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Poly(aryl ether–phenylquinoxalines)

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ABSTRACT: A general method for the preparation of poly(aryl ether–phenylquinoxalines) has been developed in which the generation of the aryl ether linkage is the polymer-forming reaction. We found that the electron-deficient pyrazine component of the quinoxaline ring system activated the 6- or 7-fluoro substituent toward nucleophilic aromatic substitution. Facile displacement occurred at these positions since the pyrazine ring can stabilize the negative charge developed in the transition state through a Meisenheimer-like complex, analogous to conventional activating groups (e.g. sulfone, carbonyl). Fluoro-substituted bisquinoxalines, 1,4- and 1,3-bis(6-fluoro-3-phenyl-2-quinoxalinyl)benzene, were prepared and subjected to fluoro displacement with various bisphenoxides in *N*-methyl-2-pyrrolidone (NMP). High molecular weight polymers were obtained, with T_g's ranging from 230 to 315 °C. The thermal stability for the resulting materials was comparable to other poly(phenylquinoxalines) with polymer decomposition temperatures in the 480–500 °C range. This synthetic route affords the poly(phenylquinoxaline) analogue of poly(ether–imide) and the polymers show many of the same desirable characteristics (e.g. processing and ductile mechanical properties).

Introduction

Poly(phenylquinoxalines), PPQs, have recently achieved commercial status since their first reports by Hergenrother and co-workers[1] in the late sixties. These materials have many desirable properties including excellent thermooxidative and hydrolytic stability, low dielectric constant, high T_g, good dimensional stability over a wide temperature range, and good mechanical properties.[2] PPQs are generally synthesized by the polycondensation of an aromatic bis(*o*-diamine) with a bis(phenyl-α-dicarbonyl) compound either in *m*-cresol at elevated temperatures or in a *m*-cresol/xylene solvent mixture at ambient temperatures.[3,4] The polymer generated in the synthesis is a fully cyclized structure and requires no further curing. Both homopolymers and statistically random copolymers have been prepared, with T_g's ranging from 284 to 420 °C depending on the polymer structure. Due to the nonselectivity of the quinoxaline ring formation in the polymer synthesis, several constitutional isomers are generated in the polymer backbone. This significantly influences the solubility characteristics, as well as disrupts the chain packing, preventing an ordered morphology. Although PPQs are soluble in selected chlorinated solvents and *m*-cresol, the toxicity of these solvents limits the use of PPQs in many applications.

We are very interested in aryl ether containing PPQs since these materials generally show better solution and melt processing characteristics, as well as improved toughness. Ether linkages are usually introduced into the PPQ backbone by using bis(phenyl-α-dicarbonyl) monomers containing aryl ethers linkages. These monomers can be prepared by a Friedel–Crafts[5a] route or by nucleophilic aromatic nitro displacement.[5b] The nitro displacement method offers the possibility of preparing monomers with greater structural variety; however, many of these monomers are low melting solids or oils and appear difficult to purify as evidenced by the low intrinsic viscosities of the resulting polymers. An alternative approach utilizes nucleophilic aromatic substitution in which generation of the aryl ether linkage is the polymer-forming reaction. Connell et al.[6] have polymerized bisphenols containing a preformed quinoxaline ring with conventional activated dihalides (e.g. 4,4′-difluorodiphenyl sulfone, 4,4′-difluorobenzophenone, etc.). High molecular weight poly(aryl ether–phenylquinoxalines) are readily synthesized in a dimethylacetamide/*o*-dichlorobenzene solvent mixture in the presence of potassium carbonate.

We recently reported[7] the synthesis of poly(aryl ether–phenylquinoxalines) by a fluoro-displacement polymerization of appropriately substituted fluorophenylquinoxaline monomers with bisphenols, somewhat analogous to poly(ether–imide) synthesis.[8] Facile displacement of aryl fluorides activated by the phenylquinoxaline ring system was demonstrated and polymerization of fluoro-substituted bis(phenylquinoxalines) with bisphenols

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yielded high polymer in the presence of potassium carbonate. Interestingly, these poly(aryl ether–phenylquinoxalines) were soluble in *N*-methyl-2-pyrrolidone (NMP), an important consideration for possible microelectronics applications. One advantage of the quinoxaline activated fluoro-displacement polymerization is the incorporation of greater structural variety in the polymer. In this paper we will describe our further work on poly(aryl ether–phenylquinoxalines), including details regarding the displacement reaction and the scope of the polymerization as well as the results from our evaluation of the thermal and mechanical properties of these materials.

Experimental Section

Materials. NMP was vacuum distilled from P_2O_5, and toluene was used without further purification. 1,2-Diamino-4-chlorobenzene (ICN Inc.) and 1,2-diamino-4-nitrobenzene (Aldrich) were used without further purification. 1,2-Diamino-4-fluorobenzene (4-fluoro-*o*-phenylenediamine; ICN Inc.) was purified by sublimation on a small scale or recrystallized from deoxygenated water for larger quantities. *m*-Cresol and *tert*-butylphenol were obtained from Aldrich and used as received. High purity 1,4-bis(phenylglyoxalyl)benzene (IFP Enterprises) and 1,3-bis(phenylglyoxalyl)benzene (ICN Inc.) were used as received.

2,3-Diphenyl-6-fluoroquinoxaline (1). A round bottom flask equipped with a condenser was charged with 1.2374 g (0.0098 mol) of 1,2-diamino-4-fluorobenzene (1.0049 g, 0.0047 mol) of benzil and 35 mL of chloroform. Note the diamine was used in excess. A nitrogen blanket was maintained during the course of the reaction so as to minimize the oxidation of the aromatic amine. The reaction was heated to approximately 50 °C followed by the addition of 1 mL of the catalyst (trifluoroacetic acid) and allowed to proceed for 24 h. Upon completion of the quinoxaline formation, the reaction was diluted with an additional 100 mL of chloroform and rinsed three times with dilute aqueous HCl to remove excess amine. The solution was dried (magnesium sulfate), filtered, and concentrated leaving the product (~90% yield). The crude product was recrystallized (ethyl acetate/hexane) to afford **1** as a white crystalline solid: mp 134–135 °C; ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 6 H), 7.45 (m, 5 H), 7.75 (m, 1 H), 8.1 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 112.4, 112.8, 128.3, 129.0, 129.8, 131.1, 131.3, 138.7, 138.8, 152.8, 154.2, 160.83, 164.8. Anal. Calcd for $C_{20}H_{13}N_2F$: C, 79.98, H, 4.36; N, 9.33. Found: C, 79.87; H, 4.50; N, 9.31.

