Synthesis of poly(arylene ether)s containing quinoxaline units

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Poly(arylene ether)s containing quinoxaline units were prepared by the aromatic nucleophilic displacement reaction of novel bis(phenolquinoxaline) compounds with activated aromatic difluoro compounds. Polymers prepared from bis(phenolquinoxaline)s that had configurational isomers were amorphous with inherent viscosity (η_{inh}) from 0.34 to 1.30 dl g^{-1} and glass transition temperature (T_g) from 213 to 283°C. Several polymers prepared from bis(phenolquinoxaline)s that did not contain configurational isomers were semicrystalline with η_{inh} from 0.24 to 0.83 dl g^{-1}, T_gs from 179 to 240°C and T_ms from 365 to 388. The molecular weights of the semicrystalline polymers were limited by their solubility in the reaction media.

(Keywords: poly(arylene ether)s; polyquinoxaline; high temperature polymers; films)

INTRODUCTION

Polyquinoxalines (PQs) and polyphenylquinoxalines (PPQs) are conventionally prepared from the reaction of aromatic bis(1,2-diamines) and bis(1,2-dicarbonyl) compounds. Polyquinoxalines were first prepared in 1964[1,2]. The preparation of PPQs was first reported in 1967[3]. Quinoxaline polymers generally possess a favourable combination of properties such as good thermo-oxidative stability, relatively high glass transition temperature (T_g) and high mechanical properties. Review articles concerning the chemistry and the mechanical and physical properties of PQ and PPQ have been published[4–7].

As part of an effort on high-performance/high-temperature polymers for potential aerospace applications, poly(arylene ether)s containing various heterocyclic units are under investigation. The approach has involved the synthesis and purification of novel heterocyclic bisphenols, which are subsequently reacted with activated aromatic dihalides by using an alkali-metal base in a polar aprotic solvent at elevated temperatures under nitrogen. In order to prepare high molecular weight polymer the heterocyclic ring must survive the polymerization conditions and the polymer must remain soluble in the reaction media. Heterocyclic rings that have been incorporated into the backbone of poly(arylene ether)s by using this approach include imidazole[8–10], benzoxazole[11], benzimidazole[12], 1,3,4-oxadiazole[13], 1,2,4-triazole[13], pyrazole[14,15] and quinoxaline[16]. The incorporation of a heterocyclic ring into the backbone of a poly(arylene ether) can increase certain properties such as the T_g, strength and modulus. Also, this synthetic approach can offer certain advantages over the conventional syntheses of some polymers by avoiding the use of an expensive or toxic reactant.

Concurrent with our effort, a different synthetic approach to prepare poly(arylene ether)s containing phenylquinoxaline[17,18] and benzoxazole[19] units was under investigation. This approach involved reacting aromatic bisphenols with aromatic difluoro phenylquinoxaline and benzoxazole compounds. The heterocyclic ring activates the fluorine atom sufficiently to permit displacement by a bisphenate and accordingly the formation of high molecular weight polymer. These reactions were generally carried out by using potassium carbonate in polar aprotic media at elevated temperatures under nitrogen.

