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Preparation of Poly(arylene ether pyrimidine)s by Aromatic Nucleophilic Substitution Reactions[†]

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ABSTRACT: As part of a continuing effort to prepare novel thermally stable high-performance polymers, poly(arylene ether pyrimidine)s have been prepared with 4,6-bis(4-(trimethylsiloxy)phenyl)pyrimidine and a series of activated bis(aryl fluoride)s using a catalytic amount of cesium fluoride in diphenyl sulfone. These polymers exhibited good thermal stability in both air and helium atmospheres with 10% weight losses in the range 480−540 °C. Moderate to high inherent viscosities (η_{inh}: 0.40−0.92 dL/g) were recorded, and clear pale yellow flexible fingernail creasable films were solution cast from these samples. A polymer in this series containing a phenylphosphine oxide linkage exhibited good thin film tensile properties and resistance to oxygen plasma. Model reactions with 4,6-bis(4-fluorophenyl)pyrimidine and *p*-cresol along with studies of this compound's ^{19}F NMR shift values indicated sufficient capacity of the pyrimidine ring to activate aryl fluorides toward polymerization with bis(phenol)s. The pyrimidine bis(aryl fluoride) monomer was used to prepare a series of polymers with selected bis(phenol)s by potassium carbonate-mediated aromatic nucleophilic substitution reactions. One example containing the fluorene moiety exhibited a high inherent viscosity (η_{inh}: 0.80 dL/g); however, only brittle films could be cast from polymers prepared by this approach.

Introduction

Poly(arylene ether)s containing heterocyclic rings have been extensively investigated over the past several years.[1] The interest in these polymers is due to the heterocycle's tendency to enhance mechanical and adhesive properties as well as glass transition temperatures of the poly(arylene ether) while retaining thermal stability and processability. Previously, we reported the preparation of poly(arylene ether)s containing isoxazoles[2] and pyrazoles.[3−5] In this report we extend our investigation to novel poly(arylene ether pyrimidine)s prepared by aromatic nucleophilic substitution reactions. The potential for utility of this heterocycle in thermally stable polymer systems was established via thermal stability values of pyrimidines, which were recorded in the range of 620−650 °C by Johns, McElhill, and Smith.[6] Despite this potential very few synthetic polymers containing the pyrimidine moiety have been reported.[7−10] The dearth of processable thermally stable high-performance materials containing the pyrimidine ring can be attributed to the difficult synthetic approaches to suitable pyrimidine-containing monomers. The various synthetic approaches to functionalized pyrimidines have been extensively reviewed by Brown.[11−14]

The pyrimidine ring, a six-membered aromatic heterocycle with nitrogen atoms β to each other, is deficient of π electrons at the 2, 4, and 6 positions due to the electronegativity of the nitrogen atoms.[15] This electron-withdrawing capacity gives the pyrimidine moiety a potential ability to activate aryl fluoride substituents toward aromatic nucleophilic displacement. This ability has been exhibited by other electron deficient heterocycles used to prepare poly(arylene ether)s. Among these are triazole[16] and oxadiazole[17−19] rings, which have been successfully utilized as activating groups to prepare high molecular weight polymers.

Several papers involving the preparation of poly(arylene ether)s by nucleophilic aromatic substitution reactions have focused on predicting the reactivity of various bis(aryl fluoride)s. The ability of the electron-withdrawing activating group to affect the electron density at the position ipso to the fluorine was used as a predictor of potential reactivity via an S_NAr mechanism. Hückel[20,21] and Hartree−Fock (RHF)[22] molecular orbital calculations as well as ^{1}H, ^{13}C, and ^{19}F NMR shift values[16,18,23−25] have been used as indicators of reactivity. In the period following our preliminary report,[26] a qualitative synopsis of the work involving predicting aryl fluoride reactivity and a quantitative analysis of the data was reported by Carter.[27] As part of our efforts to prepare and characterize novel poly(arylene ether)s containing heterocycles, the potential reactivity by aromatic nucleophilic substitution of bis(aryl fluoride)s containing pyrimidine rings has been probed by ^{19}F NMR. Model reaction and polymerization results have also been examined. In addition, a series of polymers, prepared from 4,6-bis(4-hydroxyphenyl)pyrimidine or its trimethylsilyl ether derivative and a series of bis(aryl fluoride)s, was investigated.

As a means of improving the resistance to an oxygen plasma, the phosphine oxide group has been incorporated into a variety of arylene ether[28,29] and heterocyclic polymers including imides,[30,31] benzimidazoles,[30] oxadiazoles,[30] quinoxalines,[31] benzoxazoles,[31] and benzothiazoles.[31] Upon exposure to an oxygen plasma, the phosphorus reacts with the atomic oxygen present in the plasma to form a phosphate layer which subsequently retards the erosion rate. These materials have potential applications on spacecraft in low earth orbit

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(LEO) where atomic oxygen is present at significant concentrations and energy levels to cause rapid erosion of organic polymeric materials. In addition, they have potential application as reactive ion etch barriers used in the fabrication of microelectronic components. Thus it was of interest to investigate the stability of the phenylphosphine oxide-containing poly(arylene ether pyrimidine) to an oxygen plasma.

Experimental Section

Characterization Methods. All monomers and their precursors as well as the pertinent polymers prepared were characterized by ^{1}H, ^{19}F, and ^{13}C NMR using a General Electric QE-300 Fourier transform NMR spectrometer. A Perkin-Elmer 1600 IR spectrometer was used to record IR spectra. Elemental analyses (for all new compounds) were recorded by Atlantic Microlabs Inc. (Norcross, GA).

Melting points were carried out using a Mel-Temp or a differential scanning calorimeter (DSC) at a heating rate of 10 °C/min, as noted in the text. The glass transition temperature of the polymers was determined using a Perkin-Elmer DSC-4. Thermogravimetric analyses (TGA) were performed using a Perkin-Elmer TGS-2 thermogravimetric analyzer at a heating rate of 2.5 °C/min in helium and air. Temperature values were recorded at 10% weight loss of the sample.

Inherent viscosities (η_{inh}) were recorded with 15 mL of 0.5% (w/v) solutions of the polymer sample in *N*-methyl-2-pyrrolidinone (NMP) or *N*,*N*-dimethylpropyleneurea (DMPU) at 25 °C using a size 100, Cannon 100−753B viscometer.