2,3-Diphenyl-6-chloroquinoxaline (2). Compound **2** was prepared by the procedure described for **1** by using 6.883 g (0.048 25 mol) of 1,2-diamino-4-chlorobenzene and 8.000 g (0.0386 mol) of benzil in the presence of trifluoroacetic acid catalyst (1 mL) in a chloroform/THF (50/50) solvent mixture. The product was isolated in high yield (~90%) and purified by recrystallization (chloroform) to afford **2** as a yellow crystalline solid: mp 122–123 °C; ^{1}H NMR (DMSO-d_6) δ 7.4 (m, 6 H), 7.5 (m, 4 H), 7.9 (m, 1 H), 8.2 (m, 2 H). Anal. Calcd for $C_{20}H_{13}N_2Cl$: C, 75.83; H, 4.14; N, 8.85. Found: C, 75.80; H, 4.19; N, 8.72.

2,3-Diphenyl-6-nitroquinoxaline (3). Compound **3** was prepared by an analogous procedure described for **1** using 5.000 g (0.032 65 mol) of 1,2-diamino-4-nitrobenzene and 6.7953 g (0.032 32 mol) of benzil in the presence of trifluoroacetic acid (1 mL) in chloroform. The product was isolated in high yield and recrystallized (ethyl acetate/hexane) to afford **3** as a crystalline solid, mp 193–195 °C. Anal. Calcd for $C_{20}H_{13}N_3O_2$: C, 73.38; H, 4.00; N, 12.84. Found: C, 73.01; H, 4.04; N, 12.68.

2,3-Diphenyl-6-(3-methylphenoxy)quinoxaline (4). A three-neck 50-mL flask fitted with a nitrogen inlet and Dean-Stark trap was charged with 889 mg of 23.85% aqueous sodium hydroxide [212 mg (5.30 mmol) of NaOH], 5 mL of NMP, and 25 mL of toluene. The reaction mixture was heated to 130 °C to effect dehydration of the system by azeotropic distillation of toluene and water. Water collected in the Dean-Stark trap was removed, and fresh toluene was added as needed. After complete dehydration of the system, the reaction was cooled to ambient temperature and 1.50 g (5.00 mmol) of **1** was added, followed by 3 mL of NMP. The reaction was heated to 160 °C for 17 h, at which time HPLC analysis (85:15 acetonitrile/water, carbon-18 μ-bondapak column) showed complete conversion of **1** (retention time = 5.1 min) and the presence of a single product peak (retention time = 9.0 min). The reaction mixture was partitioned between ether and water and separated, and the aqueous layer was extracted with fresh ether. The combined ether layer was washed three times with water, dried ($MgSO_4$), and concentrated on a rotary evaporator. The crude product was purified by flash chromatography (5% ethyl acetate/hexane, silica gel) to afford 1.85 g (95%) of **4** as a white crystalline solid: mp 132–133 °C; ^{1}H NMR ($CDCl_3$) δ 2.4 (s, 3 H), 7.3–7.6 (m, 13 H), 8.2 (d, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.5, 112.5, 117.5, 121.0, 123.5, 125.6, 128.2, 128.4, 129.76, 130.6, 137.7, 139.1, 140.4, 141.8, 151.4, 153.8, 155.4, 159.8. Anal. Calcd for $C_{27}H_{20}N_2O$: C, 83.48; H, 5.19; N, 7.21. Found: C, 83.46; H, 5.34; N, 7.11.

2,3-Diphenyl-6-(4-*tert*-butylphenoxy)quinoxaline (5). Compound **5** was prepared by the procedure described for **4** using 1.29 mL of a 23.85 wt % sodium hydroxide solution [308 mg (7.70 mmol) of NaOH], 1.16 g (7.70 mmol) of 4-*tert*-butylphenol, and 2.10 g (7.00 mmol) of **1** in 9 mL of NMP. The product was purified by flash chromatography (10% ethyl acetate/hexane, silica gel) to afford 2.94 g (98%) of **5** as white crystals: mp 168–169 °C; ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 9 H), 7.2 (d, 2 H), 7.3–7.7 (m, 14 H), 8.25 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 31.5, 34.5, 112.0, 120.2, 123.5, 127.0, 128.2, 128.7, 129.7, 130.6, 137.9, 139.1, 142.3, 147.8, 151.6, 152.9, 153.7, 160.05. Anal. Calcd for $C_{30}H_{26}N_2O$: C, 83.69; H, 6.09; N, 6.51. Found: C, 83.77; H, 6.04; N, 6.21.

2,3-Diphenyl-6-(3-aminophenoxy)quinoxaline (6). Compound **6** was prepared by the procedure described for **4** using 890 mg of 23.85 wt % sodium hydroxide solution [212 mg (5.30 mmol) of NaOH], 580 mg (5.30 mmol) of 3-aminophenol, and 1.50 g (5.00 mmol) of **1** in 7 mL of NMP. The product was purified by flash chromatography (1% methanol/methylene chloride) to afford 1.90 g (97%) of **6** as an off-white solid: mp 184–185 °C; ^{1}H NMR (DMSO-d_6) δ 5.4 (s, 2 H, NH) 6.3–6.6 (m, 3 H), 7.1 (t, 1 H), 7.2–7.4 (m, 11 H), 7.6 (d, 1 H), 8.1 (d, 1 H); ^{13}C NMR (DMSO-d_6) δ 105.2, 107.0, 110.8, 112.5, 123.8, 128.2, 128.8, 129.8, 130.7, 137.3, 138.9, 141.7, 151.1, 151.5, 153.4, 156.4, 159.2. Anal. Calcd for $C_{26}H_{19}N_3O$: C, 80.18; H, 4.92; N, 10.74. Found: C, 80.19; H, 5.12; N, 10.61.

1,4-Bis[2-(3-phenyl-6-fluoroquinoxalinyl)]benzene (7). 1,2-Diaminofluorobenzene (13.6867 g, 0.10862 mol) and 17.6460 g (0.0519 mol) of 1,4-bis(phenylglyoxalyl)benzene were charged into a round-bottom flask equipped with a condenser and carefully washed down with chloroform (250 mL). A nitrogen blanket was maintained during the course of the reaction so as to minimize oxidation of the aromatic amine. The reaction was heated to approximately 50 °C followed by the addition of 1 mL of the catalyst (trifluoroacetic acid) and allowed to proceed for 24 h. Upon completion of the quinoxaline formation, the reaction was diluted with an additional 100 mL of chloroform and rinsed three times with dilute aqueous HCl to remove excess amine. The solution was dried (magnesium sulfate), filtered, and concentrated to give the crude product (~90% yield) which was recrystallized from ethyl acetate yielding a yellow crystalline solid: mp 236–239 °C; IR (KBr) 3086, 1562, 1495, 1244, 1019. Anal. Calcd for $C_{34}H_{20}N_4F_2$: C, 78.14; H, 3.85; N, 10.72. Found: C, 78.17; H, 3.78; N, 10.92.