EXPERIMENTAL

Starting materials

4,4′-Difluorodiphenylsulphone (Aldrich Chemical Co.) was recrystallized from ethanol (m.p. 98–99°C). 4,4′-Difluorobenzophenone (Chemical Dynamics Corp.) was recrystallized from ethanol (m.p. 104–105°C). 1,3- and 1,4-Bis(4-fluorobenzoyl)benzene were prepared as previously described[20] (m.p. 178–179°C and 215–217°C, respectively). 3,3′,4,4′-Tetraaminobiphenyl (Acurex Corp.) and 3,3′,4,4′-tetraaminobenzophenone (Jackson and Burdick Chemical Co.) were recrystallized from deoxygenated water containing a small amount of sodium dithionite (m.p. 179–181°C and 215–217°C, respectively). 3,3′,4,4′-Tetraaminodiphenyl ether was prepared as previously described[21] (m.p. 149–151°C). 1,2-Diaminobenzene (Aldrich Chemical Co.) was recrystallized from deoxygenated water containing a small amount of sodium dithionite (m.p. 103–105°C). 4,4′-Dimethoxybenzil, 3,3′-dihydroxybenzil and 4,4′-dihydroxybenzil (Midori Kagaku Co., Ltd) were used as received (m.p. 131–133°C, 145–147°C and 248–250°C, respectively). 4,4′-Dihydroxybenzil was also prepared by the demethylation of 4,4′-dimethoxybenzil using 48% aqueous hydrobromic acid in acetic acid (m.p. 248–250°C). Benzyl(4-hydroxyphenyl)ketone was obtained from Aldrich Chemical Co. or prepared as previously described[22] and subsequently oxidized by

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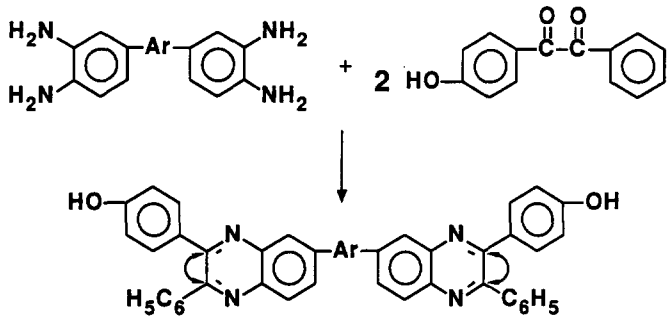
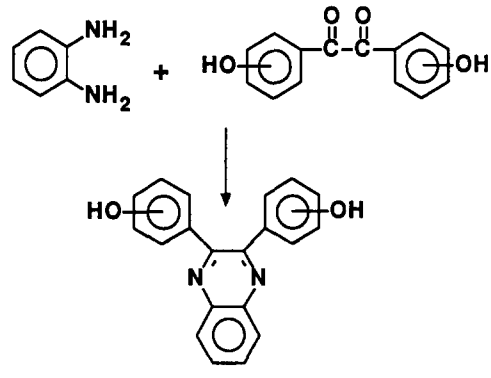
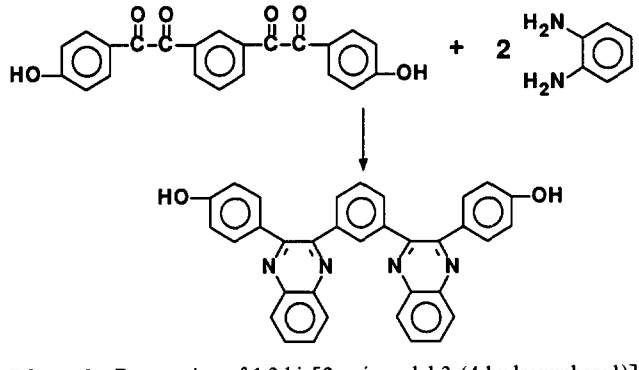


Scheme 1 Preparation of bis(phenylquinoxaline) (see *Table 1* for Ar)



Scheme 2 Preparation of 2,3-bis(3- or 4-hydroxyphenyl)quinoxaline



Scheme 3 Preparation of 1,3-bis[2-quinoxalyl-3-(4-hydroxyphenyl)]-benzene

using selenium dioxide in 1,4-dioxane to prepare 4-hydroxybenzil (m.p. 129–131°C; literature[23] m.p. 129–130°C). 1,3-Bis(4-hydroxyphenylglyoxalyl) benzene was prepared as previously described[24] (m.p. 204–206°C).

The preparation of the bis(phenolquinoxaline)s with and without configurational isomers are depicted in *Schemes 1–3*.

