Synthesis of Poly(phenylquinoxaline)s via Self-Polymerizable Quinoxaline Monomers

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ABSTRACT: The development of three new self-polymerizable quinoxaline monomers was pursued in an attempt to increase the susceptibility of the monomers toward aromatic nucleophilic substitution reactions. The polymerizations were carried out in *N*-methyl-2-pyrrolidinone in the presence of potassium carbonate, to yield high molecular weight poly(phenylquinoxaline)s (PPQs). Replacement of the 1,4-phenylene group of the phenol in the isomeric monomer mixture of 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline and 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline with the 2,6-naphthylene, 4,4′-biphenylene, and 4,4′-oxydiphenylene groups resulted in more reactive monomers as evidenced by shorter polymerization times and lower polymerization temperatures needed to obtain PPQs with high intrinsic viscosities. Polymerizations of the 1,4-phenylene-, 2,6-naphthylene-, 4,4′-biphenylene-, and 4,4′-oxydiphenylene-containing monomers led to PPQs with intrinsic viscosities ranging from 1.4 to 2.5 dL/g and glass transition temperatures ranging from 221 to 287 °C. All of the PPQs exhibited high tensile properties, with tensile strengths of ≥92 MPa, tensile moduli of ≥2.6 GPa, and elongations of ≥88%.

Introduction

Poly(phenylquinoxaline)s (PPQs) are a class of high-temperature/high-performance thermoplastics that have many desirable properties such as high glass transition temperatures (T_g's), low dielectric constants, high chemical resistance, excellent mechanical properties, and high thermooxidative stability. Since the first synthesis of conventional PPQs, which were prepared from bis(*o*-diamine) and bis(α-diketone) monomers, extensive research has been carried out in their synthesis and characterization.[1−5] A major barrier to widespread commercial use of PPQs has been the relatively high cost of the monomers involved.

An alternate approach to the synthesis of PPQs is through the polymerization of monomers containing preformed quinoxaline rings via aromatic nucleophilic substitution (S_NAr) reactions. Difluoroquinoxaline monomers were synthesized and polymerized with a series of aromatic diols to afford poly(aryl ether phenylquinoxaline)s with high intrinsic viscosities.[6−8] The electron-withdrawing pyrazine ring activates the electrophilic fluorocarbon toward substitution. The aryl−ether linkage imparts properties such as better solution and melt-processing characteristics and improved toughness compared to PPQs without aryl−ether linkages.[7]

Diol quinoxaline monomers have also been polymerized to high intrinsic viscosities with a series of activated difluoro monomers.[9,10] Highly activated difluoro monomers were necessary due to the deactivated nature of the quinoxaline monomers. This arises from the electron-withdrawing ability of the pyrazine ring, which stabilizes the phenoxide intermediate during polymerization, resulting in lower nucleophilicity.

In our laboratory, self-polymerizable quinoxaline monomers have been developed, which offers the advantage of having an inherent 1:1 stoichiometry.[5,11,12] Thus, the isomeric monomer mixture 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline and 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline was synthesized and polymerized to high intrinsic viscosities in *N*-methyl-2-pyrrolidinone (NMP). The resulting PPQ has a T_g of 251 °C and polymer decomposition temperatures above 500 °C in both nitrogen and air. This PPQ had a tensile strength of 107 MPa, tensile modulus of 3.18 GPa, and an elongation to break of approximately 4%.

Experimental Section

Materials. Anisole, phenylacetyl chloride, copper(II) bromide ($CuBr_2$), hydrobromic acid (HBr) (48%), fluorobenzene, 4-methoxyphenol, pyridine hydrochloride, potassium fluoride, trifluoroacetic acid, trifluoroacetic acid, Raney nickel, nitrobenzene, 2-methoxynaphthalene, 4-fluoro-2-nitroaniline, 4-(4-bromophenyl)phenol, palladium(II) acetate, palladium(II) chloride, phenylacetylene, triphenylphosphine, and copper(I) iodide (Aldrich Chemical Co.) were used as received. NMP (Fisher Chemical Co.) was distilled from phosphorus pentoxide under reduced pressure. Aluminum chloride ($AlCl_3$), glacial acetic acid, ethyl acetate, dimethyl sulfoxide (DMSO), chloroform ($CHCl_3$), hydrochloric acid (HCl), and methylene chloride (CH_2Cl_2) (Fisher Chemical Co.) were used as received. Potassium carbonate (Fisher Chemical Co.) was ground and dried at 100 °C under reduced pressure overnight before use. Toluene (Fisher Chemical Co.) was dried with magnesium sulfate overnight before use. All other chemicals were used as received. 1-(4-Fluorophenyl)-2-phenylethanone (**13**)[13] and 1-(4-fluorophenyl)-2-phenylethane-1,2-dione (**14**)[14] were prepared according to the literature.

Characterization. Differential scanning calorimetric (DSC) analyses were performed under nitrogen at heating rate of 10 °C/min using a DuPont model 2910 thermal analyzer equipped with a DSC cell. Thermogravimetric analyses (TGA) were performed in nitrogen and air at a heating rate of 10 °C/min using a TA Instruments model 2950 thermogravimetric analyzer. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained with a Varian Gemini 200 NMR spectrometer

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at 200 MHz. Fluorine nuclear magnetic resonance (^{19}F NMR) spectra were obtained with a Varian Gemini 300 NMR at 300 MHz. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were obtained with a Bruker ADVANCE 300 NMR spectrometer at 75 MHz. Tetramethylsilane was used as the reference for ^{1}H and ^{13}C NMR analyses. Fluorotrichloromethane was used as the reference for ^{19}F NMR analyses. The reference peaks were assigned at 0.0 ppm. Infrared spectra were obtained with an AT Mattson Genesis series FTIR. Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Intrinsic viscosities were determined with a Cannon-Ubbelohde #200 viscometer. Flow times were recorded for *m*-cresol solutions with polymer concentrations of approximately 0.50−0.25 g/dL at 30.0 ± 0.1 °C. Mechanical properties of thin films were determined on an Instron model 5567 according to ASTM D638. All calculations were performed on a Silicon Graphics Indigo2 workstation. Geometries of the monomeric molecules were calculated at the AM1 level as implemented within Gaussian94.[15] Single-point energies on all molecules were performed at the B3LYP/3-21G(d) level and are denoted as B3LYP/3-21G(d)//AM1. Mulliken populations were computed at both the AM1 and the B3LYP/3-21G(d)//AM1 levels. Dihedral angles were determined using MacSPARTAN computational package. Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN). High-performance liquid chromatographic (HPLC) analyses were performed on a Shimadzu LC-600 liquid chromatograph with a Shimadzu SPD-6A UV spectrophotometric detector, Shimadzu CD 501 Chromatopac, and YMC, Inc., HPLC reverse phase column. HPLC samples were run using a 7/3 (v/v) acetonitrile/water solvent system.

Syntheses. 1-(4-Methoxyphenyl)-2-phenylethanone (1). To a 1 L, three-neck, round-bottom flask equipped with an overhead stirrer, condenser, and addition funnel were placed $AlCl_3$ (80.00 g, 0.6000 mol) and CH_2Cl_2 (225 mL). After the stirred mixture was cooled to 0 °C in an ice bath, a mixture of phenylacetyl chloride (77.30 g, 0.5000 mol), anisole (54.05 g, 0.5000 mol), and CH_2Cl_2 (225 mL) was added dropwise, while the mixture was maintained at ≤0 °C. The mixture was stirred at 0 °C for 1 h and then allowed to warm to room temperature overnight. After the mixture was heated at reflux for 1−2 h, it was allowed to cool to room temperature and poured into a 2 L slurry of 0.1 M HCl and ice. The solution was transferred to a separatory funnel, and 250 mL of CH_2Cl_2 was added. The organic layer was washed several times with water. After the CH_2Cl_2 was removed under reduced pressure, the residue was poured into cold ethanol. After the mixture was stored in a freezer for several hours, the solid was collected by filtration. The crude solid was recrystallized from 95% ethanol. Yield 83.85 g (74%) of light tan crystals; T_m = 67−69 °C (lit.[16] T_m = 66−68 °C). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.8 (s, 3H, OCH_3), 4.2 (s, 2H, CH_2), 6.9−8.0 (m, 9H, Ar).

1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione (2). To a 2 L, three-neck, round-bottom flask equipped with an overhead stirrer and condenser were added 1-(4-methoxyphenyl)-2-phenylethanone (83.85 mol, 0.3706 mol), $CuBr_2$ (165.62 g, 0.74153 mol), DMSO (371 mL), and ethyl acetate (371 mL). The mixture was stirred and heated at reflux overnight. After the mixture was allowed to cool to room temperature, it was transferred to a separatory funnel. To the funnel was added CH_2Cl_2 (400 mL) and the organic layer washed several times with water. The organic phase was filtered through Celite to remove insoluble copper salts. The filtrate was evaporated to dryness under reduced pressure to yield a dark yellow solid. The solid residue was recrystallized from ethanol. Yield 74.26 g (83%) of yellow crystals; T_m = 62−63 °C (lit.[17] T_m = 62−63 °C). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.9 (s, 3H, OCH_3), 7.0−8.0 (m, 9H, Ar).