1,3-Bis[2-(3-phenyl-6-fluoroquinoxalinyl)]. Compound **8** was prepared in an analogous fashion to **7** and purified by solvent-induced crystallization. Although the monomer was initially soluble in ethyl acetate, heating induced solvent crystallization producing **8** as yellow crystals: mp 165–170 °C; IR (KBr) 3061, 1541, 1445, 1241. Anal. Calcd for $C_{34}H_{20}N_4F_2$: C, 78.04; H, 3.85; N, 10.72. Found: C, 78.05; H, 3.75; N, 10.81.

Reaction of 5 and Sodium Cresolate (Ether Interchange). A solution of sodium cresolate was prepared by mixing 1.08 g of *m*-cresol (0.010 mol), 1.67 mL of 23.95% aqueous sodium hydroxide (0.0101 mol), and 5 mL of NMP in a 50-mL round-bottom flask fitted with a Dean-Stark trap. Toluene (30 mL) was added and the solution heated to reflux to remove the water as the toluene azeotrope. After dehydration, the toluene was removed through the Dean-Stark trap, and 861 mg (2.00

mol) of 5 in 2 mL NMP was added. The reaction mixture was heated to 170 °C, and aliquots were taken periodically, partitioned between ethyl acetate and water, and analyzed by HPLC (85:15 acetonitrile/water, 1 mL/min). The retention times of 4 and 5 were 9.1 and 13.6 min, respectively.

Bisphenols 9. 2,2′-Bis(4-hydroxyphenyl)propane (**9a**) was purchased from Aldrich and recrystallized from toluene. Bis[(4-hydroxyphenyl)-4-phenyl]methane (**9b**) (Applied Organic Silicones) was recrystallized from toluene. 2,2′-Bis(4-hydroxyphenyl)hexafluoropropane (**9c**) (Aldrich) and 4,4′-dihydroxybenzophenone (**9d**) (Aldrich) were purified by recrystallization from a toluene/ethyl acetate (95:15) mixture. 4,4′-Dihydroxydiphenyl sulfone (**9e**) (Aldrich) was used without purification. Resorcinol (**9f**) (Aldrich) was recrystallized from deoxygenated toluene. Hydroquinone (**9g**) (Aldrich) was recrystallized from deoxygenated acetone, and 9,9′-bis(4-hydroxyphenyl)fluorene (**9h**) was kindly supplied by P. M. Hergenrother (NASA Langley).

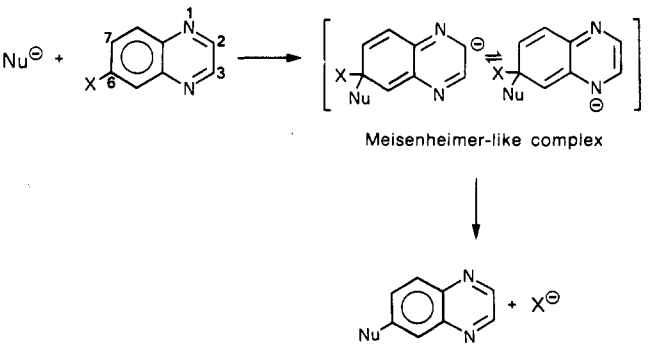
Polymer Synthesis. A typical synthesis of a poly(aryl ether–phenylquinoxaline) was conducted in a three-necked flask equipped with a nitrogen inlet, mechanical stirrer, and Dean-Stark trap and condenser. A detailed synthetic procedure designed to prepare a poly(aryl ether–phenylquinoxaline) based on **9c** is provided. The flask was charged with 3.5000 g (0.0104 mol) of 5.4391 g (0.0104 mol) of **7** and carefully washed in with 35 mL of NMP. Toluene (20 mL) was added, followed by 2.1568 g (0.0156 mol) of K_2CO_3. Note that K_2CO_3 was used in a 40–50% excess. The reaction mixture was then heated until the toluene began to reflux. An optimum reflux temperature range was achieved when the oil bath was maintained between 140 and 150 °C. Toluene was periodically removed from the Dean-Stark trap and replaced with deoxygenated dry toluene to ensure dehydration. The reaction mixture was maintained at 140 °C until the presence of water was no longer observed in the Dean-Stark trap, which may take 4–8 h. During this stage of the reaction the solution underwent several color changes. For example, during the initial formation of the phenoxide, a yellow-brown color was observed, and as the refluxing proceeded, the color changed to dark brown. Upon dehydration the temperature was slowly increased to 180 °C, and the toluene was removed through the Dean-Stark trap. However, the Dean-Stark trap was substantially full and a small amount of toluene was present in the reaction so as to ensure complete dehydration. The reaction mixture was heated to 180 °C for approximately 20 h. Completion or near completion was qualitatively estimated by the point where the viscosity increased dramatically. The reaction mixture was diluted with NMP and filtered hot to remove inorganic salts. The filtered solution was cooled, and several drops of weak acid (e.g., acetic acid) were added to neutralize phenoxide end groups. The polymer solution was then coagulated in about 10× volume of methanol and then boiled in water to remove any trapped salts. The polymer was then dried in a vacuum oven (80 °C) to a constant weight. The yield was essentially quantitative.

Characterization. Glass transition temperatures, taken as the midpoint of the change in slope of the baseline, were measured on a Du Pont DSC 1090 instrument with a heating rate of 10 °C/min. Films for thermal analysis were cast from NMP and heated to 325 °C (5 °C/min heating rate) and held for 30 min. Thermal gravimetric analysis (TGA) on the polymer films was conducted with a heating rate of 5 °C/min for the variable-temperature scans, and the isothermal scans were performed at 400 °C over an 8-h period. Intrinsic viscosity measurements were determined by using a Cannon-Ubbelohde dilution viscometer in NMP (25 °C). Mechanical property measurements on solution cast films were made on an Instron tensile tester at a strain rate of 10 mm/min. Dynamic mechanical behavior was assessed on a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) in the tension with a heating rate of 10 °C/min (10 Hz).