2,3-Bis(4-hydroxyphenyl)quinoxaline

The title compound was prepared as depicted in *Scheme 2* by the following procedure. Into a 1 l three-neck round-bottom flask equipped with a mechanical stirrer, thermometer and reflux condenser, was placed 4,4'-dihydroxybenzil (60.5 g, 0.25 mol), 1,2-diaminobenzene (27.04 g, 0.25 mol) and absolute ethanol (450 ml, 15% solids). The solids dissolved rapidly to give a clear yellow solution and a bright yellow precipitate formed after ~10 min. The mixture was stirred at room temperature for ~1 h and then heated to reflux overnight. The mixture was poured into water, washed in water and dried at 125°C for 6 h under vacuum to give 77 g (98% yield) of yellow solid (m.p. 325–330°C). The material was recrystallized from ethanol/water (3.5:1) to give yellow needles (65 g, 83% yield) (m.p. 336–338°C; literature[25] m.p. 326–328°C).

2,3-Bis(3-hydroxyphenyl)quinoxaline

The title compound was prepared from 3,3'-dihydroxybenzil (6.09 g, 0.025 mol) and 1,2-diaminobenzene (2.72 g, 0.025 mol) in refluxing ethanol (40 ml). The crude material was recrystallized from ethanol/water (1:1) to give 6 g (78% yield) of yellow crystals (m.p. 249–251°C). Elemental analysis for $C_{20}H_{14}N_2O_2$: calculated C, 76.42%; H, 4.49%; N, 8.91%. Found: C, 76.80%; H, 4.50%; N, 8.63%.

1,3-Bis[2-quinoxalyl-3-(4-hydroxyphenyl)]benzene

The title compound was prepared from 1,3-bis(4-hydroxyphenylglyoxalyl)benzene (5.14 g, 0.0137 mol) and 1,2-diaminobenzene (2.97 g, 0.0275 mol) in refluxing ethanol (45 ml), as depicted in *Scheme 3*. The crude product was recrystallized from ethanol/water (5:1) to give ~6 g of yellow crystalline solid; sharp peak at 320°C by differential thermal analysis (d.t.a.). Elemental analysis for $C_{34}H_{22}N_4O_2$: calculated C, 78.75%; H, 4.28%; N, 10.80. Found: C, 78.31%; H, 4.34%; N, 10.62%.

6,6'-Bis[2-(4-hydroxyphenyl)-3-phenylquinoxaline] and isomers

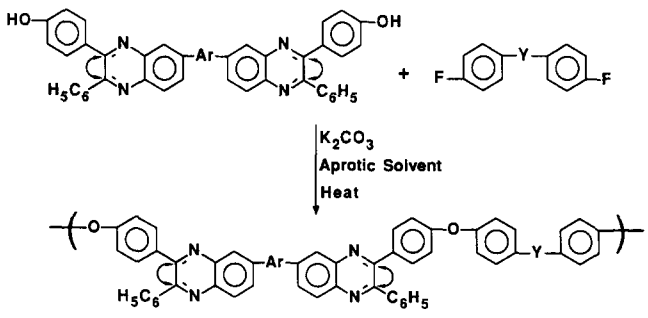
The title compound was prepared from 3,3',4,4'-tetraaminobiphenyl (10.71 g, 0.05 mol) and 4-hydroxybenzil (22.72 g, 0.10 mol) in a mixture of ethanol/benzene (1:1, 85 ml each) at reflux temperature for ~12 h. The solvent mixture was removed by vacuum distillation to give a quantitative yield of product. The compound was subsequently dissolved in ethanol, treated with activated charcoal, filtered and precipitated into water. The bis(phenolquinoxaline) was obtained as a yellow amorphous solid (28 g, 95% yield) (m.p. over 360°C). Elemental analysis for $C_{40}H_{26}N_4O_2$: calculated C, 80.79%; H, 4.41%; N, 9.42%. Found: C, 80.56%; H, 4.22%; N, 9.48%.