Oxygen plasma exposures were performed on thin films (0.5 in. × 0.5 in., ~1−3 mils thick) of the polymer and a standard (Kapton HN) in a Tegal Plasmod asher. The asher was operated at 500 mTorr, 100 W of radio frequency, an oxygen pressure of 3 psi, and a flow rate of 50 cm^3/min. Since the asher was not calibrated, a simultaneous exposure of Kapton HN film was performed with the experimental polymer. The Kapton HN film served as a standard allowing for direct comparison with the experimental polymer film. Duplicate exposures were performed. The samples were dried to constant weight under vacuum prior to testing to remove absorbed moisture. The samples were periodically removed, weighed, and replaced in the asher over a 24 h period and the weight losses of the films monitored as a function of exposure time.

X-ray photoelectron spectroscopic anaylses (XPS) were performed at Virginia Polytechnic Institute and State University under NASA-Langley grant NAG1-1186. XPS was performed using a Perkin-Elmer PHI 5300 spectrometer with a magnesium Kα X-ray source (1253 eV) operated at 15 kV with an emission current of 20 mA. Typical operating pressures were $<1 \times 10^{-7}$ Torr. Analyses were made at a takeoff angle of 45°. The carbon 1s photopeak was set to 285.0 eV for calibration.

Chloroform or *N*,*N*-dimethylacetamide (DMAc) solutions (7−15% solids) of the polymers were centrifuged, and the decantate was doctored onto clean, dry plate glass and dried to a tack free form in a low-humidity chamber. The films on glass were dried at 100, 200, and ~50 deg above their respective glass transition temperatures (T_g) for 1 h at each temperature. Thin film tensile properties were measured according to ASTM D882.

All commercially available chemicals (Aldrich Co.) were used as received with the exceptions of 4,4′-difluorobenzophenone, **a**, and 4,4′-difluorodiphenyl sulfone, **b**, which were recrystallized from benzene/hexanes. Diphenyl sulfone was recrystallized from high-boiling petroleum ether. The bis(aryl fluoride)s, 1,3- and 1,4-bis(4-fluorobenzoyl)benzene, **c** and **d**, respectively, and 4,4′-bis(4-fluorobenzoyl)diphenyl ether, **e**, were prepared by known procedures.[32] The required bis(4-fluorophenyl)phenylphosphine oxide, **f**, was obtained from Daychem Laboratories and used as received. The bis(phenolic) monomers, Bisphenol A, **g**, Bisphenol A6F, **h**, 9,9′-bis(4-hydroxyphenyl)fluorene, **i**, and 4,4′-thiodiphenol, **j**, were recrystallized from toluene. The diketone, 1,3-bis(4-methoxyphenyl)-1,3-propanedione, **1**, was prepared by Anselme's method[33] and 1,3-bis(4-methoxyphenyl)-2-phenyl-1,3-propanedione was prepared by the procedure reported previously by Anstead *et al.*[34] DMAc, NMP, tetramethylene sulfone (sulfolane), and DMPU were dried over 4 Å molecular sieves.

Pyrimidines: Monomers, Precursors, and Model Reactions. 4,6-Bis(4-methoxyphenyl)pyrimidine (2). A 500 mL round-bottom reaction kettle containing a magnetic stirrer and fitted with a condenser and a thermometer was charged with 27.72 g (97.5 mmol) of **1** and 194 mL of formamide. The reaction was heated at 180−190 °C for 6 h. The dark amber solution was poured into about 1 L of a 7:3 ethanol/water solution. The crude product was vacuum filtered, washed with water, and oven dried to yield 17.55 g (62%) of **2** as a crude light brown powder. A hot extraction was subsequently performed on the crude product with high-boiling petroleum ether (50−110 °C) in a Soxhlet extractor for 6 h. The solution was concentrated to saturation, and the straw yellow product crystallized and was vacuum filtered to yield 7.93 g (28%) of **2** (mp: 143−145 °C, DSC). IR (KBr pellet, cm^{-1}): 3005.1 (*H*−*C*=C); 2840.1 (*H*−*C*−C); 1601.7, 1590.4 (*C*=*C*); 826.7, 778.3 (*Ar*−*H*). ^{1}H NMR (DMSO-d_6, ppm): 9.18 (s, 1H, pyrimidine C$_2$−*H*); 8.19 (d, 2H, Ar−*H*); 7.90 (s, 1H, pyrimidine C$_5$−*H*); 6.98 (d, 2H, Ar−*H*); 3.83 (s, 6H, OC−*H*). ^{13}C NMR (DMSO-d_6, ppm): 163.72, 161.88, 158.88 (pyrimidine C$_2$); 129.39 (pyrimidine C$_5$); 128.6, 114.24, 110.82, 55.33 (O*C*H$_3$). Anal. Calc for $C_{18}H_{16}N_2O_2$: C, 73.96; H, 5.52; N, 9.58. Found: C, 73.79; H, 5.43; N, 9.47.

4,6-Bis(4-hydroxyphenyl)pyrimidine (3). A 2 L single-necked round-bottom flask containing a mechanical stirrer and fitted with a condenser was charged with 7.93 g of **2** (27.1 mmol) and 350 mL of glacial acetic acid. A 400 mL solution of aqueous 48% hydrobromic acid was added, and the solution was brought to reflux temperature. The reaction was allowed proceed at reflux temperature for 17 h and subsequently cooled to room temperature. The solution was poured into about 1 L of water to precipitate the product. A yellow solid was collected by vacuum filtration, washed with water, and oven dried. The crude solid was recrystallized from ethanol to yield 5.83 g (81%) of **3** as a white powder (mp: 327−329 °C, DSC). IR (KBr pellet, cm^{-1}): 2500−3100 (Ar−O−*H*); 1597.6, 1576.3 (*C*=*C*), 830.0, 779.4 (*Ar*−*H*). ^{1}H NMR (DMSO-d_6 ppm): 10.12 (s, 2H, O−*H*, CH$_3$OD exchangeable); 9.14 (s, 1H, pyrimidine C$_2$−*H*); 8,39 (s, 1H, pyrimidine C$_5$−*H*); 8.29 (d, 4H, Ar−*H*); 7.00 (d, 4H, Ar−*H*). ^{13}C NMR (DMSO-d_6, ppm): 163.34, 160.52, 158.81 (pyrimidine C$_2$); 129.16 (pyrimidine C$_5$); 127.51, 115.90, 109.98. Anal. Calc for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60. Found: C, 72.73; H, 4.62; N, 10.54.