Results and Discussion

The synthesis of poly(aryl ethers) is based on the nucleophilic displacement of an aryl halide with a phenoxide in polar aprotic solvents. The aryl halide is activated by an electron-withdrawing group like carbonyl or sulfone.[9,10] In addition, these activating groups can accept a negative charge lowering the activation energy for the displacement through a Meisenheimer complex. The reaction we sought to use for the synthesis of poly(aryl ether–phenylquinoxalines) was the nucleophilic aromatic substitution of a halide from the 6- or 7-positions of a quinoxaline ring system with a phenoxide (Scheme I). The rationale for facile nucleophilic aromatic substitution from the benzo ring of a quinoxaline was 2-fold: (1) the electron-poor pyrazine ring would have the effect of an electron-withdrawing group; (2) due to resonance of the negative charge in the pyrazine ring, a Meisenheimer-like complex would form as a stabilized intermediate (and/or transition state) during the transformation (Scheme I). Presumably, the resonance stabilization of the negative charge will be greatest if the displacement occurs para to the pyrazine ring, (i.e. the 6- or 7-positions). The electronic effect of pyrazine on a quinoxaline ring system can be evaluated by ^1H NMR, as the deshielding of the protons ortho to a substituent is indicative of an electron-withdrawing group. Comparison of the ^1H NMR spectral assignments for 2,3-diphenyl-6-fluoroquinoxaline (**1**) with a conventional activated dihalide, 4,4′-difluorobenzophenone, shows the protons ortho to the pyrazine (H_a) have a chemical shift of δ 8.2, as compared to δ 7.9 for the protons ortho to the ketone in 4,4′-difluorobenzophenone (Figure 1). This demonstrates the electron-withdrawing affect of the pyrazine ring on the fused benzo ring in the ground state is comparable to a ketone and portends the likelihood of facile nucleophilic aromatic substitution at the 6- or 7-positions of a quinoxaline, as these positions are para to the pyrazine ring.

Scheme I



To demonstrate the feasibility of the quinoxaline activated aryl ether synthesis, the reaction of phenoxides with 1, 2,3-diphenyl-6-chloroquinoxaline (**2**), and 2,3-diphenyl-6-nitroquinoxaline (**3**), were investigated (Scheme II). An anhydrous solution of sodium cresolate in NMP was treated with **1** at room temperature and then heated to 160 °C. After 1 h, HPLC analysis showed quantitative conversion of **1** had occurred with the formation of a single product peak. The expected 2,3-diphenyl-6-(3-methylphenoxy)quinoxaline (**4**) was isolated as a single homogeneous product in high yield (95%) after flash chromatography (95:5 hexane/ethyl acetate, silica gel). Likewise, the reaction of **1** with the sodium salt of 4-*tert*-butylphenol or 3-aminophenol afforded the desired aryl ethers **5** and **6** in >95% yield. The analogous reaction of the chloro derivative **2** did not occur with complete conversion, even after extended heating at 180 °C. In the case of the nitro displacement, the reaction of **3** with sodium cresolate at 160 °C occurred with the formation of many products, possibly due to reaction of the nitrite ion generated in the displacement with the quinoxaline ring analogous to the side reactions observed in poly(ether–

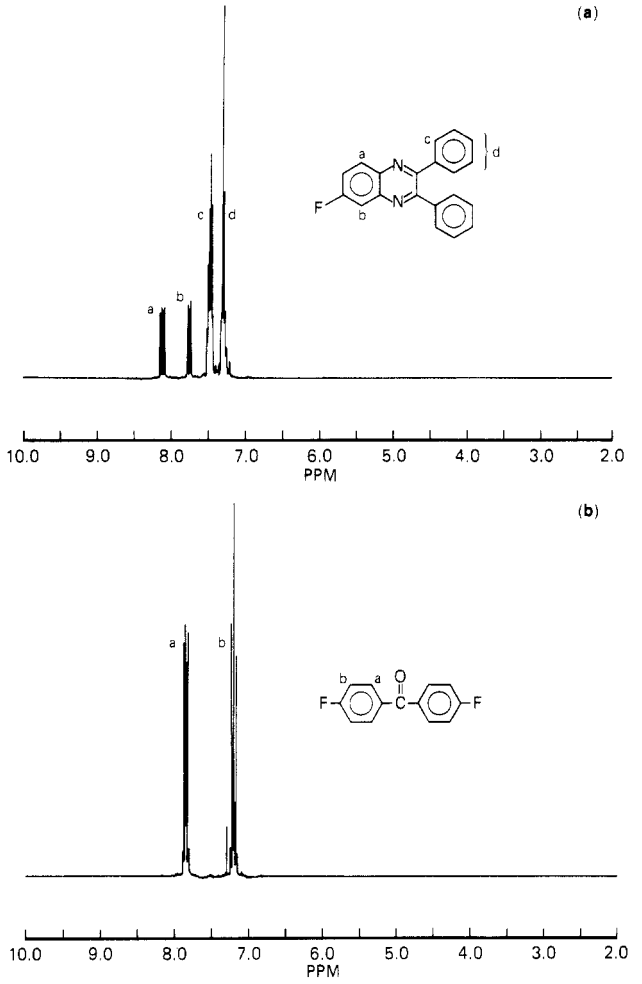
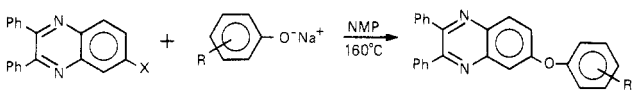


Figure 1. (a) ^{1}H NMR spectrum of 3,4′-diphenyl-6-fluoroquinoxaline. (b) ^{1}H NMR spectrum of 4,4′-difluorobenzophenone.

Scheme II



1 : X = F
2 : X = Cl
3 : X = NO_2

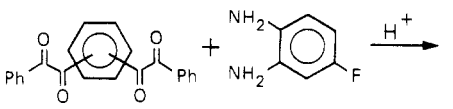
R = 3-Me
= 4-t-Bu
= 3-NH_2

4 : R = 3-Me
5 : = 4-t-Bu
6 : = 3-NH_2

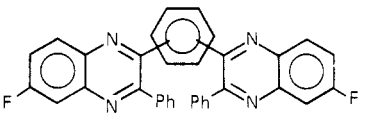
imide) synthesis. The model reactions demonstrated that the fluoro group at the 6-position of a quinoxaline is cleanly displaced by phenoxides, as a result of the activation by the adjacent pyrazine ring. Although facile halo displacement is known to occur with 2- and 3-haloquinoxalines[11] (i.e. positions adjacent to nitrogen), this represents the first example of nucleophilic aromatic substitution on the fused benzene ring in these systems. The high selectivity and yield observed for the fluoro displacement demonstrates that this transformation is a suitable polymer-forming reaction; however, the chloro and nitro displacements are not good reactions for polymer formation from the results of the model study.