1-(4-Hydroxyphenyl)-2-phenylethane-1,2-dione (3). In a 500 mL, three-neck, round-bottom flask equipped with an overhead stirrer and condenser were added 1-(4-methoxyphenyl)-2-phenylethane-1,2-dione (33.16 g, 0.1380 mol), glacial acetic acid (128 mL), and HBr (255 mL). The solution was stirred and heated at reflux for 4 h and then allowed to cool to room temperature. The solution was poured into 1 L of water and ice. The precipitate was collected by filtration and dissolved in 350 mL of an aqueous 10% NaOH solution. The aqueous layer was extracted three times with ethyl ether and acidified with dilute HCl. The resulting precipitate was collected by filtration and washed with water until the wash had a neutral pH. The solid was recrystallized from toluene. Yield 21.22 g (68%) of yellow needles; T_m = 131−132 °C (lit.[18] T_m = 129−130 °C). ^{1}H NMR ($CDCl_3$) δ (ppm): 6.6 (s, 1H, OH) and 6.8−7.9 (m, 9H, Ar).

1,2-Diamino-4-fluorobenzene (4). To a 250 mL Parr bottle were added 4-fluoro-2-nitroaniline (5.00 g, 0.0320 mol), ethanol (100 mL), and a 50% slurry of Raney nickel/water (2.0 mL). The bottle was placed in a hydrogenation apparatus and agitated under hydrogen (60 psi) at room temperature for 4 h. The mixture was filtered through Celite and the residue rinsed with ethanol until the rinse was no longer colored. The filtrate was evaporated to dryness under reduced pressure. The solid residue was sublimed twice at 80 °C to yield 2.61 g (65%) of a white powder, which was immediately used in monomer synthesis; T_m = 92−93 °C (lit.[19] T_m = 88−89 °C). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.3 (s, 4H, NH_2), 6.4−6.6 (m, 3H, Ar).

3-(4-Hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline and 2-(4-Hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline (5a,b). To a 250 mL, round-bottom flask equipped with a magnetic stirring bar, nitrogen inlet, and condenser were added 1-(4-hydroxyphenyl)-2-phenylethane-1,2-dione (26.96 g, 0.1192 mol), 4-fluoro-1,2-phenylenediamine (15.03 g, 0.1192 mol), $CHCl_3$ (184 mL), and five drops of trifluoroacetic acid. The solution was magnetically stirred and heated at reflux under a nitrogen blanket for 5 h. After the solution was allowed to cool to room temperature, it was transferred to a separatory funnel. The organic layer was washed with dilute HCl and then with water several times. The organic layer was evaporated to dryness under reduced pressure. The crude residue was recrystallized from 85% aqueous ethanol to yield a yellow powder. The powder was then recrystallized from toluene. Yield 35.55 g (94%) of yellow crystals; T_m's (DSC) = 126, 172 °C (lit.[12] T_m = 110−130 °C). ^{1}H NMR ($CDCl_3$) δ (ppm): 6.8 (s, 1H, OH), 6.6 and 7.3−8.1(m, 12H, Ar).

1-(6-Methoxynaphthalen-2-yl)-2-phenylethanone (6). To a 1 L, three-neck, round-bottom flask equipped with a nitrogen inlet, an addition funnel, and an overhead stirrer were added 2-methoxynaphthalene (150.0 g, 0.9543 mol), CH_2Cl_2 (630 mL), $AlCl_3$ (168.0 g, 1.260 mol), and nitrobenzene (37.37 g, 0.3117 mol). After the stirred solution was cooled to 0 °C in an ice bath, phenylacetyl chloride (146.6 g, 0.9482 mol) was added dropwise, while the mixture was maintained at 0 °C. The mixture was stirred at 0 °C for 1 h and then allowed to warm to room temperature over 19 h. The mixture was poured into a 2 L slurry of 0.1 M HCl and ice. The mixture was transferred to a separatory funnel, and 500 mL of CH_2Cl_2 was added to aid in the workup. The organic layer was washed several times with water. After the solvent was removed under reduced pressure, the residue was recrystallized from ethanol. Yield 169.0 g (64%) of a dark yellow powder; T_m = 119−120 °C (lit.[20] T_m = 117 °C). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.9 (s, 3H, OCH_3), 4.4 (s, 2H, CH_2), 7.16−7.41 (m, 7H, Ar), 7.80 (q, 2H, Ar), 8.04 (dd, 1H, Ar), 8.48 (d, 1H, Ar).

1-(6-Methoxynaphthalen-2-yl)-2-phenylethane-1,2-dione (7). In a 1 L, three-neck, round-bottom flask equipped with an addition funnel and overhead stirrer were placed 1-(6-methoxynaphthalen-2-yl)-2-phenylethanone (70.00 g, 0.2648 mol), $CuBr_2$ (118.3 g, 0.5297 mol), DMSO (310 mL), and ethyl acetate (310 mL). The compound was prepared according to **2**. Yield 60.7 g (82%) of yellow needles; T_m = 107−108 °C. IR (KBr) ν (cm^{-1}): 3067 (Ar−H), 2939 (aliphatic C−H), 1670 (C=O), 1595 (Ar). ^{1}H NMR ($CDCl_3$) δ (ppm): 4.0 (s, 3H, $-OCH_3$), 7.2−8.02 (m, 10H, Ar), 8.32 (d, 1H, Ar). ^{13}C NMR ($CDCl_3$) δ (ppm): 194.8, 194.3, 160.6, 138.3, 134.7, 133.2, 131.5, 129.9, 129.0, 128.4, 127.8, 127.7, 124.5, 120.0, 106.0, 77.4, 77.0, 76.6, 55.4. Anal. Calcd for $C_{19}H_{14}O_3$: C, 77.60; H, 4.86. Found: C, 77.48; H, 4.83.

1-(6-Hydroxynaphthalen-2-yl)-2-phenylethane-1,2-dione (8). To a 2 L, three-neck, round-bottom flask equipped with an overhead stirrer and condenser were added 1-(6-

methoxynaphthalen-2-yl)-2-phenylethane-1,2-dione (40.00 g, 0.138 mol), HBr (56 mL), and glacial acetic acid (856 mL). The solution was stirred and heated at reflux for 23 h and then allowed to cool to room temperature. The workup followed the procedure for **3**. Yield 21.52 g (57%) of a yellow powder; T_m = 118−120 °C. IR (KBr) ν (cm^{-1}): 3383 (O−H), 3063 (Ar−H), 1650 (C═O), 1622 (Ar). ^{1}H NMR ($CDCl_3$) δ (ppm): 6.00 (s, 1H, OH), 7.05−8.00 (m, 10H, Ar), 8.12 (d, 1H, Ar). ^{13}C NMR ($CDCl_3$) δ (ppm): 195.3, 194.7, 157.1, 138.3, 135.0, 133.7, 133.1, 132.1, 130.0, 129.0, 128.2, 127.4, 124.3, 119.3, 109.9 Anal. Calcd for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38. Found: C, 78.19; H, 4.39.

3-(2-(6-Hydroxynaphthalenyl))-2-phenyl-6-fluoroquinoxaline and 2-(2-(6-Hydroxynaphthalenyl))-3-phenyl-6-fluoroquinoxaline (9a,b). In a 250 mL, three-neck, round-bottom flask equipped with an overhead stirrer and condenser were placed 1-(6-hydroxynaphthalen-2-yl)-2-phenylethane-1,2-dione (17.54 g, 0.06349 mol), 4-fluoro-1,2-phenylenediamine (8.01 g, 0.0635 mol), $CHCl_3$ (167 mL), and five drops of trifluoroacetic acid. The compound was prepared according to **5a,b**. Yield 13.57 g (58%) of a light yellow powder; T_m = 180−181 °C. IR (KBr) ν (cm^{-1}): 3171 (O−H), 1625 and 1605 (Ar). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.00 (m, 1H, OH), 7.23−7.40 (m, 7H, Ar), 7.50−7.60 (m, 4H, Ar), 7.83 (m, 1H, Ar), 7.90 (m, 1H, Ar), 8.22 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$) δ (ppm): 164.1, 163.9, 160.8, 160.6, 156.7, 156.6, 154.1, 153.9, 152.8, 152.7, 152.6, 141.5, 141.2, 141.0, 138.9, 138.8, 138.1, 137.8, 134.7, 134.6, 132.8, 132.7, 131.5, 131.4, 131.3, 130.3, 130.2, 129.8, 129.7, 129.5, 129.1, 128.9, 128.2, 127.3, 127.2, 127.1, 125.7, 120.7, 120.5, 120.4, 119.3, 112.5, 112.4, 112.2, 112.1, 108.7. Anal. Calcd for $C_{24}H_{15}FN_2O$: C, 78.67; H, 4.13; N, 7.65. Found: C, 78.66; H, 4.13; N, 7.69.

4′-Phenylethynylbiphenyl-4-ol (10). To a 500 mL, three-neck, round-bottom flask equipped with an overhead stirrer and a condenser were added 4-(4-bromophenyl)phenol (50.00 g, 0.2007 mol), phenylacetylene (22.58 g, 0.2211 mol), cuprous iodide (0.20 g), triphenylphosphine (2.00 g), palladium(II) acetate (0.0856 g), and triethylamine (300 mL). After the solution was stirred and heated at reflux for 15 h, it was allowed to cool to room temperature. The solution was poured into 2 L of a dilute aqueous HCl solution. The brown precipitate that formed was collected by filtration, dissolved in acetone, and precipitated in water. This procedure was repeated twice, yielding a light tan solid. The crude solid was recrystallized from ethanol to yield 39.20 g (72%) of a light tan powder; T_m = 227−229 °C. IR (KBr) ν (cm^{-1}): 3417 (O−H), 3032 (Ar−H), 2217 (alkyne), 1607 and 1593 (Ar). ^{1}H NMR (DMSO-d_6) δ (ppm): 6.85 (d, 2H, 3-Ar*H*), 7.40−7.70 (m, 11H, Ar), 9.6 (s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ (ppm): 157.6, 140.3, 131.8, 131.3, 129.7, 128.7, 128.6, 127.7, 126.0, 122.4, 120.0, 115.8, 89.7, 89.5. Anal. Calcd for $C_{20}H_{14}O$: C, 88.97; H, 5.30. Found: C, 88.86; H, 5.22.