4,6-Bis(4-(trimethylsiloxy)phenyl)pyrimidine (4). A flame-dried 1000 mL three-necked round-bottom flask containing a magnetic stirrer and equipped with a nitrogen inlet, a condenser with drying tube, and a stoppered 125 mL pressure-equalizing drop funnel was charged with 7.88 g (29.8 mmol) of **3** and 530 mL of dioxane. The solution was brought to reflux temperature under a nitrogen atmosphere and 24.06 g (149 mmol) of 1,1,1,3,3,3-hexamethyldisilazane was added dropwise over 5 min. After 17 h at reflux temperature under nitrogen, the IR of the crude product, obtained from the reaction solution by drying on a NaCl plate, no longer showed an −OH stretching band. The solution was cooled to room temperature, and the solvent was removed by a rotoevaporator to yield a white solid. The crude product was recrystallized from *n*-hexane to yield 12.18 g (85%) of **4** as white needles (mp: 97−99 °C). The pure product was dried at 80 °C under vacuum for 18 h and stored under N$_2$. The material was very sensitive to hydrolysis from moisture in the air and was used within a couple days of preparation. Although high molecular weight polymer could be formed from the purified product, elemental analyses exhibited values consistent with partially hydrolyzed material. IR (neat on NaCl plate, cm^{-1}): 3043.5 (C=C−*H*); 2959.2, 2900.2 (C−C−*H*); 1603.5, 1585.5, 1510.5 (*C*=*C*); 1270.8 (*Ar*−*O*−*Si*); 912.9, 845.5 (Ar−*H*). ^{1}H NMR (CDCl$_3$ ppm): 9.28 (s, 1H, pyrimidine C$_2$−*H*); 8.1−8.2 (m, 4H, Ar−*H*); 8.00 (s, 1H, pyrimidine C$_5$−*H*); 7.18−7.27 (m, 4H, Ar−*H*).

1,3-Bis(4-fluorophenyl)-1,3-propanedione (5). A three-necked 1000 mL round-bottom flask fitted with a mechanical stirrer and two glass stoppers was charged with 9.07 g (227 mmol) of 60% sodium hydride in mineral oil and 100 mL of hexanes. The mixture was stirred for 15 min at room temperature to extract the mineral oil. The hexanes was decanted, and this extraction process was repeated four more times. After the last decantation the glass stoppers were removed and a nitrogen inlet and a condenser with an attached drying tube were fitted to the flask. Nitrogen was blown through the flask until the bottom was no longer cool to the touch, and the NaH was a fine dry off-white powder. The nitrogen inlet was replaced with a stoppered 500 mL pressure equalizing drop funnel, and 200 mL of dried THF was added. A solution of 20.86 g (151 mmol) of 4-fluoroacetophenone in 200 mL of THF was added over 1.5 h. A 200 mL solution of methyl-4-fluorobenzoate was subsequently added over 45 min. The reaction was heated at reflux for 17 h. At completion the reaction solution was cooled to room temperature and a few drops of methanol were added. The solution was subsequently cooled with an ice bath and a dilute aqueous hydrochloric acid solution was added dropwise with stirring until the aqueous solution was acidic to pH paper. The layers were separated in a 2000 mL separatory funnel, and the organic layer was set aside. The aqueous layer was extracted three times with 300 mL portions of diethyl ether, and the organic portions were combined. The organic solution was washed three times with 250 mL of dilute aqueous sodium bicarbonate solution and three times with 250 mL portions of water. The organic solution was dried over molecular sieves and distilled on the rotoevaporator to yield a pale yellow waxy solid. The crude product was recrystallized from high-boiling petroleum ether (50−110 °C) to yield 21.33 g (54%, mp 109.5−111.5 °C, DSC) of **5** as pale yellow needles. IR (neat on NaCl plate, cm^{-1}): 1603.5 (*C*—*O* enolic); 1503.9 (*C*=*C*); 844.6, 781.5 (Ar—*H*). NMR (CDCl$_3$, ppm): 8.0 (m, 4H, Ar—*H* meta to carbonyl); 7.1−7.2 (m, 4H, Ar—*H* meta to −F); 6.72 (s, 1.75H, CH$_3$OD exchangeable); 3.87 (s, 0.25H, CH$_3$OD exchangeable). ^{13}C NMR (CDCl$_3$, ppm): 184.49 (C=O); 167.14 (C ipso to −F); 163.78, 131.7, 129.64, 116.00, 115.71, 114.03, 92.49. Anal. Calc for $C_{15}H_{10}F_2O_2$: C, 69.23; H, 3.87. Found: C, 69.16; H, 3.87.

4,6-Bis(4-fluorophenyl)pyrimidine (6). A 250 mL round-bottomed flask containing a magnetic stirrer and equipped with a thermometer inlet and a single neck was fitted with a condenser and a thermometer. The flask was charged with 10.00 g (38.4 mmol) of **5** and 70 mL of formamide. The reaction was heated at 180−190 °C for 6 h. The dark amber solution was subsequently poured into about 750 mL of a 25% ethanol/water solution. The crude product was vacuum filtered, washed with water, and oven dried to yield a of crude off-white powder. A hot extraction was performed on the crude product with high-boiling petroleum ether (50−110 °C) in a Soxhlet extractor for 6 h. The solvent was removed by a rotoevaporater, and the crude product was recrystallized from low-boiling petroleum ether to yield 2.66 g (26%) of **6** as white needles (mp: dimorphic; 88.9−91.0 °C, 95.2−97.4 °C, a recrystallization exotherm was recorded at 92.0 °C, DSC). A second measurement of the mp by DSC after quick cooling recorded a single mp: 88.1−90.6 °C. IR (KBr pellet, cm^{-1}): 3044.1, 3001.5 (*H*—*C*=C); 1600.7, 1582.2 (*C*=*C*); 830.9, 768.3 (*Ar*—*H*). ^{1}H NMR (DMSO-d_6, ppm): 9.25 (s, 1H, pyrimidine C$_2$—*H*); 8.60 (s, 1H, pyrimidine C$_5$—*H*); 8.4−8.5 (m, 4H, Ar protons ortho to isoxazole); 6.98 (m, 4H, Ar protons ortho to F). ^{13}C NMR (DMSO-d_6, ppm): 166.42 (C ipso to F); 163.56, 163.09, 159.18, 129.31, 116.21, 111.78. ^{19}F NMR (DMSO-d_6, ppm) −109.42 (F para to pyrimidine). Anal. Calc for $C_{16}H_{10}N_2F_2$: C, 71.64; H, 3.76; N, 10.44. Found: C, 71.40; H, 3.76; N, 10.42.