The quinoxaline-activated poly(aryl ether) synthesis required the preparation of bis(6-fluoroquinoxalinyl) monomers. This involved the acid-catalyzed reaction of various bis(dicarbonyl) compounds with 1,2-diamino-4-fluorobenzene in refluxing chloroform (Scheme III). The structure of the monomer, and hence the polymer, may be varied by the choice of the bis(dicarbonyl) compound. The use of 1,4- or 1,3-bis(phenylglyoxal)benzene as the

Scheme III

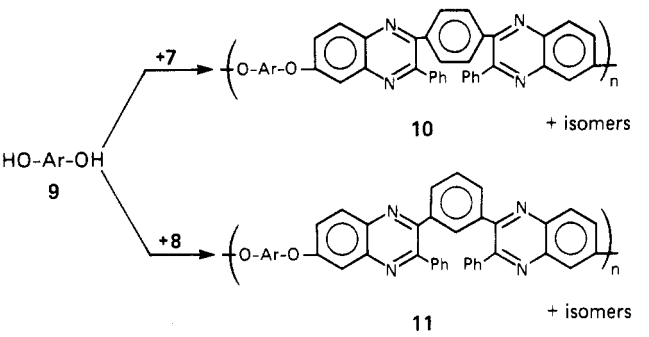


1,4 or 1,3



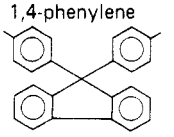
7 : 1,4-benzene + isomers
8 : 1,3-benzene + isomers

Scheme IV



Ar

9,10,11 a : -PhC$(CH_3)_2$Ph-
b : -PhC$(Ph)_2$Ph-
c : -PhC$(CF_3)_2$Ph-
d : -Ph CO Ph-
e : -PhSO_2Ph-
f : 1,3-phenylene
g : 1,4-phenylene
h :



bis(dicarbonyl) compounds afforded 1,4- and 1,3-bis[2-(3-phenyl-6-fluoroquinoxolinyl)]benzene (7 and 8), respectively. Both 7 and 8 were isolated in approximately 90% yield and recrystallized (ethyl acetate) to give polymer grade monomers. Due to the nonselectivity of the quinoxaline formation, three distinct isomers are possible for each of the bis(dicarbonyls) used, analogous to the multiple isomeric phenylquinoxaline moieties formed in PPQ synthesis.

Polymerization of 7 and 8 with various bisphenols was carried out in the presence of K_2CO_3 in an NMP/toluene (2/1) solvent mixture[12] (Scheme IV). As in the case for most polyether syntheses, the solids composition was maintained between 20 and 25 wt %. The water generated by bisphenoxide formation in the initial stages of the polymerizations was removed as an azeotrope with toluene. The reaction mixture was observed to reflux at the desired rate when the oil bath was maintained at 140–150 °C. Toluene was periodically removed through the Dean-Stark trap and replaced with fresh deoxygenated toluene. Upon completion of bisphenoxide formation and dehydration, the polymerization mixtures were heated to 180–190 °C to effect the displacement reaction. In

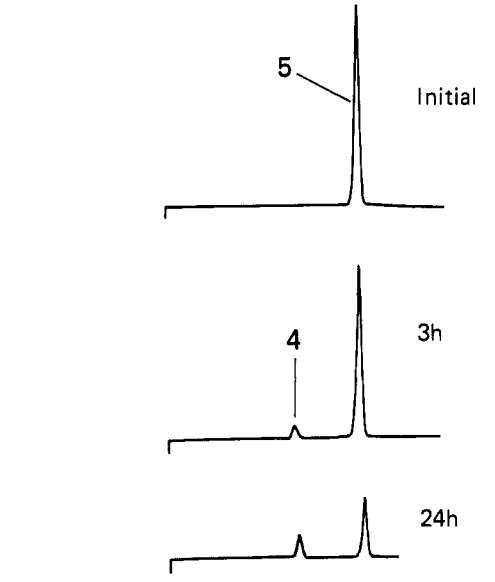
Table I
Characteristics of Poly(aryl ether–phenylquinoxalines)

polymer	[η]NMP, 25 °C dL/g	T_g, °C
10a	1.20	255
10b	1.45	270
10c	1.20	255
10d	0.70	252
10e	0.55	285
10f	0.50	250
10g	1.66	273
10h	1.10	315
11a	1.23	230
11b	0.65	250
11c	0.44	240

each case, high molecular polymer was attained within 24 h as judged by the dramatic increase in viscosity. The resulting mixtures were diluted, filtered, coagulated in excess methanol, washed with boiling water (to remove any remaining salts), and dried in a vacuum oven at 80 °C for 24 h.

This general procedure was applied to a number of bisphenols (**9a–h**) for each of the activated difluorides, **7** and **8**, yielding polymer series **10** and **11**, respectively (Scheme IV). High molecular weight polymer was achieved in each case as indicated by the intrinsic viscosity measurements (Table I). Polymerization of **7** with bisphenols **9a–d** and **9f** proceeded readily affording polymers **10a–d** and **10f**. Likewise, polymerization of **8** with bisphenols **9a–c** afforded high molecular weight polymers **11a–c** by this procedure. In contrast, polymers derived from **7** and bisphenols **9e–g** required modification of the polymerization conditions. For instance, polymer **10e** required longer reaction times since the nucleophilicity of **9e** is considerably weaker than other bisphenoxides since the sulfone moiety is strongly electron-withdrawing. In fact, high molecular weight polymer, as judged by the viscosity increase, was not obtained for 48 h, substantially longer than other fluoro-displacement polymerizations. Interestingly, long reaction times were not necessary for polymer **10d** derived from **9d** which has the electron-deficient ketone group. Polymerization with **9f** and **9g** were complicated by the sublimation of the bisphenols at temperatures required for dehydration. In these syntheses, the monomers K_2CO_3 and NMP were charged and heated to 85 °C with a nitrogen blanket in an effort to form the phenoxide salt which did not sublime. After 2–3 h at 85 °C, deoxygenated toluene was added to the reaction mixture. The reaction mixture was subsequently dehydrated and heated as described previously. In each case, **10f** and **10g**, high molecular weight polymer was achieved. In contrast to many PPQs, poly(aryl ether–phenylquinoxalines) prepared by the quinoxaline activated displacement were soluble in NMP, except polymer **10g**. This polymer was soluble at the polymerization temperature but only marginally soluble at room temperature. Solubility in NMP is important since it is frequently used for polymer processing in the microelectronics industry. In addition high molecular weight poly(aryl ether–phenylquinoxalines) were formed by using conventional polymerization conditions, whereas poly(ether–imide) synthesis requires milder conditions to avoid side reactions associated with the nitrite ion generated in the polymerization.