1-(4′-Hydroxybiphenyl-4-yl)-2-phenylethane-1,2-dione (11). In a 250 mL, three-neck, round-bottom flask equipped with an overhead stirrer and a condenser were placed 4′-phenylethynylbiphenyl-4-ol (24.42 g, 0.09034 mol), palladium(II) chloride (1.60 g, 0.00902 mol), and DMSO (100 mL). The solution was stirred at 140 °C for 22 h and then allowed to cool to room temperature. The solution was poured into 600 mL of water and ice, transferred to a separatory funnel, and extracted with ether. The ether layer was washed with brine several times and then with water several times. The ether was removed under reduced pressure to afford a dark oil, which solidified upon standing. Yield 14.52 g (52%) of a dark yellow powder; T_m = 118−120 °C. IR (KBr) ν (cm^{-1}): 3323 (O−H), 1729 and 1669 (C═O), 1593 (Ar). ^{1}H NMR (DMSO-d_6) δ (ppm): 6.90 (d, 2H, 3-Ar*H*), 7.61−7.92 (m, 11 H, Ar), 9.80 (s, 1H, OH). Anal. Calcd for $C_{19}H_{14}O_3$: C, 79.45; H, 4.67. Found: C, 79.54; H, 4.79.

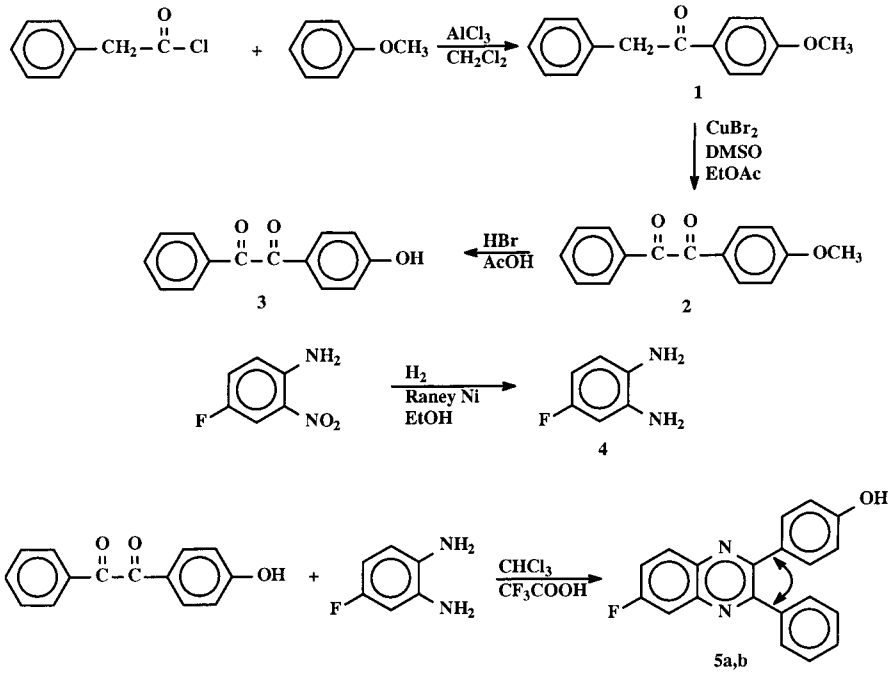
3-(4-(4′-Hydroxybiphenyl)-yl)-2-phenyl-6-fluoroquinoxaline and 2-(4-(4′-Hydroxybiphenyl)-yl)-3-phenyl-6-fluoroquinoxaline (12a,b). To a 50 mL, round-bottom flask equipped with a magnetic stirring bar, condenser, and nitrogen inlet were placed 1-(4′-hydroxybiphenyl-4-yl)-2-phenylethane-1,2-dione (4.09 g, 0.0135 mol), 1,2-diamino-4-fluorobenzene (1.71 g, 0.0135 mol), $CHCl_3$ (21 mL), and five drops of trifluoroacetic acid. The compound was prepared according to **5a,b**. Yield 4.25 g (80%) of a light orange powder; T_m's (DSC) 145, 181, 193 °C. IR (KBr) ν (cm^{-1}): 3409 (O−H), 1606 (Ar). ^{1}H NMR (DMSO-d_6) δ (ppm): 6.91 (d, 2H, Ar), 7.18−7.79 (m, 10H, Ar), 7.91 (dd, 2H, Ar), 8.20 (dd, 2H, Ar), 9.61 (s, 1H, OH). Anal. Calcd for $C_{26}H_{17}FN_2O$: C, 79.57; H, 4.37; N, 7.14. Found: C, 79.51; H, 4.28; N, 6.99.

1-(4-Methoxyphenoxy)-2-phenylethane-1,2-dione (15). To a 200 mL, three-neck, round-bottom flask equipped with an overhead stirrer, nitrogen inlet, Barrett trap, condenser, and nitrogen outlet were placed 4-methoxyphenol (6.00 g, 0.0483 mol), K_2CO_3 (8.02 g, 0.0580 mol), NMP (64 mL), and toluene (50 mL). The mixture was stirred and heated at 140 °C overnight under a nitrogen flow to aid in azeotropic removal of water, which collected in the Barrett trap. The nitrogen flow was increased to distill the toluene from the system. After removal of toluene, 1-(4-fluorophenyl)-2-phenylethane-1,2-dione (10.00 g, 0.04382 mol) was added. The reaction was allowed to proceed at 140 °C for 4 h and then poured onto ice containing HCl (50 mL). The brown, gummy solid was collected by filtration and recrystallized from ethanol to afford brown needles. The solid was decolorized with charcoal in acetone. Yield 11.35 g (78%) of a pale yellow solid; T_m = 85−86 °C (lit.[21] T_m = 85−86 °C). IR (KBr) ν (cm^{-1}): 3062 (Ar−H), 2933 (aliphatic C−H), 1673 (C═O), 1590 (Ar). ^{1}H NMR (DMSO-d_6) δ (ppm): 3.83 (s, 3H, OCH_3), 7.05 (dd, 4H, Ar), 7.14 (d, 2H, Ar), 7.62 (t, 2H, Ar), 7.79 (t, 1H, Ar), 7.87−7.96 (m, 4H, Ar). ^{13}C NMR (DMSO-d_6) δ (ppm): 195.7, 194.1, 165.1, 157.3, 148.1, 136.2, 133.3, 130.5, 130.3, 127.3, 122.8, 122.6, 117.6, 116.2, 56.3. Anal. Calcd for $C_{21}H_{16}O_4$: C, 75.89; H, 4.85. Found: C, 75.92; H, 4.84.

1-(4-Hydroxyphenoxy)-2-phenylethane-1,2-dione (16). To a 100 mL, three-neck, round-bottom flask equipped with an overhead stirrer, condenser, and gas outlet were placed 1-(4-methoxyphenoxy)-2-phenylethane-1,2-dione (5.00 g, 0.0150 mol) and pyridine hydrochloride (13.07 g). The solution was stirred at 230 °C for 4 h and then poured onto ice. The brown/gray precipitate was collected by filtration and dissolved in ether. The ether layer was extracted with 200 mL of an aqueous 10% NaOH solution. The aqueous layer was washed with ether (100 mL) and acidified with dilute HCl. The gummy solid was collected by filtration and dissolved in $CHCl_3$. The $CHCl_3$ layer was washed twice with water. The organic layer was evaporated to dryness under reduced pressure to afford a dark oil, which solidified upon cooling. The solid was decolorized with charcoal in acetone. Yield 3.40 g (71%) of a dark yellow solid; T_m = 124−125 °C (lit.[21] T_m = 84−85 °C). IR (KBr) ν (cm^{-1}): 3397 (O−H), 3066 (Ar−H), 1681 (C═O), 1592 (Ar). ^{1}H NMR (DMSO-d_6) δ (ppm): 6.84 (d, 2H, Ar), 7.03 (dd, 4H, Ar), 7.62 (t, 2H, Ar), 7.79 (t, 1H, Ar), 7.91 (dd, 4H, Ar), 9.57 (s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ (ppm): 193.3, 191.7, 162.9, 153.5, 144.4, 133.8, 130.9, 130.8, 128.0, 127.8, 124.7, 123.1, 120.4, 115.0. Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.26; H, 4.43.

3-(4-Hydroxyphenoxyphenyl)-2-phenyl-6-fluoroquinoxaline and 2-(4-Hydroxyphenoxyphenyl)-3-phenyl-6-fluoroquinoxaline (17a,b). To a 50 mL, round-bottom flask equipped with a magnetic stirring bar and a condenser were placed 1-(4-hydroxyphenoxy)-2-phenylethane-1,2-dione (2.00 g, 0.00628 mol), 1,2-diamino-4-fluorobenzene (0.80 g, 0.0063 mol), $CHCl_3$ (10 mL), and three drops of trifluoroacetic acid. The compound was prepared according to **5a,b**. Yield 2.40 g (93%) of an orange solid; T_m(DSC) 209 °C (lit.[21] T_m = 202−204 °C). IR (KBr) ν (cm^{-1}): 3220 (O−H), 1618 (Ar). ^{1}H NMR (DMSO-d_6) δ (ppm): 6.86 (dd, 4H, Ar), 6,96 (d, 2H, Ar), 7.40−7.58 (m, 7H, Ar), 7.83 (m, 1H, Ar), 7.94 (m, 1H, Ar), 8.24 (m, 1H, Ar), 9.46 (s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ (ppm): 161.6, 158.5, 158.3, 157.1, 157.0, 152.1, 152.0, 151.6, 151.0, 150.3, 150.2, 149.7, 149.6, 145.0, 144.9, 139.1, 139.0, 138.9, 138.7, 136.5, 136.4, 135.7, 135.5, 130.1, 129.9, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 127.5, 126.9, 126.7, 126.0, 119.1, 119.0, 118.4, 118.1, 117.9, 114.2, 114.0, 113.9, 110.2, 110.1, 109.9, 109.8. Anal. Calcd for $C_{26}H_{17}FN_2O_2$: C, 76.46; H, 4.20; N, 6.86. Found: C, 76.22; H, 4.21; N, 6.67.