3,5-Bis(4-fluorophenyl)isoxazole (7). A 500 mL single-necked round-bottom flask containing a magnetic stirrer and fitted with a condenser and drying tube was charged with 5.00 g of **5** (19.2 mmol), 2.03 g (29.2 mmol) of hydroxylamine hydrochloride, 100 mL of absolute ethanol, and 50 mL of pyridine. The solution was heated under reflux for 17 h and subsequently poured into about 1 L of water. The white solid was collected by vacuum filtration and washed with water. The crude solid was oven dried and crystallized from ethanol to yield 4.05 g (82%) of **7** as white needles (mp: 188−190 °C). IR (KBr pellet, cm^{-1}): 3112.2 (*H*—C); 1616.9, 1506.0 (*C*=*C*); 845.7, 812.0 (*H*—Ar). ^{1}H NMR (THF-d_4, ppm): 8.2−8.0 (s, 4H, Ar protons ortho to isoxazole); 7.65 (s, 1H, isoxazole proton); 7.5 (d, 4H, Ar protons ortho to fluorine). ^{13}C NMR (THF-d_4, ppm): 99.01 (isoxazole C$_4$). ^{19}F NMR (THF-d_4, ppm): −109.813 (F para to isoxazole 5 position); −110.729 (F para to isoxazole 5 position). Anal. Calc for $C_{15}H_9F_2O$: C, 70.03; H, 3.53; N, 5.45. Found: C, 69.88; H, 3.59; N, 5.32.

4,6-Bis{4-(methylphenoxy)phenyl}pyrimidine (8). A three-necked 50 mL round-bottom flask fitted with a mechanical stirrer, Dean-Stark trap filled with toluene and fitted with a condenser and drying tube, and a thermometer adapter fitted with a thermometer and a nitrogen inlet was charged with 0.4971 g of *p*-cresol (4.597 mmol), 0.6166 g of **6** (2.298 mmol), 1.27 g of potassium carbonate (9.19 mmol), 4.45 mL of DMPU (25% solids, w/v), and 2.25 mL of toluene. Water was azeotropically removed under a nitrogen flow and a temperature of 110 °C for 3.0 h. The toluene was distilled off, and the reaction temperature was raised to 180−190 °C and allowed to proceed at this temperature under nitrogen for 24 h, at which time there was no longer a spot on a TLC plate with the same R_f value as **6**. The reaction solution was subsequently poured into a 250 mL dilute aqueous acetic acid solution. A white solid precipitated and was isolated by vacuum filtration and washed with water. The product was recrystallized from dioxane/water and then ethanol to yield 0.85 g (83%; mp 143−145 °C) of white crystals. IR (KBr pellet, cm^{-1}): 3030.0 (*H*—*C*=C); 2919.3 (*HC*—C); 1585.2 (*C*=*C*); 1234.9 (*C*—*O*—*C*); 873.8, 832.5, 773.0 (*H*—Ar). ^{1}H NMR (DMSO-d_6, ppm): 9.2 (s, 1H, pyrimidine C$_2$—*H*); 8.1 (d, 4H, Ar—*H*); 7.95 (s, 1H, pyrimidine C$_5$—H); 7.19 (d, 4H, Ar—*H*); 7.09 (d, 4H, Ar—*H*); 6.98 (d, 4H, Ar—*H*); 2.35 (s, 6H, Ar—C—*H*). ^{13}C NMR (DMSO-d_6, ppm): 163.76, 160.62, 159.04, 153.68, 133.75, 131.20, 128.73, 119.77, 111.35, 20.74 (Ar—*C*—H). Anal. Calc for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30. Found: C, 80.89, H, 5.43; N, 6.29.

Polymers. Poly(arylene ether)s Prepared from Pyrimidine-Containing Bis(trimethylsilyl) Ethers. Using the typical polymerization procedure for the bis(trimethylsilyl) ether monomer, a three-necked 50 mL round-bottom flask fixed with a condenser with an attached drying tube, a mechanical stirrer, and a thermometer with a nitrogen inlet was charged with 0.6086 g (1.489 mmol) of **4**, 0.4680 g (1.489 mmol) of **f**, 0.011 g (1% solids) of cesium fluoride, and 2.15 g of diphenyl sulfone (50% solids). After an initial 10 min at 180−190 °C the reaction was heated for 2 h at 320 °C at which time the solution became viscous and was diluted stepwise to 25% solids with diphenyl sulfone. The hot reaction solution was diluted with DMPU and poured into a dilute acetic acid solution in methanol. The precipitated polymer was blended in a Waring commercial blender to complete maceration, vacuum filtered and washed with methanol, boiled in methanol 1 h, vacuum filtered, and oven dried 17 h in a vacuum oven at 100 °C to give 0.69 g (86%) of fibrous white polymer. The polymer was soluble in chloroform and polar aprotic solvents at room temperature. A colorless, tough, fingernail creasable film was obtained from a chloroform solution. η_{inh}: 0.92 dL/g (DMPU, 25 °C, 0.5 g/dL). T_g: 179 °C TGA: 513 °C (air), 541 °C (helium). IR (neat film, cm^{-1}): 3056.3 (*H*—*C*=C); 1573.9 (*C*=*C*); 1197.1 (*C*—*O*—*C*); 872.3, 779.4, 730.9 (*H*—Ar).