6,6'-Carbonylbis[2-(4-hydroxyphenyl)-3-phenylquinoxaline] and isomers

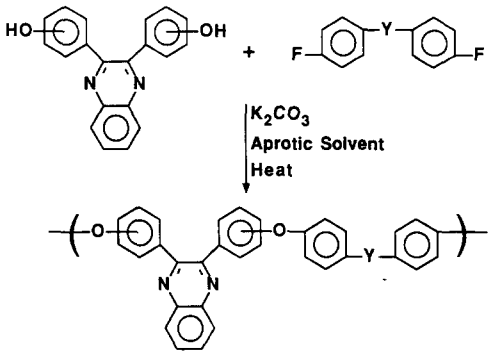
The title compound was prepared from 3,3',4,4'-tetraaminobenzophenone (12.11 g, 0.05 mol) and 4-hydroxybenzil (22.72 g, 0.10 mol) in refluxing ethanol (175 ml, 15% solids). The product was obtained as a tan solid (29.8 g, 96% yield), m.p. 165–175°C. Elemental analysis for $C_{41}H_{26}N_4O_3$: calculated C, 79.08%; H, 4.21%; N, 8.99%. Found: C, 79.92%; H, 4.11%; N, 9.23%.

6,6'-Oxybis[2-(4-hydroxyphenyl)-3-phenylquinoxaline] and isomers

The title compound was prepared from 3,3',4,4'-tetraaminodiphenyl ether (11.51 g, 0.05 mol) and 4-hydroxybenzil (22.72 g, 0.10 mol) in refluxing ethanol (175 ml, 15% solids). The product was obtained as a yellow solid (28.3 g, 93% yield) (m.p. 155–167°C). Elemental analysis for $C_{40}H_{26}N_4O_3$: calculated C, 78.67%; H, 4.29%; N, 9.17%. Found: C, 79.83%; H, 4.56%; N, 9.63%.



Scheme 4 Preparation of PAEQs with configurational isomers (see *Table 1* for Ar and Y)



Scheme 5 Preparation of PAEQs without configurational isomers

Polymers

The following experimental procedure is representative of that used for the preparation of the poly(arylene ether phenylquinoxaline)s (PAEQ) as depicted in *Schemes 4* and *5*. In some cases 1,2-dichlorobenzene was used as a co-solvent to maintain polymer solubility.

Into a 100 ml three-neck round-bottom flask equipped with a mechanical stirrer, thermometer, nitrogen gas inlet, Dean–Stark trap and reflux condenser, was placed 1,3-bis(4-fluorobenzoyl)benzene (3.2231 g, 0.01 mol), 6,6′-bis[2-(4-hydroxyphenyl)-3-phenylquinoxaline] and isomers (5.9464 g, 0.01 mol), pulverized anhydrous potassium carbonate (3.2 g, 0.023 mol, 15% excess), toluene (35 ml) and a 1:1 mixture of 1,2-dichlorobenzene and N,N-dimethylacetamide (DMAc, 18 ml each, ~20% solids). The mixture was heated to ~135°C for 4 h to remove water. The toluene was subsequently removed and the reaction mixture was heated to ~160°C for 16 h under nitrogen. The viscous solution was diluted with DMAc (25 ml), filtered through coarse porosity sintered glass and precipitated into methanol containing acetic acid. The polymer was washed in hot methanol, hot water and dried for 8 h at 150°C under vacuum to give 8 g (91%) of yellow polymer. The polymer exhibited a T_g of 240°C by d.s.c. A 0.5% solution in *m*-cresol at 25°C had an inherent viscosity of 1.09 dl g^{-1}.

Films

Meta-cresol solutions of the polymers (15–20% solids) were centrifuged and doctored onto plate glass and dried to a tack-free form in a flowing-dry-air chamber. The films on glass were subsequently stage-dried in a forced-air oven to a temperature ~50°C above the T_g of the polymer and held for 0.5 h. Thin-film tensile properties were determined according to ASTM D882 by using four specimens per test condition.