Scheme 1. Synthesis of 5a,b



General Polymerization. To a 100 mL, three-neck, round-bottom flask equipped with an overhead stirrer, a nitrogen inlet, a Barrett trap, and a condenser were added self-polymerizable quinoxaline monomer (3.00 g), potassium carbonate (1.2 equiv), NMP (12 mL), and toluene (12 mL). The mixture was stirred at 150 °C for 4 h under a nitrogen flow to aid in azeotropic removal of water, which collected in the Barrett trap. The solution was heated to 170−180 °C, and the nitrogen flow increased to remove the toluene. After 1 h, the nitrogen flow was decreased, and the mixture was raised to 202 °C for 3 h. The brown mixture was diluted with NMP and cooled to room temperature. The polymer was precipitated in 600 mL of a 5/1 (v/v) methanol/acetic acid solution. The white, fibrous PPQ was collected by filtration and reprecipitated twice from $CHCl_3$ with methanol. The polymer was stirred overnight in refluxing methanol and overnight in refluxing water. The polymer was dried overnight at 180 °C under reduced pressure.

PPQ (**18**) from monomer mixture **5a,b**. Yield: 94%. IR (film) ν (cm^{-1}): 3056 (Ar−H), 1600 (Ar), 1220 (Ar−O).

PPQ (**19**) from monomer mixture **9a,b**. Yield 88%. IR (film) ν (cm^{-1}): 3059 (Ar−H), 1599 (Ar), 1240 (Ar−O).

PPQ (**20**) from monomer mixture **12a,b**. Yield 92%. IR (film) ν (cm^{-1}): 3059 and 3034 (Ar−H), 1600 (Ar), 1219 (Ar−O).

PPQ (**21**) from monomer mixture **17a,b**. Yield 93%. IR (film) ν (cm^{-1}): 3060 (Ar−H), 1600 (Ar), 1222 (Ar−O).

General Procedure for Degradation of PPQ. A polymer sample (0.50 g) was dissolved in 5 mL of NMP. To this solution was added potassium carbonate or potassium fluoride (0.50 g). The solution was stirred under reflux for 1 h. The polymer was precipitated in 300 mL of a 5/1 (v/v) methanol/acetic acid solution. The light yellow powder was collected by filtration and reprecipitated from $CHCl_3$ with methanol. The polymer was stirred overnight in refluxing methanol and overnight in refluxing water. The polymer was dried at 150 °C under reduced pressure overnight.

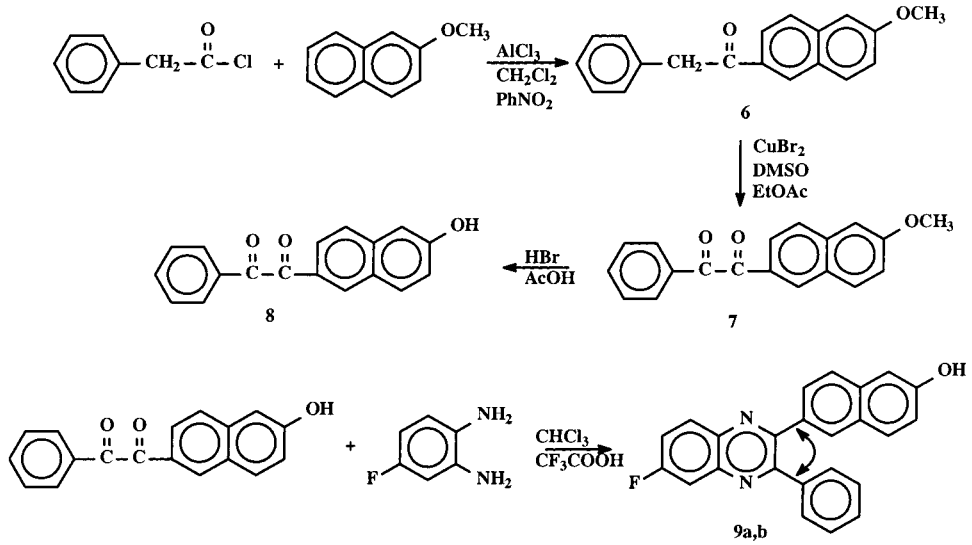
General Procedure for the Preparation of Films for Mechanical Testing. A polymer sample (1.00 g) was dissolved in $CHCl_3$ (15 mL) to give a 7.5 wt % solution. The solution was filtered through cotton and poured onto a clean glass plate. The plate was stored in a dust-free chamber until tack free. After the film was removed from the plate using hot water, it was dried under reduced pressure overnight at 160 °C and cut using a dumbbell shaped die (type V). The dumbbell shaped samples, which were approximately 0.040−0.100 mm thick, were tested at room temperature according to ASTM D638 with a crosshead speed of 1 mm/min. A minimum of five specimens were tested for each polymer.

Results and Discussion

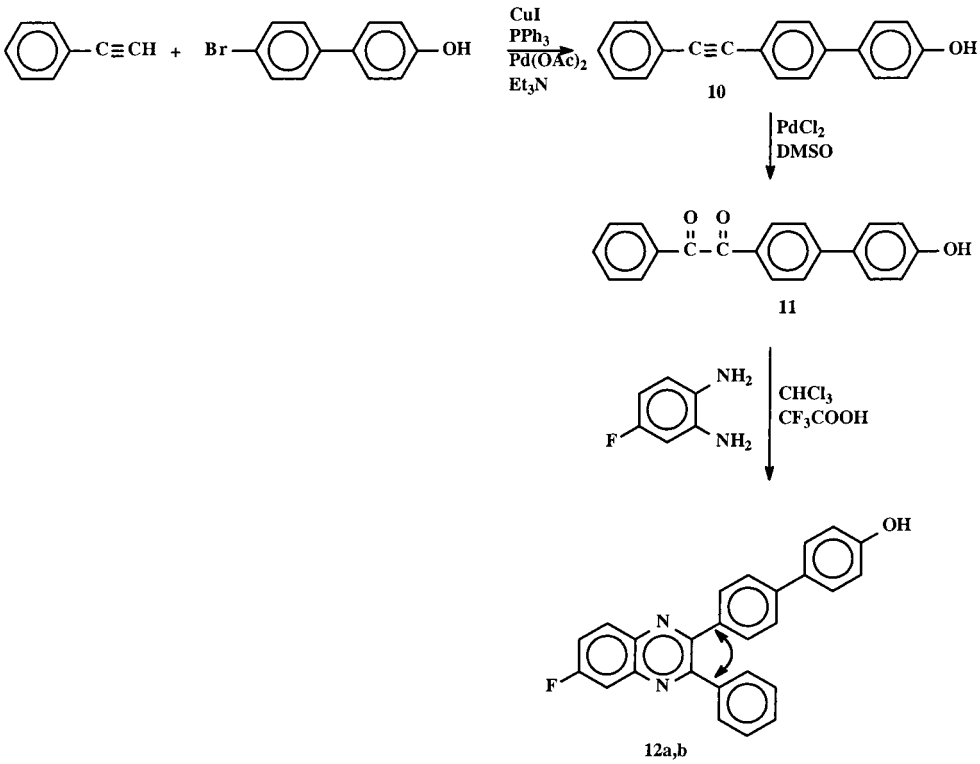
Monomer mixtures **9a,b 12a,b**, and **17a,b** were synthesized in an attempt to increase the reactivity relative to **5a,b**. Introduction of the 2,6-naphthylene, 4,4′-biphenylene, and 4,4′-oxydiphenylene groups were incorporated into the self-polymerizable quinoxaline monomers in an attempt to decrease charge delocalization into the pyrazine ring. Charge delocalization into the pyrazine ring would lead to a less nucleophilic monomer. It was believed that the 2,6-naphthylene ring system would have a larger dihedral angle with the pyrazine ring relative to the 1,4-phenylene ring system, which would lead to less charge delocalization. The 4,4′-biphenylene ring system was added because the second twist between the two phenyl rings would also lead to less charge delocalization into the pyrazine ring. The 4,4′-oxydiphenylene ring system contains an ether linkage, which shields the quinoxaline ring system from delocalization of the negative charge from resonating into the quinoxaline ring.

Monomer Synthesis. The synthetic route to **5a,b** (Scheme 1) has been independently established previously in this laboratory[5,11,12] and elsewhere.[22] The synthesis of **9a,b** (Scheme 2) began through a synthesis of 1-(6-methoxynaphthalen-2-yl)-2-phenylethanone (**6**), which has been described previously.[20] The Friedel−Crafts acylation of 2-methoxynaphthalene with phenylacetyl chloride yielded only **6** at long reaction times. Shorter reaction times yielded a mixture of **6** with 1-(2-methoxynaphthalen-2-yl)-2-phenylethanone. HPLC analysis of **6** revealed only one product under the conditions employed. Oxidation of **6** to 1-(6-methoxynaphthalen-2-yl)-2-phenylethane-1,2-dione (**7**) was carried out in a mixture of DMSO and ethyl acetate with $CuBr_2$. Demethylation to 1-(6-hydroxynaphthalen-2-yl)-2-phenylethane-1,2-dione (**8**) was carried out using HBr and acetic acid.