Poly(arylene ether)s Prepared from Pyrimidine-Containing Bis(aryl halide)s. Using the typical polymerization procedure for the bis(aryl fluoride) monomer, a three-necked 50 mL round-bottom flask fitted with a mechanical stirrer, Dean-Stark trap fitted with a condenser and drying tube, and a thermometer adapter fixed with a thermometer and a nitrogen inlet was charged with 0.3853 g (1.708 mmol) of Bisphenol A (**g**), 0.94 g of (6.8 mmol) potassium carbonate, 4.19 g (20% solids, w/v) of diphenyl sulfone, and 2 mL of 1,2-dichlorobenzene. The reaction mixture was refluxed at 170 °C for 18 h under nitrogen to remove water via azeotropic distillation into a Dean-Stark trap. The 1,2-dichlorobenzene was removed by distillation and 0.4905 g (1.708 mmol) of **6** was added and the reaction temperature was increased to 230 °C. The solution did not become viscous after 3 h at this temperature and concentration. The temperature was subsequently increased to 320 °C. After 2 h the viscosity increased and the solution was diluted to 15% solids. No additional increase in viscosity was observed, and after 2 h the polymerization was quenched and precipitated by pouring the hot solution into a dilute acetic acid solution in methanol. The crude polymer was macerated in a Waring commercial blender, and the brown solid was vacuum filtered, oven dried, and boiled in a methanol/water solution to yield 0.70 g (90%), which was soluble in polar aprotic solvents at room temperature. A brittle film was obtained from a DMAc solution. η_{inh}: 0.17 dL/g (NMP, 25 °C, 0.5 g/dL). T_g: 122 °C. TGA: 490 °C (air), 483 °C (helium). IR (KBr pellet, cm^{-1}): 3037.6 ($C{=}C{-}H$); 2965.3 ($C{-}C{-}H$); 1586.5, 1500.3 ($C{=}C$); 1233.8 ($C{-}O{-}C$); 874.6, 833.7 ($Ar{-}H$).

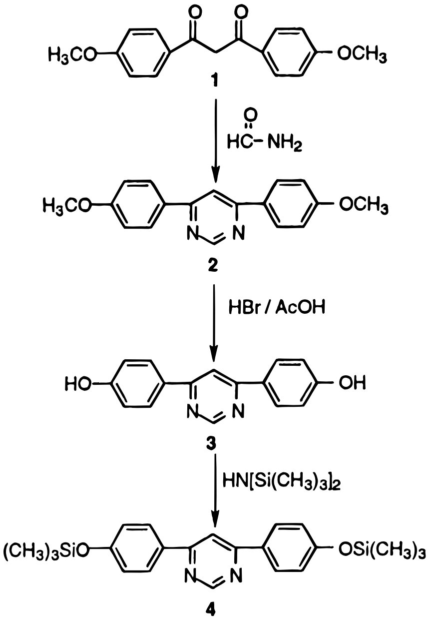
Results and Discussion

Pyrimidine Monomers and Precursors. (a) Bis(phenol)s and Synthons. The preparation of pyrimidines by reacting a C−C−C fragment with a N−C−N fragment is known as the "Principal Synthetic Method". This approach is the most widely utilized and the most versatile for the synthesis of a variety of compounds containing the pyrimidine ring.[13] The C−C−C fragment is necessarily a β-diketone or other functionality that reacts in an equivalent manner. The N−C−N fragment is necessarily a dinucleophile such as an amidine.

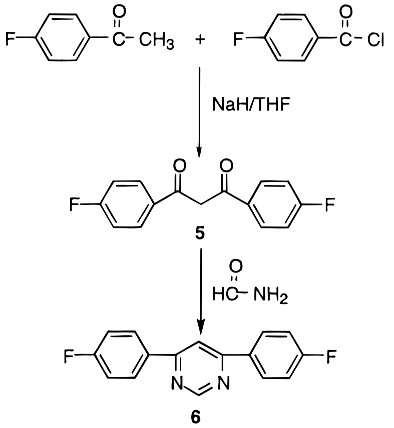
Our previous synthesis of novel pyrazole-[3−5] and isoxazole-containing[2,35] monomers demonstrated the versatility in the preparation of novel heterocycle-containing bis(phenol)s starting with a β-diketone synthon. Therefore, initial efforts to prepare pyrimidine-containing bis(phenol)s involved the attempted cyclization of the β-diketones, 1,3-bis(4-methoxyphenyl)-1,3-propanedione, **1**, and 1,3-bis(4-methoxyphenyl)-2-phenyl-1,3-propanedione (MPPPD). The N−C−N fragments investigated were formamidine and benzamidine. It has been reported by Anker and Cook that a similar reaction between benzamidine and the diaryl β-diketone, dibenzoylmethane, did not produce any pyrimidine product under various conditions ranging from highly basic to acidic.[36] However, another report by Capuano and Giammanco claims that this reaction proceeds to form 4,5,6-triphenylpyrimidine when an excess of sodium hydroxide is utilized.[37] These conflicting reports necessitated the investigation of the viability of an approach wherein amidines are condensed with diaryl and triaryl β-diketones to prepare 4,6-diphenyl- and 4,5,6-triphenylpyrimidines. In our hands it was found that, under a variety of reaction conditions ranging from highly basic to acidic and from temperatures of 80−200 °C, benzamidine and formamidine do not react with **1** or MPPPD, to form their corresponding pyrimidines.

A different preparation of 4,6-diarylpyrimidines from β-diketones has been reported by Bredereck *et al.*[38] In their approach, dibenzoylmethane was cyclized with excess formamide at 180−190 °C to form 4,6-diphenylpyrimidine in 30% yield. The formamide cyclization reaction therefore was investigated for the preparation of pyrimidine derivatives of **1** and MPPPD. It was found that 4,6-bis(4-methoxyphenyl)pyrimidine, **2**, could be prepared in 28% yield by cyclizing formamide with **1** at 180−190 °C. This cyclization, however, was unsuccessful for the preparation of 4,6-bis(4-methoxyphenyl)-5-phenylpyrimidine by cyclization of MPPPD with formamide at 180−190 °C. This result is probably due to the steric bulk provided by the phenyl ring at the C$_2$ position of the β-diketone. The bis(phenolic) and bis(trimethylsilyl) ether monomers were then prepared from **2** by HBr cleavage of the methyl groups and silylation of the bisphenol with hexamethyldisilazane (Scheme 1).