Poly(aryl ether) synthesis is often accompanied by an ether-interchange processes. Activated by para-electron-withdrawing substituents, aryl ether linkages are subject to nucleophilic attack, resulting in phenoxide interchange.[9,13] The ether exchange process is a major deterrent in preparing block, multiphase polyethers. Although



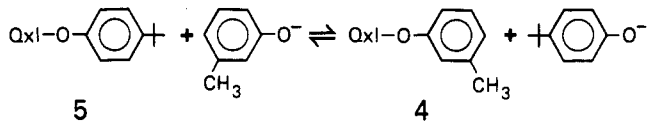
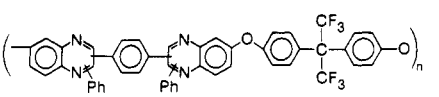


Figure 2. HPLC analysis of ether interchange product of sodium cresolate with 2,3-diphenyl-6-(4-*tert*-butylphenoxy)quinoxaline in NMP (160 °C).



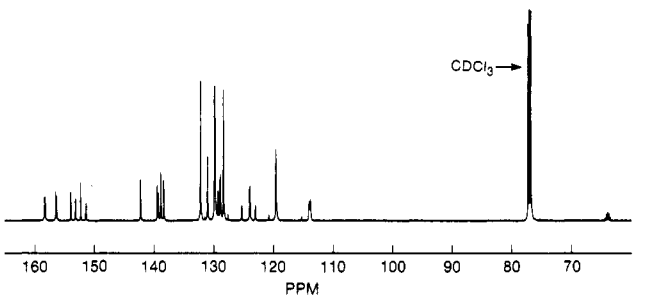


Figure 3. ^{13}C NMR spectrum of poly(aryl ether–phenylquinoxaline) based on **9c**.

this process occurs readily for conventional activating groups, we wanted to determine if poly(aryl ether–phenylquinoxalines) were susceptible to ether interchange. This process was examined by heating a sample of **5** with 5 equiv of sodium cresolate in NMP at 170 °C. The reaction was monitored by HPLC and the product analysis showed formation of **2** due to the exchange of the cresolate for the 4-(*tert*-butylphenoxide) (Figure 2). After 24 h approximately 30% of **5** had converted to **4**, demonstrating that poly(aryl ether–phenylquinoxalines) will undergo ether interchange like conventional poly(aryl ethers).

The structure of the polymers was confirmed by both ^{13}C NMR and FT-IR. Initially the ^{13}C NMR of **10c** was perplexing owing to the many peaks (Figure 3). The complexity observed in the ^{13}C NMR of **10c** was reflective of the constitutional isomers in the polymer. Future publications will include an extended analysis of this and related spectra. The FT-IR spectrum of the **10c** is shown in Figure 4, and the key characteristics bands are pointed out, including the aryl ether linkage that is generated in

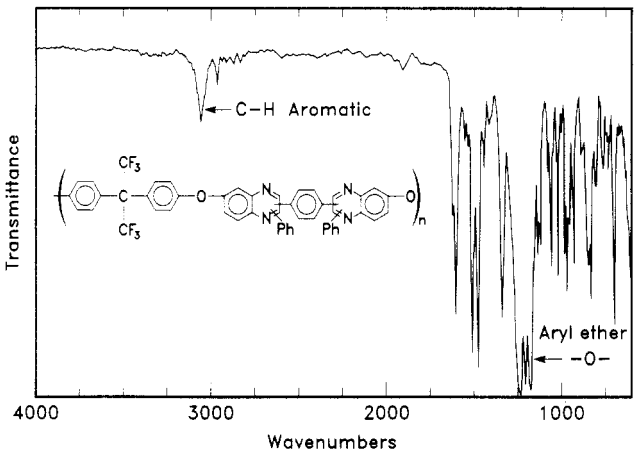


Figure 4. FT-IR spectrum of poly(aryl ether–phenylquinoxaline) based on **9c** .

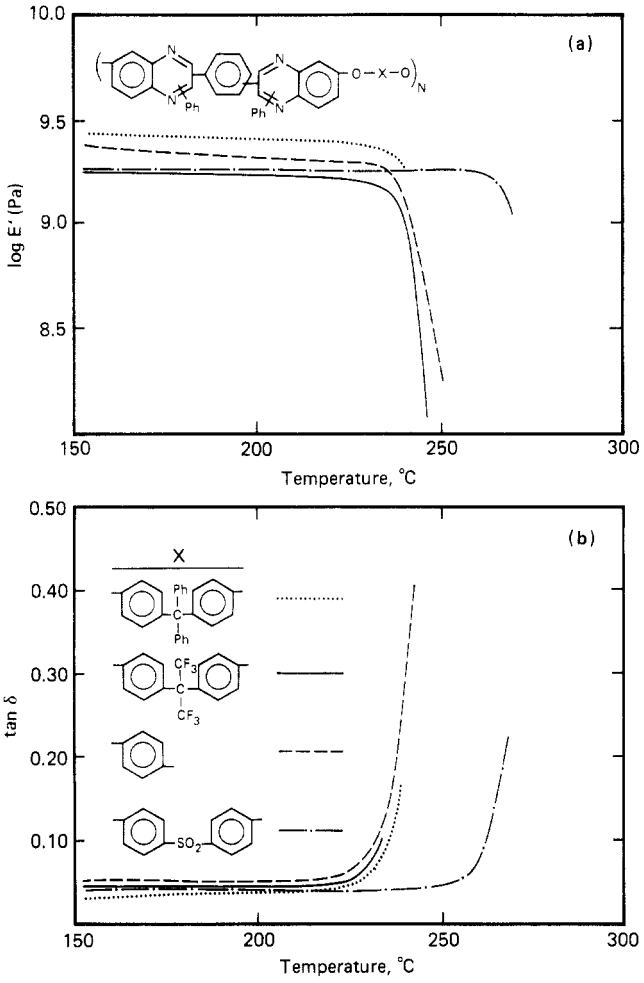


Figure 5. (a) Storage tensile modulus versus temperature. (b) tan δ versus temperature for various poly(aryl ether–phenylquinoxalines).

the polymer-forming reaction.

The T_g's ranged from 230 to 315 °C depending on the bisphenol and activated difluoride used in the polymer synthesis (Table I). Polymer series **10** showed the the highest T_g's, with **10c** and **10e** being somewhat higher than the polymers derived from the other bisphenols (Table I). Polymer series **11** had T_g's generally 20–30 °C lower than those of polymer series **10** with the same bisphenols. These data are consistent with the dynamic mechanical thermal analysis (Figure 5). The dynamic mechanical behavior for several of the copolymers is shown in

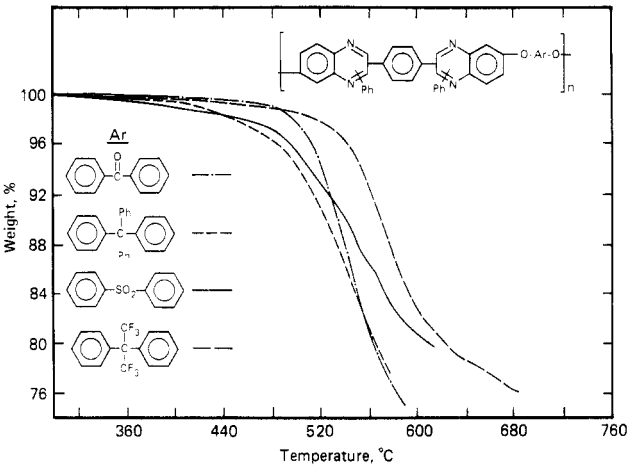


Figure 6. TGA thermograms (weight loss versus temperature) for various poly(aryl ether–phenylquinoxalines) prepared with different bisphenols.