Scheme 2. Synthesis of 9a,b



Scheme 3. Synthesis of 12a,b

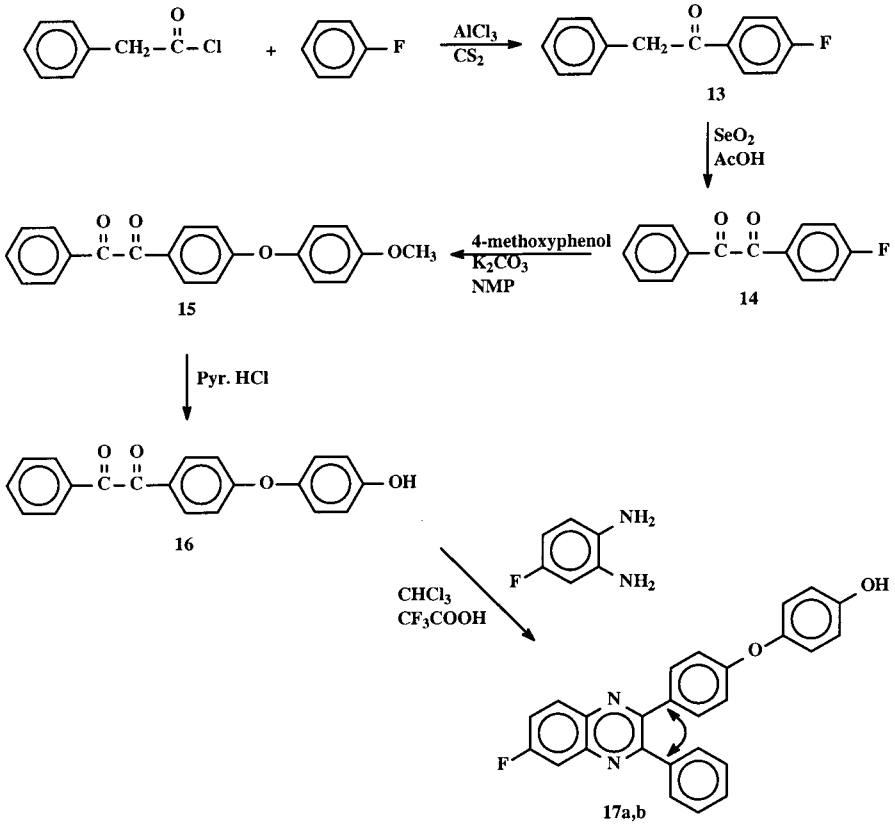


Monomer mixture **12a,b** (Scheme 3) had to follow a different route to the α-diketone than for **5a,b** and **9a,b**. A coupling reaction of phenylacetylene with 4-(4-bromophenyl)phenol yielded 4′-phenylethynylbiphenyl-4-ol (**10**). Oxidation of the acetylene group was carried out in DMSO using palladium(II) chloride to yield 1-(4′-hydroxybiphenyl-4-yl)-2-phenylethane-1,2-dione (**11**). An attempt to oxidize the acetylene group using iodine/DMSO resulted in the oxidation of the phenolic OH to the quinone.

Monomer mixture **17a,b** (Scheme 4) began with a Friedel−Crafts acylation reaction of phenylacetyl chloride with fluorobenzene to give 1-(4-fluorophenyl)-2-phenylethanone (**13**). Oxidation of **13** to 1-(4-fluorophenyl)-2-phenylethane-1,2-dione (**14**) was carried out in acetic acid in the presence of SeO_2. A condensation of **14** with 4-methoxyphenol formed 1-(4-methoxyphenoxy)-2-phenylethane-1,2-dione (**15**). Demethylation of **15** using pyridine hydrochloride formed 1-(4-hydroxyphenoxy)-2-phenylethane-1,2-dione (**16**).

Monomer mixtures **5a,b**, **9a,b 12a,b**, and **17a,b** were synthesized in a similar fashion. Each respective α-diketone was treated with 1,2-diamino-4-fluorobenzene in chloroform containing a few drops of trifluoroacetic acid as a catalyst to yield the desired monomers. Because of the isomeric forms of the monomers, the isomer ratio could be determined using ^{19}F NMR spectroscopy, since each isomer form of the monomer will have its own set of resonances. Figure 1a−d shows the ^{19}F NMR spectra of the monomer mixtures. The isomer ratios can be determined in (a), (b), and (d), but in (c) it cannot be determined due to the overlapping peaks. The isomer ratios were 75/25, 62/38, and 70/30 for **5a,b**, **9a,b**, and

Scheme 4. Synthesis of 17a,b



17a,b, respectively, all in favor of the more symmetric isomer.

Figure 2a−d shows the ^{19}F NMR spectra of the potassium phenoxide salts of monomer mixtures **5a,b**, **9a,b 12a,b**, and **17a,b**. A comparison of each monomer vs the potassium phenoxide salts shows an upfield shift when the monomer is in its potassium phenoxide form. This topic will be discussed later in this paper.

Labadie et al. synthesized **5a,b** and attempted to assign the isomer ratio utilizing ^{13}C NMR.[22] A ratio of 60:40 of the isomers was determined based upon peak heights. However, no determination of the structure of the predominant isomer was reported.

It is believed that the use of ^{19}F NMR to determine the isomer ratio is easier and more reliable than ^{13}C NMR. One reason is that the ^{19}F atom has a high natural abundance, unlike the ^{13}C atom. Therefore, fewer scans are required to get a reasonable ^{19}F NMR spectrum. The ^{19}F NMR spectrum contains a less noisy baseline, which makes integration of peaks more accurate. For ^{13}C NMR inverse-gated decoupling techniques are required to obtain a spectrum that can be accurately integrated. Therefore, the isomer ratio determined by ^{19}F NMR spectroscopy is more straightforward and accurate than the ratio determined by ^{13}C NMR spectroscopy.

Previously in our laboratory, it was determined that the symmetric monomer is upfield from the asymmetric monomer.[11] This was accomplished through an alternate synthetic route leading to a predominately symmetric isomer. 1-(4-Hydroxyphenyl)-2-phenylethane-1,2-dione was treated with 1,2-diamino-4-nitrobenzene to form 2-(4-hydroxyphenyl)-3-phenyl-6-aminoquinoxaline. The electron-donating OH group of the 1-(4-hydroxyphenyl)-2-phenylethane-1,2-dione causes a decreased reactivity of the carbonyl group *para* to it, as well as the electron-withdrawing nitro group in 1,2-diamino-4-nitrobenzene decreasing the reactivity of the amino group *para* to it, resulting in the predomination of one isomer. After reduction of the nitro group to the amine, conversion to 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline was carried out through a diazonium fluoroborate salt. The ^{19}F NMR spectrum revealed only a trace of the asymmetric isomer downfield from the symmetric isomer. One would expect the more symmetric monomer upfield since the fluorine is shielded by the direct resonance of the phenoxide to the carbon−fluorine site.

Monomer Melting Behavior. The self-polymerizable quinoxaline monomers in this research exhibited interesting melting behavior. Monomer mixture **5a,b** had been previously analyzed by DSC to determine the melting point. It was shown that this monomer exhibited two melting endotherms.[12] This same behavior was found in **5a,b** (Figure 3a) synthesized in this research. Two strong melting endotherms at peak maxima of 126 and 172 °C were determined along with a small melting endotherm at 178 °C. Monomer mixture **9a,b** (Figure 3b) only displays one sharp melting endotherm at 182 °C. Monomer mixture **12a,b** (Figure 3c) displays three melting endotherms with peak maxima at 145, 181, and 193 °C. Monomer mixture **17a,b** (Figure 3d) displays a small melting endotherm at 186 °C and a large melting endotherm at 208 °C. Each monomer displayed >98.5% purity as determined by HPLC analyses; therefore, it is unlikely that the multiple melting endotherms are due to impurities. It is postulated that the multiple melting endotherms are due to either polymorphism exhibited by the monomer or the presence of the two isomers. X-ray analyses of the isomeric monomer mixtures could not be determined due to the inability to grow crystals.