Scheme 1. Synthesis of Bis(phenol)s and Bis(trimethylsilyl) Ethers Containing Pyrimidine Rings



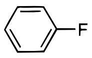
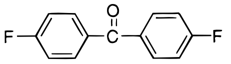
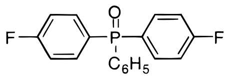
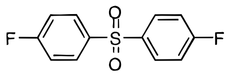
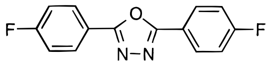
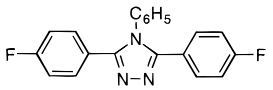
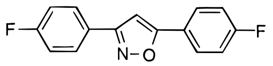
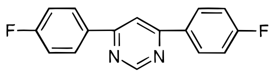
Scheme 2. Synthesis of a Bis(aryl fluoride) Containing the Pyrimidine Ring



(b) Bis(aryl halide)s. As part of an investigation into the electron-withdrawing capacity of the pyrimidine ring for activation of bis(aryl fluoride)s toward aromatic nucleophilic substitution reactions with bis(phenolate)s, 4,6-bis(4-fluorophenyl)pyrimidine was prepared and characterized. Due to the success in the preparation of the above pyrimidine-containing compound, **2**, by cyclization of the β-diketone with formamide, this approach was also adopted for the preparation of the pyrimidine-containing bis(aryl halide) monomer (Scheme 2).

The β-diketone, 1,3-bis(4-fluorophenyl)-1,3-propanedione, **5**, was prepared by a Claisen type condensation procedure similar to that used in the preparation of **1**. The desired material was prepared in 54% yield. This material was subsequently condensed with formamide at 180−190 °C to prepare 4,6-bis(4-fluorophenyl)pyrimidine, **6** in 26% yield. For comparison, an isoxazole-containing bis(aryl fluoride) was also prepared from **5** in order to investigate this heterocyclic ring's electron-withdrawing capacity. The desired 3,5-bis(4-fluorophenyl)isoxazole was prepared in 82% yield by cyclizing with hydroxylamine.

Table 1. Comparison of ^{19}F NMR Shift Values of Aryl Fluorides

Arylfluoride	^{19}F NMR Shift Values*
	-112.70 (-112.77)
	-106.01 (-106.01)
	-106.97
	-104.26 (-104.08)
	(-106.81)
	(-110.49)
	-109.81, -110.73
	-109.42

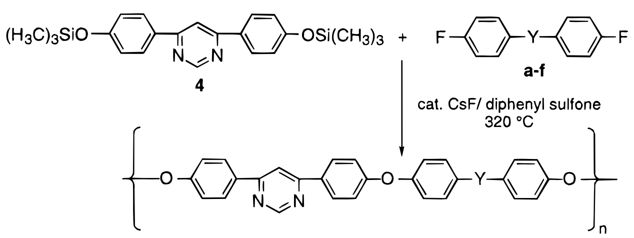
*Shift values were recorded in ppm relative to a CFCl3 standard. Values in parentheses are reported from the literature.[16,22]

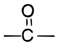
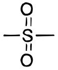
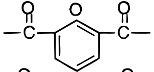
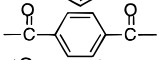
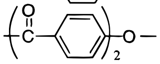
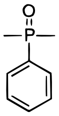
A study of the ^{19}F shift values of the fluorine leaving groups of the above heterocycle-containing bis(aryl fluoride)s was conducted to determine the relative electron densities at the ipso carbon position. The NMR spectra of these monomers were then compared with those of activated bis(aryl fluoride)s known to be sufficiently reactive to form high molecular weight poly(arylene ether)s. Fluorobenzene was also analyzed as a nonreactive model. The more deshielded the nuclei the lower the electron density, and thus, the more reactive the monomer.

Table 1 gives the values obtained from the ^{19}F study as well as literature values from similar investigations conducted by researchers at IBM.[16,23] The highly reactive conventional activated bis(aryl halide)s such as 4,4′-difluorophenyl sulfone and 4,4′-difluorobenzophenone exhibited shift values in the range of about −104 to −106 ppm, while the value for unactivated fluorobenzene was shifted to −112.7 ppm. The pyrimidine monomer exhibited an ^{19}F shift of −109.4 ppm, while the isoxazole's nonequivalent fluorines exhibited values of −109.8 and −110.7 ppm. It was observed by Carter that bis(aryl fluoride)s in the range of −110 to −111 ppm could be used to prepare high molecular weight poly(arylene ether)s at high reaction temperatures (above 200 °C) in DMPU.[23] On the basis of these results it was determined that these heterocycles had sufficient electron-withdrawing capacity to warrant further investigation into their use for the preparation of high molecular weight materials. Model reaction and polymerization results are discussed below.

Poly(arylene ether pyrimidine)s. (a) Polymers Resulting from Bis(phenol)s and Trimethylsilyl Ethers Containing the Pyrimidine Ring. Initial attempts to polymerize bis(phenol) **3** with the activated bis(aryl fluoride)s **a**−**f** in the presence of potassium carbonate in polar aprotic solvents resulted in precipitation of the bis(phenolate) salt of the monomers or an oligomeric material during the azeotropic distillation of water with toluene. It was necessary to heat the reaction in diphenyl sulfone in excess of 300 °C in order to redissolve this material. When the salt was redissolved at this high temperature there was almost immediate gelation of the polymer even at low solids content (10−15%, w/v). Other aprotic solvents including NMP and DMPU, which are known to have good solvent power for dissolution of poly(arylene ether)s, were ineffective for redissolving this material. An alternative route was therefore sought.