Table II
Thermal Analysis of Poly(aryl ether–phenylquinoxalines)

polymer	wt loss on isothermal aging at 400 °C, wt %/h	polymer decomp temp, °C
10b	0.15	485
10c	0.05	500
10d	0.08	480
10e	0.13	470
10f	0.17	480

Figure 5. These data, consistent with the calorimetry results, clearly show the high T_g's and good dimensional stability exhibited by these materials. In contrast to many polyimides and other rigid-rod structures that do not show a T_g, the poly(aryl ether–phenylquinoxalines) all manifest a T_g, indicative of an amorphous or glassy morphology. The T_g's of these polymers are among the highest reported for poly(aryl ethers) prepared by nucleophilic aromatic substitution and are comparable to those reported by Connell et al.[6] on similar structures.

The poly(aryl ether–phenlquinoxalines) demonstrated excellent thermal stability with polymer decomposition temperatures in excess of 450 °C (Figure 6). The bisphenol from which the polymer was derived significantly influenced the thermal stability. Those structures based on **9c** and **9d** were among the most thermally stable polymers as judged by variable temperature TGA. Isothermal TGA (400 °C, under nitrogen atmosphere) was also used to assess the thermal stability of the polymers (Table II). The data, consistent with the variable-temperature TGA scans, demonstrate that the structures based on **9d** and **9e** are the most thermally stable and have comparable thermal stability to that of the aromatic polyimides.

The poly(aryl ether–phenylquinoxalines) behave in many respects as engineering thermoplastics with characteristics similar to those of polysulfone, poly(ether–imide), and others. In contrast to conventional PPQ, the poly(aryl ether–phenylquinoxalines) can be thermoformed via compression molding. Samples were molded at approximately 350 °C, about 50–100 °C above their T_g's. The good thermal stability allows for this high thermoplastic processing conditions in spite of their high T_g.

Unfortunately, the poly(aryl ether–phenylquinoxalines) were susceptible to environmental stress cracking.[14-16] This phenomenon occurs when a stressed polymer is exposed to solvents. Environmental stress cracking can render an otherwise strong material useless; therefore, many engineering thermoplastics have lim-

Table III
Mechanical Properties of
Poly(aryl ether–phenylquinoxalines)

polymer	modulus, MPa	yield stress, MPa	tensile stress, MPa	elongatn, %
10c	2300	85	80	23
10e	2800	100	108	13
10f	2400	87	82	50
11b	2350		90	4
11c	2400		90	5
PPQ	2700		128	10

ited utility in applications which require exposure to chemical environments. Poly(aryl ether–phenylquinoxalines) failed catastrophically under mild loads (even a fingernail crease) in the presence of acetone, chloroform, and 2-propanol. This may limit their utility in applications that require multiple solvent coatings or exposures.

The mechanical properties of the poly(aryl ether–phenylquinoxalines) varied substantially depending on chemical structure as well as the casting or curing temperature. Films of the polymers were cast from NMP and cured (5 °C/min) to either 275 or 350 °C for 30 min. Samples cured to 275 °C did not show the expected ductile mechanical behavior characteristic of many materials containing aryl ether linkages and were somewhat brittle with elongations under 5%. Crazing was observed prior to failure, which is often denoted as a precursor to brittle failure. In contrast, samples cured to 350 °C showed tough ductile mechanical properties as judged by higher elongations without evidence of crazing. We believe the NMP is bound to the polymer backbone, and the NMP may induce stress cracking as evidenced by the crazing and low elongations. Higher temperatures (350 °C) were required to remove the NMP. Similar effects are observed with PPQ cast from *m*-cresol.

Table III contains the mechanical properties of the poly(aryl ether–phenylquinoxalines) based on each of the activated difluorides with a number of bisphenols. Interestingly, the moduli and tensile strengths were in the 2500 and 80 MPa range which is comparable to that of PPQ. The polymers of series **10** showed the expected ductile mechanical properties with elongations ranging from 12 to 50% depending on the bisphenol used which is comparable to the poly(ether–imide) analogue. The poly(aryl ether–phenylquinoxalines) showed yield points with necking and drawing typical of many other ductile engineering thermoplastics; in contrast, PPQ shows only 11% elongation and no distinguishable yield point. Furthermore, many of the engineering polymers that show these ductile deformation processes have a major secondary relaxation (β transition) in the dynamic mechanical spectra.[17] Both the origin of the β relaxation as well as its effects on the ductile mechanical behavior remain controversial even though the phenomenon has been investigated by a variety of dynamic mechanical[17-19] and NMR techniques.[20] The poly(aryl ether–phenylquinoxalines) show a major secondary relaxation at −100 °C (110 Hz) (Figure 7) that is very similar to those observed for poly(aryl ether–sulfone) and related structures. In contrast, polymers **9a–c** were brittle with elongations below 5% which is characteristic of many structures composed of meta linkages. The moduli and tensile strengths were higher than those of the polymer series **10** (Table III).

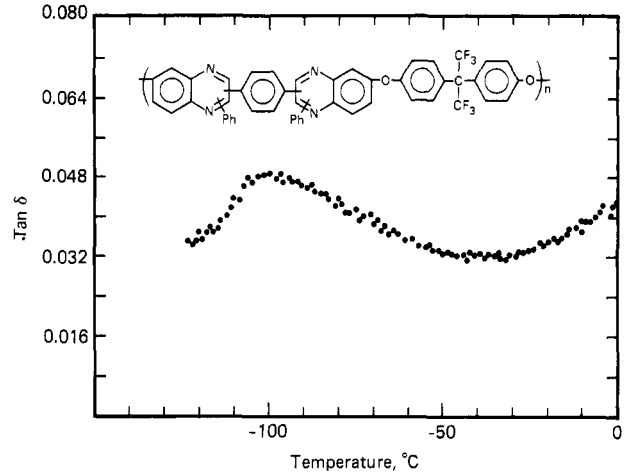


Figure 7. tan δ versus temperature for **10c**.