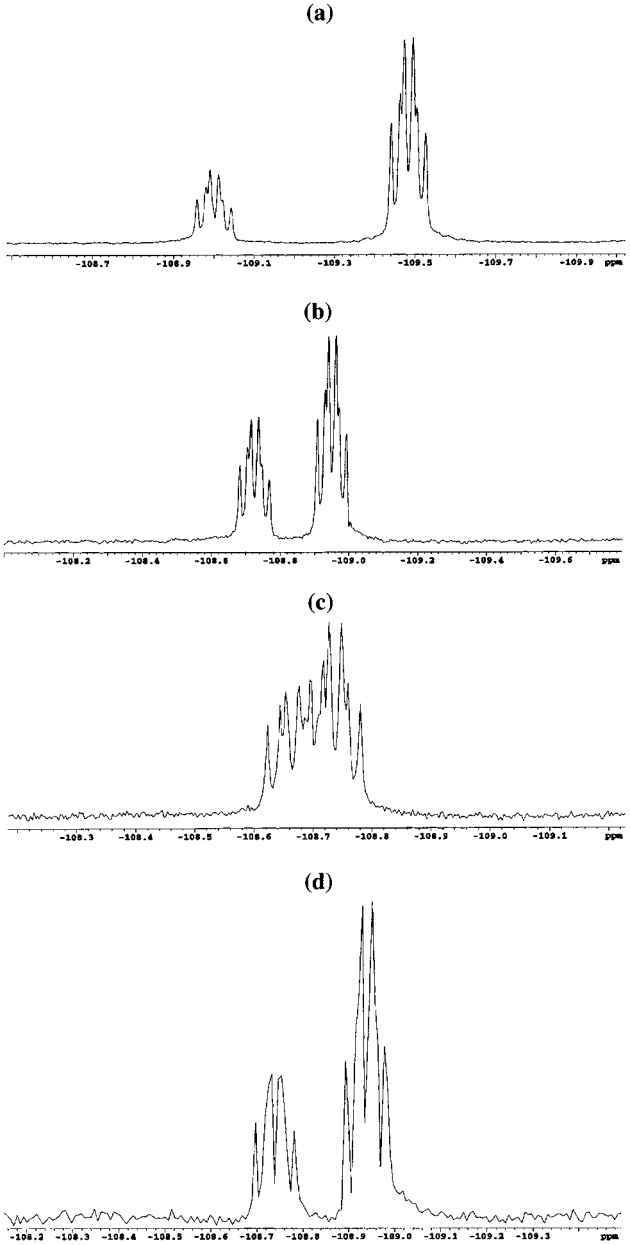


Figure 1. ^{19}F NMR spectra of (a) **5a,b**; (b) **9a,b**; (c) **12a,b**; and (d) **17a,b**.

An unexpected result was obtained in the second DSC scan after quenching the sample from 250 °C. Upon heating, no melting endotherms were detected for monomers **5a,b**, **9a,b**, and **12a,b**. Only a T_g was found for **5a,b** at 83 °C, **9a,b** at 98 °C, and **12a,b** at 101 °C. It is believed that the monomer is trapped in its amorphous form after quenching from 250 °C. This theory was examined in the laboratory by melting **5a,b**, recrystallizing from toluene, and analyzing the sample using DSC. Two melting endotherms were found and no T_g. The lack of the T_g after this experiment suggests that the monomer does not oligomerize in the solid state at high temperatures. Also, a mixture of isomeric quinoxaline monomers that do not self-polymerize was found to only exhibit a T_g on the second DSC scan after melting the sample and quenching.[23] Monomer mixture **17a,b** displays a T_g at 81 °C, a crystallization exotherm at 180 °C, and two melting endotherms at 189 and 207 °C after quenching from 250 °C. The third run on **17a,b** displays a T_g at 81 °C and a melting endotherm at 192 °C.

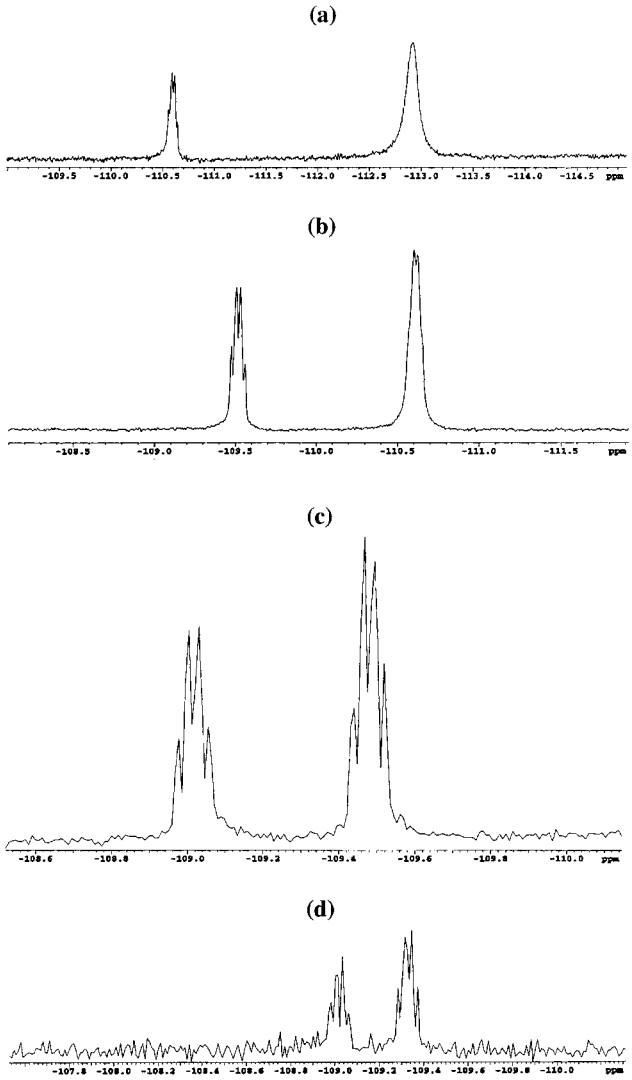


Figure 2. ^{19}F NMR spectra of the potassium phenoxide salts of (a) **5a,b**; (b) **9a,b**; (c) **12a,b**; and (d) **17a,b**.

Polymer Synthesis. The polymerization procedure for **5a,b** has been established in our laboratory[5,11,12] and elsewhere.[22] The polymerization was carried out in NMP/toluene containing potassium carbonate (Scheme 5) for 4 h at 160 °C to convert the monomer to its phenoxide salt. The temperature was raised to 180 °C for 1 h to remove toluene from the system. Finally, the polymerization was carried out at 202 °C for 2−3 h to effect displacement of the fluoro groups. At times less than 2 h lower molecular weight PPQs are obtained presumably due to the lack of sufficient time necessary to maximize chain growth. At polymerization times greater than 3 h, the molecular weight decreases probably due to transetherification reactions,[7,24] KF attacking the polymer chains causing chain scission,[24] or carbonate from the base causing scission. Therefore, polymerization times were carried out in the 2−3 h range for monomer mixture **5a,b** to achieve the highest molecular weight PPQs.

The polymerization of **9a,b** was drastically different than **5a,b**. Under the same polymerization conditions as for **5a,b** the reaction mixture containing **9a,b** solidified before the 202 °C polymerization temperature was reached. This polymer exhibited an intrinsic viscosity

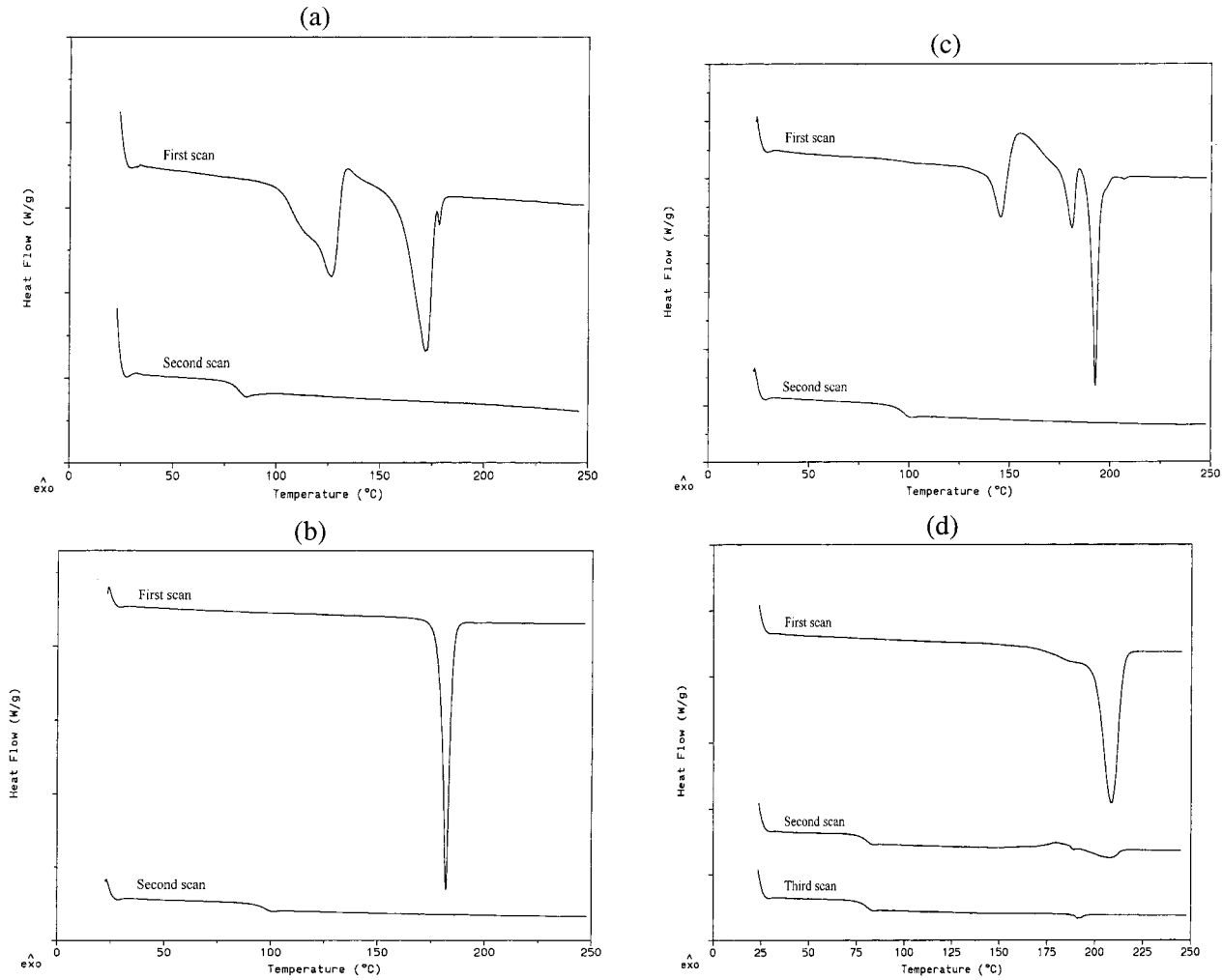
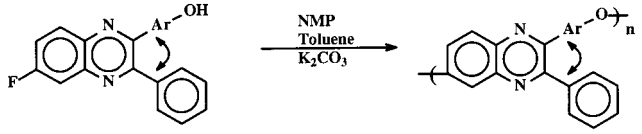


Figure 3. DSC thermograms of (a) **5a,b**; (b) **9a,b**; (c) **12a,b**; and (d) **17a,b**.