Table 2. Poly(arylene ether pyrimidine)s Prepared from Monomer 4



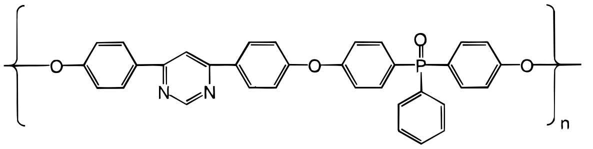
	Y	T_g^{i} (°C)	η_{inh}^{ii} (dL/g)	TGA^{ii} (°C) Air	He
a		185	0.52*	515	494
b		225	0.42	513	481
c		176	0.41	512	490
d		197	0.71*	473	515
e		179	0.54*	506	510
f		242	0.92	513	541

i) Heating rate of 25°C/min.
ii) 0.5 g/dL in NMP or DMPU, when noted with *
iii) Heating rate of 2.5 °C/min., 10% wt. loss

Previously, we reported polymerizations with bis(trimethylsilyl) ethers and activated bis(aryl halide)s in the presence of a catalytic amount of cesium fluoride, resulting in high molecular weight poly(arylene ether isoxazole)s.[2,35] This synthetic approach to poly(arylene ether)s was originaly reported by Kricheldorf *et al.*[39−43] without the formation of a potassium bis(phenolate) salt during the polymerization; this approach was also investigated for the preparation of poly(arylene ether pyrimidine)s. The lower nucleophilicity of the bis(trimethylsilyl) ether moiety in comparison with the phenolate ion gives the added advantage of the use of comparatively higher reaction temperatures with lower risk of gelation due to cross-linking or the formation of exceedingly high molecular weight fractions.

Polymers prepared from **4** and **a**−**f** had T_g's ranging from 176 to 242 °C. The T_g's follow the same trend previously reported for poly(arylene ether)s containing flexible activating groups: phenylphosphine oxide > sulfone > terephthaloyl, carbonyl > isophthaloyl. Good thermal stability was observed, with 10% weight loss values in air and helium, ranging from 480 to 540 °C (Table 2). Inherent viscosities ranging from 0.41 to 0.92 dL/g and the ability to obtain creasable films from DMAc indicated medium to high molecular weight materials. Polymers **4a**−**f** were soluble in polar aprotic solvents only upon heating. Polymer **4f**, containing the

Table 3. Unoriented Thin Film Tensile Properties of 4f



test temp (°C)	tensile strength (MPa)	tensile modulus (GPa)	elongation (%)
25	85.77	2.331	52.14
177	43.38	1.599	50.54
200	40.93	1.379	68.43

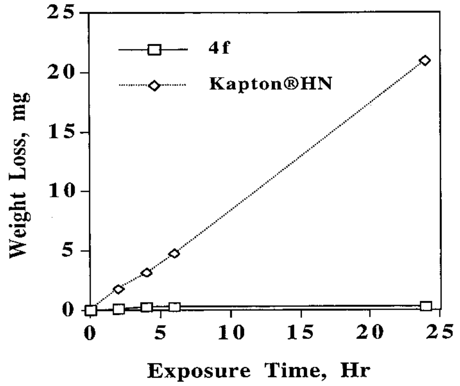


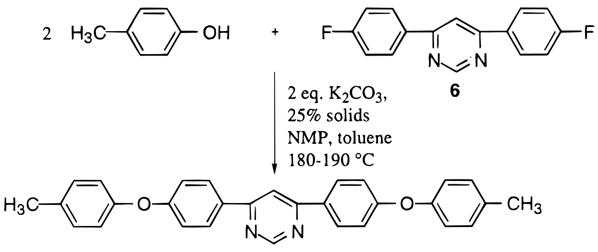
Figure 1. Oxygen plasma testing of **4f** thin film versus Kapton HN.

phenylphosphine oxide linkage, however, showed good solubility, and a strong, clear pale yellow fingernail creasable film could be cast from chloroform or DMAc without initial warming of the solvent.

A thin film of **4f**, cast from DMAc exhibited good mechanical strength (Table 3). A tensile strength of 85.77 MPa (12 440 psi) was recorded at room temperature. This value is consistent with other poly(arylene ether)s containing heterocyclic rings without hydrogen bonding between the chains. As the temperature approached the glass transition temperature of the polymer (242 °C), the strength dropped precipitously to half of its room temperature value. The moduli exhibited similar behavior. Elongation at break was about 50%. As expected, the elongation at break increased as the glass transition temperature was approached.

An unoriented thin film of the phenylphosphine oxide-containing poly(arylene ether pyrimidine) was exposed to an oxygen plasma under vacuum. Since the asher was not calibrated, a simultaneous exposure of Kapton HN film was performed. The erosion rate of Kapton HN film is well documented and thus serves as a standard allowing for relative comparison with the experimental polymer. Exposures were performed for 24 h, with the sample being periodically removed and weighed. The results are represented graphically in Figure 1. The phenylphosphine oxide-containing poly(arylene ether pyrimidine) exhibited excellent resistance (i.e., weight retention) to the oxygen plasma. As seen with other aromatic polymers containing this group, this material exhibited a nonlinear weight loss rate.[28−31] The sample exhibited most of the weight loss during the first 2 h of exposure and exhibited negligible weight loss for the remainder of the experiment. In contrast, Kapton HN exhibited a relatively constant, linear weight loss rate throughout the duration of the oxygen plasma exposure. The weight loss rates of the phenylphosphine oxide-containing film over the 0−24 h exposure period was 0.0034 mg/h as normalized to the Kapton HN weight loss rate of 0.87 mg/h.

Scheme 3. Model Reaction for the Nucleophilic Substitution of a Fluoride Atom Activated by a Pyrimidine Ring



8

This change in weight loss rate is due to formation of a higher oxidized phosphate-type surface layer upon exposure which is resistant to the oxygen plasma. Apparently, an induction period is necessary for the chemical changes to occur which result in a reduction in the erosion rate. An inorganic phosphate-type surface layer has been shown to form on poly(arylene ether phosphine oxide)s[28,29] and poly(arylene ether heterocycle)s[30,31] exposed to oxygen plasma.