Summary

Poly(aryl ether–phenylquinoxalines) have been prepared by nucleophilic aromatic substitution generating aryl ether linkages as the polymer-forming reaction. We have demonstrated that the electron-deficient pyrazine component of the quinoxaline ring system activated the 6- and 7-fluoro substituents toward displacement by a variety of nucleophiles. Fluoro-substituted bisquinoxalines, 1,4-bis[2-(3-phenyl-6-fluoroquinoxalinyl)]benzene and related monomers, were prepared and subjected to fluoro displacement with various bisphenols in NMP in the presence of K_2CO_3. High molecular weight polymer was readily achieved, and structural variety could be introduced through the use of different bisquinoxalines and bisphenols. The polymers could be processed from NMP or from the melt (compression molding). T_g's ranging from 230 to 315 °C were observed depending on the monomers used in the synthesis, and the thermal stability was comparable to other PPQs with thermal decomposition temperatures in the 480–500 °C range. As expected, the incorporation of the aryl ether linkage induced ductile mechanical behavior with elongations ranging from 12 to 50%, and the structures showed a major secondary relaxation characteristic of many engineering thermoplastics. This represents one of the first examples of poly(aryl ether) synthesis based on aryl fluorides activated by an adjacent heterocyclic ring, and this synthesis can be considered the quinoxaline analogue of the poly(ether–imide) synthesis. Moreover, heterocyclic activated nucleophilic displacement chemistry should prove effective with monomers derived from other ring systems, providing a general synthetic methodology to high temperature, high T_g arylene ether–heterocyclic polymers.

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Registry No. **1**, 114583-79-8; **2**, 36305-60-9; **3**, 7466-45-7; **4**, 114583-80-1; **5**, 124942-74-1; **6**, 117684-98-7; **7**, 124921-91-1; **(7)(9c)** (copolymer), 124921-96-6; **(7)(9c)** (SRU), 114633-53-3; **8**, 124921-92-2; **10a** (copolymer), 124921-97-7; **10a** (SRU), 114633-54-4; **10b** (copolymer), 124921-98-8; **10b** (SRU), 118899-69-7; **10d** (copolymer), 124921-99-9; **10d** (SRU), 125048-58-0; **10e** (copolymer), 124922-00-5; **10e** (SRU), 118899-68-6; **10f** (copolymer), 124922-01-6; **10f** (SRU), 125048-56-8; **10g** (copolymer), 124922-02-7; **10g** (SRU), 125048-57-9; **10h** (copolymer), 124922-03-8; **10h** (SRU), 125048-61-5; **11a** (copolymer), 124922-04-9; **11a** (SRU), 125048-60-4; **11b** (copolymer), 124922-05-0; **11b** (SRU), 125048-62-6; **11c** (copolymer), 124922-06-1; **11c** (SRU), 125048-59-1; 1,2-diamino-4-fluorobenzene, 367-31-7; benzil, 134-81-6; 1,2-diamino-4-chlorobenzene, 95-83-0; 1,2-diamino-4-nitrobenzene, 99-56-9; toluene, 108-88-3; 4-*tert*-butylphenol, 98-54-4; 3-aminophenol, 591-27-5; 1,4-bis(phenylglyoxalyl)benzene, 3363-97-1; *m*-cresol, 108-39-4.

New Polymer Syntheses. 39. Thermotropic Copolyesters of 4-Hydroxybenzoic Acid and 3-Chloro-4-hydroxybenzoic Acid

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ABSTRACT: Numerous cocondensations of 3-chloro-4-acetoxybenzoic acid and 4-acetoxybenzoic acid were conducted at 320 °C in an inert reaction medium so that the molar ratio of the comonomers varied between 5:1 and 1:10. A second series of copolyesters with a molar composition near 1:1 was prepared under a variety of reaction conditions. All copolyesters prepared from acetoxybenzoic acids were crystalline, whereas those synthesized from (trimethylsiloxy)benzoyl chloride were mainly amorphous. DSC and WAXS measurements revealed that crystalline copolyesters rich in 4-hydroxybenzoic acid (4-Hybe) possess a first-order phase transition at temperatures between 200 and 340 °C, which represents a change from orthorhombic to pseudohexagonal chain packing. At compositions around 1:1, WAXS measurements conducted with synchrotron radiation indicate a melting process above 330 °C. Films can be pressed at 390 °C, and thermomechanical analyses yield heat distortion temperatures (HDT) in the range 290–320 °C for 1:1 copolyesters and HDTs around 390 °C for 1:4 copolyesters. The melting point rises with increasing fraction of 3-chloro-4-hydroxybenzoic acid (3-Cl-4-Hybe) up to temperatures above 400 °C. TGA measurements indicate thermostabilities (5% loss of weight measured in air) up to 500 °C.

Introduction

Poly(4-oxybenzoate), $(4\text{-Hybe})_n$, is an interesting thermostable engineering plastic.[1-12] Unfortunately, it is difficult to process, because its high crystallinity and high melting point (T_m) require temperatures around or above 450 °C, where thermal degradation competes with processing.[5,6] Incorporation of a comonomer may reduce the melting point and ease mechanical processing. Incorporation of a comonomer also influences the crystallinity and the first-order solid–solid phase transition which is typical for pure $(4\text{-Hybe})_n$. The present work, which is part of a systematic study of copolyesters of 4-Hybe, was aimed at studying the influence of 3-chloro-4-Hybe on the properties of 4-Hybe containing copolyesters. Chlorine is the smallest, thermostable and easily accessible substituent that may be introduced into poly(4-Hybe).

Experimental Section

Materials. 3-Chloro-4-hydroxybenzoic acid (Aldrich, St. Louis) and 4-hydroxybenzoic acid (gift of Bayer AG, D-4150 Krefeld) were acetylated with an excess of acetic anhydride in boiling toluene. They were recrystallized from toluene and dried over P_4O_{10}. The (trimethylsiloxy)benzoyl chlorides were prepared as described previously.[13] Marlotherm-S, a mixture of isomeric dibenzyl benzenes, was a gift of Chemische Werke Hüls (Marl, FRG).

Polycondensations. A. In Solution (Table I). A mixture of 3-chloro-4-acetoxybenzoic[14] acid and 4-acetoxybenzoic acid (100 mmol total) was suspended in 200 mL of Marlotherm-S and rapidly heated to 320 °C with stirring under a slow stream of nitrogen. When the elimination of acetic acid became vigorous (at ca. 240–260 °C), heating was stopped for approximately 15 min and then continued. After 16 h, the reaction miture was cooled and diluted with acetone. The crystallized polyester was isolated by filtration, extracted with hot acetone, and

0024-9297/90/2223-1568$02.50/0