Scheme 5. Polymerization of PPQ Monomers



of 2.46 dL/g. In an attempt to keep the polymer in solution for a longer time, the polymerization conditions were altered. After removal of toluene from the system, the polymerization was carried out at about 170 °C. After approximately 4 h the reaction mixture solidified due to high molecular weight polymer formation. The polymer exhibited an intrinsic viscosity of 2.51 dL/g. A decrease in the solids content from 25% (w/v) to 10% (w/v) kept the polymer in solution during the polymerization; however, a PPQ with an intrinsic viscosity of only 1.00 dL/g was achieved.

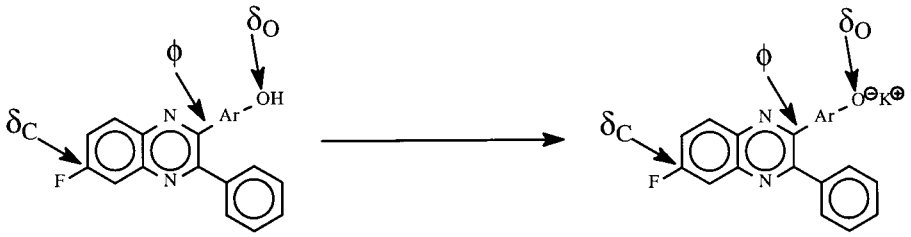
Polymerization of **12a,b** was carried out following the procedure for **9a,b** at 170 °C after removal of toluene for about 5 h. No solidification of the polymer mixture occurred in this reaction. A polymer with an intrinsic viscosity of 1.29 dL/g resulted. Next, the polymerization of **12a,b** was carried out at 202 °C for 1 h after removal of toluene to yield a polymer with an intrinsic viscosity of 1.97 dL/g. No solidification was observed in the polymerization of **12a,b**.

Polymerization of monomer **17a,b** was carried out similar to that of **5a,b** with the exception that the polymerization time was kept below 1 h. A drastic increase in viscosity occurs when approaching 202 °C. At reaction times longer than 1 h the solution starts to lose viscosity and turns black. When kept below 1 h, intrinsic viscosities of 1.41 dL/g can be reached. However, at longer polymerization times (2.5 h), the intrinsic viscosity drops to 0.54 dL/g. It is believed that the decrease in intrinsic viscosity can be attributed to transetherification reactions due to the high nucleophilicity of the 4,4′-phenoxyphenolate group.

Polymer Degradation Studies. To test whether potassium fluoride or potassium carbonate was a cause of polymer degradation during polymerization, the polymer from **5a,b** was dissolved in NMP, and then an equal mass of potassium carbonate or potassium fluoride was added. The mixture was stirred under reflux for 1 h. The initial polymer had an intrinsic viscosity of 1.00 dL/g. After degradation with potassium fluoride the intrinsic viscosity dropped to 0.80 dL/g. Degradation with potassium carbonate led to a more drastic decrease in intrinsic viscosity, dropping to 0.46 dL/g. On the basis of the larger drop in the intrinsic viscosity of **5a,b** when in the presence of potassium carbonate as compared to potassium fluoride, it appears that potassium carbonate plays a more important role than potassium fluoride in the decrease of the intrinsic viscosity as the polymerization time increases.

Correlation of Electron Densities with ^{19}F NMR Shifts. To correlate the observed polymerization rates

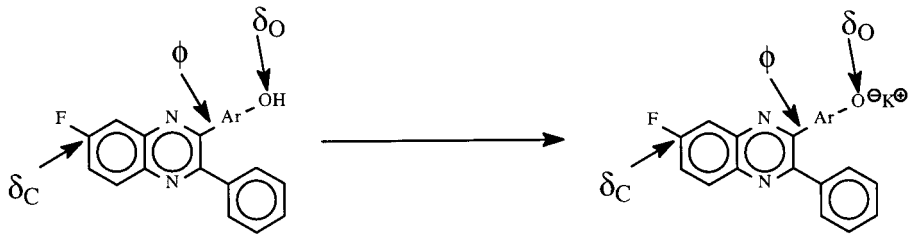
Table 1. ^{19}F NMR Chemical Shifts, Electron Densities, and Dihedral Angles for Isomer 1



	monomer isomer 1				monomer isomer 1-phenoxide salt			
Ar	δ_c[a]	δ_O[a]	ϕ (deg)[b]	δ (ppm)[c]	δ_c[a]	δ_O[a]	ϕ (deg)[b]	δ (ppm)[c]
1,4-phenylene	0.095	−0.043	−51.7	−109.50	0.029	−0.483	−30.6	−112.90
2,6-naphthylene	0.096	−0.044	−68.4	−108.96	0.054	−0.485	−43.1	−110.60
4,4′-biphenylene	0.096	−0.045	−55.7	−108.72	0.068	−0.490	−45.4	−109.50
4,4′-oxydiphenylene	0.095	−0.302	−52.1	−108.93	0.077	−0.515	−52.7	−109.32

[a] Electron density. [b] Dihedral angle. [c] ^{19}F NMR chemical shift relative to $CFCl_3$.

Table 2. ^{19}F NMR Chemical Shifts, Electron Densities, and Dihedral Angles for Isomer 2



	monomer isomer 2				monomer isomer 2-phenoxide salt			
Ar	δ_c[a]	δ_O[a]	ϕ (deg)[b]	δ (ppm)[c]	δ_c[a]	δ_O[a]	ϕ (deg)[b]	δ (ppm)[c]
1,4-phenylene	0.097	−0.043	−51.2	−109.00	0.080	−0.481	−29.8	−110.60
2,6-naphthylene	0.095	−0.044	−70.3	−108.72	0.078	−0.484	−42.3	−109.50
4,4′-biphenylene	0.096	−0.045	−55.4	−108.66	0.080	−0.490	−47.3	−109.00
4,4′-oxydiphenylene	0.096	−0.302	−51.8	−108.74	0.082	−0.515	−52.4	−109.02

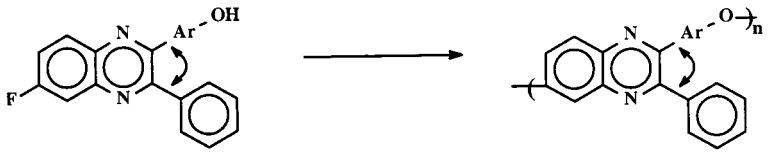
[a] Electron density. [b] Dihedral angle. [c] ^{19}F NMR chemical shift relative to $CFCl_3$.

and ^{19}F NMR data with monomer electronic structure, we decided to examine the electron densities at the C−F carbons in both the neutral and salt forms of the monomers. These molecules were optimized with Gaussian94[15] at the semiempirical (AM1) level,[25] followed by single-point calculations with the 3-21g* basis set using Becke's three-parameter hybrid method of the Lee−Yang−Parr correlation function,[26,27] denoted as B3LYP/3-21G(d)//AM1. Vibrational analyses were performed at the AM1 level for all structures indicating energetic minima for each geometry. Mullikin population analysis of the phenoxide salts at both the AM1 and B3LYP/3-21g* levels reveals a linear correlation between the electron density at the C−F carbon and the ^{19}F NMR shift (Tables 1 and 2). As expected, the largest amount of electron density is observed when the aryl group is 1,4-phenylene and decreases with decreasing conjugation of the aryloxy group with the quinoxaline ring. Analysis of the parent phenols did not yield a clean correlation of ^{19}F NMR shift to Mullikin population using the AM1 method. Calculations with the B3LYP functional did lead to a better correlation, but only when the oxydiphenylene derivative is excluded from the analysis. We speculate that only a weak interaction between the aryl alcohol group and the C−F carbon exists and does not show up in the computational data. The lack of a substantial shift in the fluorine chemical shift data supports this speculation. The better correlation of the experimental data with the B3LYP/3-21G(d)//AM1 calculations is not surprising. Density functional calculations have been demonstrated to give superior results in terms of both geometries and energies relative to semiempirical and Hartree−Fock calculations and indeed are often more accurate than calculations at the Møller−Plesset level at a fraction of the computational time.[28]

Carter[29] studied the S_NAr polymerizations of a series of fluorine-containing monomers and correlated their reactivities with their ^{19}F NMR shifts. Monomers with ^{19}F NMR chemical shifts below −110 ppm needed high temperatures and long reaction times to yield high molecular weight polymers due to their limited reactivity. From Tables 1 and 2, it would appear that the monomers would readily undergo S_NAr reactions because the ^{19}F NMR chemical shifts are downfield from −110 ppm. However, these monomers are not in their phenolic form during polymerization, but rather in the form of their phenoxide salt. Thus, the monomers were converted to their potassium phenoxide salts, which were analyzed with ^{19}F NMR.