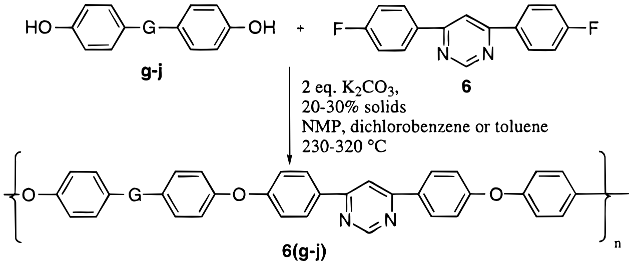
The phenylphosphine oxide-containing poly(arylene ether pyrimidine) film was analyzed by X-ray photoelectron spectroscopy. Relative to the control film, the exposed film exhibited increases in the relative concentrations and binding energies of both phosphorus and oxygen. The ratio of oxygen to phosphorus was ~5:1 in the exposed film, these observed changes in surface chemistry are consistent with the formation of a phosphate-type surface layer and are similar to those described in previous reports.[28−31]

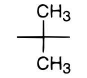
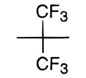
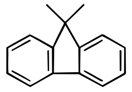
The use of oxygen plasma ashers to assess the stability of materials to atomic oxygen in LEO has been reviewed.[44,45] The LEO environment is not accurately simulated by an oxygen plasma asher. Conditions such as oxygen flux and energy level, high-energy particles, ultraviolet radiation, and thermal cycling need to be addressed to assess material stability in LEO. However, the asher is useful for determining relative stabilities of materials to the oxygen plasma and thereby aids in determining structure/property relationships in polymers.

(b) Polymers Resulting from a Bis(aryl fluoride) Containing the Pyrimidine Ring. As discussed above in the Results and Discussion concerning bis(aryl halide)s, the ^{19}F shift value of −109.42 ppm for **6** indicates that this bis(aryl halide) monomer should be reactive in the preparation of poly(arylene ether)s with bis(phenol)s by nucleophilic aromatic substitution reactions. Therefore, the reactivity of this compound toward nucleophilic substitution was first investigated via a model reaction. A model compound (Scheme 3) was prepared by reacting monomer **6** with *p*-cresol in the presence of potassium carbonate in DMPU at 180−190 °C after azeotropic distillation of water with toluene. A similar synthetic approach by workers at IBM[46] has been used to conduct the above mentioned heterocycle-activated S_NAr reactions to form arylene ethers. The required 4,6-bis{4-(4-methylphenoxy)phenyl}pyrimidine (**8**) was isolated in 83% yield after purification and fully characterized.

Similar preliminary investigations using the above isoxazole-containing bis(aryl fluoride) indicated instability of the isoxazole moiety toward the reaction conditions. In earlier work we established the instability of

Table 4. Physical Properties of Poly(arylene ether pyrimidine)s by Heterocycle Activated Aromatic Nucleophilic Substitution Reactions



	G	$T_g{}^{i}$ (°C)	$\eta_{inh}{}^{ii}$ (dL/g)	TGA^{ii} (°C) Air	He
g	 $-C(CH_3)_2-$	122	0.17	490	483
h	 $-C(CF_3)_2-$	122	0.20	514	502
i		244	0.80	511	542
j	—S—	170	-----	430	452

i) Heating rate of 25°C/min.
ii) 0.5 g/dL in NMP
iii) Heating rate of 2.5 °C/min., 10% wt. loss

isoxazole bis(phenol)s to aromatic nucleophilic substitution conditions in the presense of potassium carbonate.[2]

The success of the model reaction with the pyrimidine bis(aryl fluoride) prompted investigation into the polymerizations involving **6** and a series of bis(phenol)s. Initially, polymerizations were investigated using conditions similar to those of the model reaction. Due to the insolubility of pyrimidine oligomers formed in the early stages of the polymerization, it became necessary to use diphenyl sulfone and higher reaction temperatures to maintain homogeneous solutions throughout the polymerizations. The required reaction temperature ranged from 210 to 320 °C, depending on the solubility of the resulting materials. The isopropylidene- and aryl sulfide-containing bis(phenol)s required temperatures in excess of 300 °C, while the bulky fluorene-containing bis(phenol) required temperatures in the range of 200 °C to maintain a homogeneous solution. A similar solubility problem was encountered by Waldbauer in the course of attempted polymerizations of bis(amidine)s with bis(propynone)s, resulting in precipitation of pyrimidine-containing oligomers before a high polymer could be formed.[8]

Polymers prepared from **6** and bis(phenol)s **g** and **h** were low molecular weight materials with relatively low T_g's. The high reaction temperature in the presence of base may have been detrimental to the isopropylidene functionality, resulting in lower MW materials. Polymer **6i**, prepared with the bis(phenol) containing the fluorene moiety, **i**, had a T_g of 244 °C and an inherent viscosity of 0.80 dL/g, but the film cast from DMAc solution was not creasable. This is probably due to either crystallinity or light cross-linking of the polymer chain. The absence of a crystalline melting point indicates the latter; however, WAXS was not performed. The reaction temperature in these polymerizations is sufficiently high for cross-linking to occur in arylene ethers.[47] Polymer **6j** exhibited poor solubility in polar aprotic solvents, even upon heating. Therefore, no inherent viscosity value could be obtained. Thermal stabilities of **6g**–**j** were generally in the same temperature range as for polymers **4a**–**f** prepared from the bis(trimethylsilyl) ether monomers containing the pyrimidine ring. Physical properties are recorded in Table 4.

Conclusions

Poly(arylene ether pyrimidine)s were prepared in medium to high molecular weights with good thermal stability by aromatic nucleophilic displacement reactions between a bis(trimethylsilyl) ether containing a pyrimidine ring and a series of activated bis(aryl fluoride)s. The silyl ether approach is preferred to using the pyrimidine-containing bis(phenol) due to gelation of the polymer prepared by the latter approach. This gelation probably results from the lability of the bis(phenolate) monomer to cross-linking at the high reaction temperatures necessary for solvation of the reactants. A thin film of a poly(arylene ether pyrimidine) containing a phenylphosphine linkage exhibited good tensile properties and resistance to oxygen plasma.

The pyrimidine ring has sufficient ability to activate aryl fluorides toward polymerization with bi(phenol)s. However, the high reaction temperatures required to maintain a homogeneous polymerization solution likely caused side reactions to occur, resulting in cross-linked and low molecular weight materials.

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(29) Smith, J. G.; Connell, J. W.; Hergenrother, P. M. *Polymer* **1994**, *35* (13), 2834.
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(31) Connell, J. W.; Smith, J. G.; Hedrick, J. L. *Polymer* **1995**, *36* (1), 13.
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(34) Anstead, G. M.; Altenbach, R. J.; Wilson, S. R.; Katzenellenbogen, J. A. *J. Med. Chem.* **1988**, *31*, 1316.
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