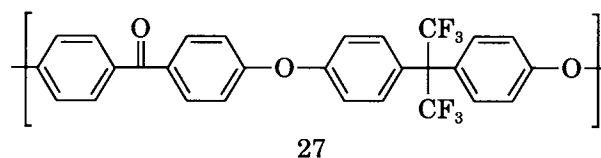
Size exclusion chromatagraphy of **23, 24**, and **25** showed that the polymers were of high molecular weight and displayed very high polydispersity. A low molecular weight fraction, which we attribute to cyclic oligomers, was observed for all three polymers tested. However, the presence of the oligomeric species did not have an especially negative effect on the polymer properties because all the polymers yielded flexible, creasable films showing good mechanical integrity. Tables V and VI presents the characterization data of the poly(ether ketone pyridazine)s.

The key structural features of the polymers can be identified by FT-IR and ^{13}C-NMR spectroscopy. The key features in the FT-IR spectrum of **26** include the following absorptions: aromatic C—H, 3069 cm^{-1}; aliphatic C—H, 2971 cm^{-1}; ketone C=O, 1659 cm^{-1}; aromatic C=C, 1588 and 1497 cm^{-1}; and aromatic ether Ar-O-Ar, 1245 cm^{-1}.

Table VII [13]C **Chemical Shifts for Poly(ether ketone pyridazine) 26**

Carbon	[13]C Chemical Shift (ppm)
1 and 7	42.3
2 and 8	30.9
3 and 6	147.0
4, 5, and 10	128.4
11, 23, and 24	117.1
12	161.3
13	163.0
14 and 20	119.4
15 and 19	132.1
16 and 18	132.5
17	194.1
21	163.1
22	149.9
25	152.7
26 and 29	161.5
27 and 28	126.3

The ^{13}C spectrum for **26** is dominated by signals ranging from 117 to 163 ppm corresponding to the numerous aromatic carbons in the polymer. However, the ketone and pyridazine ring carbons centered at 194.1, 161.5, and 126.3 ppm, respectively, and the isopropylidene carbons centered at 42.3 and 30.9 ppm are readily identifiable. The ^{13}C chemical shift assignments were made based on comparisons with the model compounds 3,6-diphenoxypyridazine and 4,4'-(p-phenylenediisopropylidene)diphenol (bisphenol P) and from calculations based on substituted benzenes.[36] The chemical shifts for the ^{13}C proton-decoupled spectrum of polymer **26** are listed in Table VII.

CONCLUSION

Twenty-one novel poly(ether ketone)s were synthesized in high yield by the reaction of a bisphenol with **1, 2, 3, 4**, or **5** using potassium carbonate in N,N-dimethylacetamide. All 21 poly(ether ketone)s were soluble in polar aprotic solvents and could be cast into flexible, creasable films showing good thermal stability. We have demonstrated that amide, imide–amide, cyano, oxadiazole, and pyridazine moieties are stable to Friedel–Crafts acylation conditions and can be incorporated into difluoro-containing monomers. The appropriately substituted monomers were prepared and subjected to displacement polymerizations with various bisphenols. High molecular weight was readily achieved, and structural variety could be introduced by selection of the appropriate difluoro-containing monomer and bisphenol.

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