As can be seen from Tables 1 and 2, the chemical shifts changed when the monomers were converted to their potassium phenoxide salts. On the basis of the work of Carter, which states that monomers with chemical shifts upfield from −110 ppm require long polymerization times and high temperatures to achieve high molecular weights, while those downfield do not require these conditions to achieve high molecular weight polymers, the phenoxide salts of the monomers in this research were compared to these data. The upfield shifts of the phenoxide salts from their monomeric forms indicate that the salts are less reactive than

Table 3. Intrinsic Viscosities and Thermal Properties of PPQs



monomer	polymer	Ar	$[\eta]$ (dL/g)[a]	T_g (°C)[b]	T_d (°C), air[c]	T_d (°C), N_2[c]
5a,b	**18**	1,4-phenylene	1.64	251	514	542
9a,b	**19**	2,6-naphthylene	2.51	278	497	552
12a,b	**20**	4,4′-biphenylene	1.97	287	520	530
17a,b	**21**	4,4′-oxydiphenylene	1.41	206	491	535

[a] Intrinsic viscosity determined in *m*-cresol at 30.0 ± 0.1 °C. [b] Determined by DSC with a heating rate of 10 °C/min. [c] Temperature at which polymer underwent a 5% weight loss when subjected to TGA with a heating rate of 10 °C/min.

when they are in their phenolic form. This is due to the fact that the lone pair electrons from the phenoxide shield the C−F site to a greater extent than when the monomers are in the phenolic state.

It can be seen when comparing Tables 1 and 2 that there is less of a ^{19}F NMR chemical shift when going from the monomer form to the phenoxide salt in isomer 2 (Table 2) than in isomer 1 (Table 1). This is due to the fact that in isomer 2 the lone pair electrons of the oxygen cannot reach the C−F carbon site. In isomer 1, however, the lone pair electrons of the oxygen can reach the C−F carbon. Therefore, one would expect that isomer 2 of each of the monomers in this research to have a similar reactivity. The limitation in the reactivity of the monomers seems to be due to isomer 1, which shows a greater change in ^{19}F NMR chemical shifts, as well as in electron density at the C−F carbon (δ_C).

The electron density calculations of the C−F carbon predicted that the reactivity of the phenoxide salts would be less toward S_NAr reactions than their respective phenolic form. The ^{19}F NMR chemical shifts also supports the electron density calculations for the phenoxide salts. Both the electron density calculations and the ^{19}F NMR chemical shifts were supported in the laboratory through the relative ease of polymerizability of monomers **9a,b**, **12a,b**, and **17a,b** relative to **5a,b**. From these data it is believed that ^{19}F NMR and electron density calculations can be effective tools for predicting relative ease of polymerizability of existing and potential monomers. However, instead of relating ^{19}F NMR chemical shifts of fluorine-containing phenolic monomers vs reactivity in aromatic nucleophilic substitution polymerization reactions, a more reliable approach would be to relate the ^{19}F NMR chemical shifts of the phenoxide salts vs reactivity.

Thermal Properties of PPQs. The T_g's of polymers are strongly affected by the structure of the polymer backbone. It was believed that the introduction of the 2,6-naphthylene and 4,4′-biphenylene groups into the PPQ backbone would increase the T_g and introduction of the 4,4′-oxydiphenylene group would decrease the T_g relative to **18** (Table 3). As noted previously,[11,12] as well as in this research, the T_g of **18** is 251 °C. Analysis of PPQ **19** showed a T_g of 278 °C. PPQ **20** displayed a T_g of 287 °C. The T_g of PPQ **21** (206 °C) is approximately 45 °C below the T_g of **18**, which is expected due to the greater flexibility of the 4,4′-oxydiphenylene substituent compared to the 1,4-phenylene substituent.

Thermogravimetric analysis of the PPQs obtained from the self-polymerizable monomers in this study revealed that all had nearly equal polymer decomposition temperatures. All three PPQs have 5% weight losses in the 500 °C range in nitrogen as well as in air.

Table 4. Tensile Properties of PPQs

polymer	$[\eta]$ (dL/g)[a]	σ (MPa)[b]	E (GPa)[b]	ϵ (%)[b]
18	1.64	109	3.7	93
19	2.51	104	2.6	88
20	1.97	95	3.0	93
21	1.41	92	3.3	100

[a] Intrinsic viscosity determined in *m*-cresol at 30.0 ± 0.1 °C. [b] Tensile properties obtained on a thin film with a crosshead speed of 1 mm/min according to ASTM D638.

The increased T_g's of PPQs **19** and **20**, the similar decomposition temperatures relative to **18**, and the increased reactivity of monomers **9a,b** and **12a,b** relative to **5a,b** show that the self-polymerizable quinoxaline monomers containing the 2,6-naphthylene group and the 4,4′-biphenylene groups offer many advantages relative to the 1,4-phenylene group.

Tensile Properties of PPQs. PPQs typically exhibit high tensile properties.[30] PPQ **18** has been shown to have a tensile modulus of 3.18 GPa, a tensile strength of 107 MPa, and an elongation of 3.8%.[11] The low elongation of this polymer was surprising since typical poly(arylene ether)s display higher elongations.

Reevaluation of **18** revealed similar tensile properties (Table 4) to that previously reported; however, the elongation was much higher. The 93% elongation exhibited by this PPQ is atypically high among all PPQs, even PPQs that contain arylene ether linkages.

The tensile properties of PPQs obtained from monomers **9a,b, 12a,b,** and **17a,b** were also determined. In all these cases the tensile moduli and tensile strengths were lower than for **5a,b**. Additionally, the PPQs exhibited high elongations (~90%). It is the combination of excellent tensile properties along with high T_g's that makes the PPQs obtained in this research very attractive for high-temperature and high-performance applications.

Conclusions

Three new self-polymerizable quinoxaline monomers were synthesized and polymerized to high intrinsic viscosity PPQs. Monomer mixture **9a,b** polymerized rapidly under relatively mild polymerization conditions in NMP. It is believed that the 2,6-naphthylene group has a larger dihedral angle than the 1,4-phenylene group, thereby allowing less charge delocalization into the pyrazine ring, resulting in a more reactive monomer mixture than **5a,b**. Monomer mixture **12a,b** also polymerized faster than **5a,b**. Monomer mixture **17a,b** polymerized rapidly as well but also depolymerized rapidly. It is postulated that addition of other extended aromatic ring systems will also increase the reactivity

of the self-polymerizable quinoxaline monomers relative to **5a,b**.

Characterization of the PPQs revealed that the T_g's increased as the rigidity of the substituent between the pyrazine ring and the phenolic substituent of the monomer increased. All of the PPQs displayed similar 5% polymer decomposition temperatures above 500 °C in both nitrogen and air. All of the PPQs had high tensile properties comparable to those of many high-performance thermoplastics.

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References and Notes

(1) Hergenrother, P. M.; Levine, H. H. *J. Polym. Sci., Part A-1* **1967**, *5*, 1453.
(2) Wrasidlo, W.; Augl, J. M. *J. Polym. Sci., Part A-1* **1969**, *7*, 3393.
(3) Wrasidlo, W. *J. Polym. Sci., Part A-1* **1970**, *8*, 1107.
(4) Fang, T. *Macromolecules* **1991**, *24*, 444.
(5) Korleski, J. E.; Harris, F. W. *Polym. Mater. Sci. Eng. Prepr.* **1989**, *6*, 870.
(6) Hedrick, J. L.; Labadie, J. W. *Macromolecules* **1988**, *21*, 1883.
(7) Hedrick, J. L.; Labadie, J. W. *Macromolecules* **1990**, *23*, 1561.
(8) Hedrick, J. L.; Labadie, J. W.; Matray, T.; Carter, K. *Macromolecules* **1993**, *26*, 4833.
(9) Connell, J. W.; Hergenrother, P. M. *Polym. Prepr.* **1988**, *29* (1), 172.
(10) Connell, J. W.; Hergenrother, P. M. *Polymer* **1992**, *33*, 3739.
(11) Korleski, J. E. Ph.D. Dissertation, The University of Akron, 1991.
(12) Kim, B. S. Ph.D. Dissertation, The University of Akron, 1993.
(13) Buu-Hoi; Hoan; Jacquignon *Recl. Trav. Chim. Pays-Bas* **1949**, *781*, 788.
(14) Lalezari, I. *J. Med. Chem.* **1971**, *14*, 1138.
(15) Gaussian 94, Revision E.2: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.
(16) Imaki, K.; Okada, T.; Nakayama, Y.; Nagao, Y.; Kobayashi, K. *Bioorg. Med. Chem.* **1996**, *12* (4), 2115.
(17) Arnold, R. T.; Fuson, R. C. *J. Am. Chem. Soc.* **1936**, *58*, 1295.
(18) Gorvin, J. H. *Nature (London)* **1948**, *161*, 208.
(19) Suschitzky, H. *J. Chem. Soc.* **1953**, 3042.
(20) Giordano, C.; Villa, M. *Synth. Commun.* **1990**, *20* (3), 383.
(21) Baek, J. B. Ph.D. Dissertation, The University of Akron, 1998.
(22) Labadie, J. W.; Hedrick, J. L.; Boyer, S. K. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 519.
(23) Klein, D. J. Unpublished results.
(24) Attwood, T. E.; Newton, A. B.; Rose, J. B. *Br. Polym. J.* **1972**, *4*, 391.
(25) Dewar, M. J. S.; Reynolds, C. H. *J. Comput. Chem.* **1986**, *2*, 140.
(26) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(27) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(28) Frisch, M. J.; Trucks, G. W.; Cheeseman, J. R. *Theor. Comput. Chem.* **1996**, *4*, 679.
(29) Carter, K. *Macromolecules* **1995**, *28*, 6462.
(30) Connell, J. W.; Hergenrother, J. W. In *International Encyclopedia of Composites*; Lee, S. M., Ed.; VCH Publishers: New York, 1991; Vol. 4, p 334.

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