Other characterization

Differential thermal analysis (d.t.a.) was performed at a heating rate of 10°C min^{-1} with the melting point taken at the endothermic peak temperature. Differential scanning calorimetry (d.s.c.) was performed at a heating rate of 20°C min^{-1} with the glass transition temperature (T_g) taken at the inflection point of the ΔT *versus* temperature curve. Thermogravimetric analysis (t.g.a.) was performed on powder samples at a heating rate of 2.5°C min^{-1} in air or nitrogen at a flow rate of 15 cm^3 min^{-1}. Wide-angle X-ray diffraction (WAXS) data were obtained on polymer powder and thin films. The X-ray diffractometer was operated at 45 kV and 40 mA by using a copper radiation source with a flat sample holder and a graphite monochromator. The intensity of one second counts was taken every 0.01° (2θ) and was recorded on hard disc for the angular range of 10–40° (2θ). An external α quartz standard was used in the goniometer alignment. Inherent viscosities (η_{inh}) were determined for 0.5% solutions in *m*-cresol at 25°C. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

RESULTS AND DISCUSSION

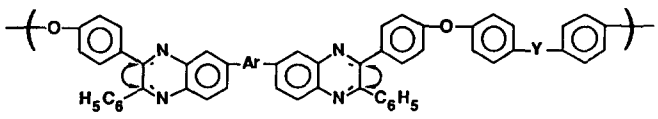
Bis(phenolquinoxaline)s

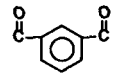
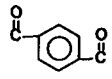
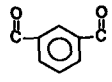
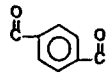
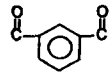
Two different types of bis(phenolquinoxaline)s were prepared (i.e. with and without configurational isomers, *Schemes 1–3*). The bis(phenolquinoxaline)s prepared from 4-hydroxybenzil and aromatic tetraamines were isolated as a mixture of three configurational isomers and as such exhibited relatively broad melting ranges. Owing to their amorphous character these compounds were not successfully recrystallized. The bis(phenolquinoxaline)s were either obtained directly from the reaction mixture or by reprecipitation. Polymers prepared from 6,6′-carbonylbis[2-(4-hydroxyphenyl)-3-phenylquinoxaline] were of high viscosity even though the elemental analysis for carbon was off by ~0.9%. Elemental analysis of 6,6′-oxybis[2-(4-hydroxyphenyl)-3-phenylquinoxaline] did not agree with the theoretical values. This bis(phenolquinoxaline) provided PAEQs with the lowest inherent viscosities, presumably due to purity. The bis(phenolquinoxaline)s prepared from the dihydroxybenzils did not contain configurational isomers and were obtained as yellow crystalline solids which exhibited sharp melting points.

Polymers

Polymers with configurational isomers. Medium to high molecular weight PAEQs that contained configurational isomers were prepared as depicted in *Scheme 4* by the nucleophilic displacement reaction of activated aromatic difluoro compounds with bis(phenolquinoxaline)s using potassium carbonate in polar aprotic media. Initially toluene was used as an azeotroping agent to remove water. The toluene was removed after ~4 h and the reaction temperature was increased to ~160°C overnight under nitrogen. The polymer solutions were diluted with DMAc, filtered through coarse-porosity sintered glass to remove any gel particles and precipitated into methanol containing a small amount of acetic acid. The polymers were subsequently washed in hot methanol, hot water and dried under vacuum. The PAEQs were soluble in *m*-cresol, but only swelled in DMAc or chloroform.

Table 1 Polymer characterization



Polymer	Ar	Y	η_{inh} (dl g^{-1})	T_g(°C)
P1	nil	SO_2	0.94	283
P2	nil	CO	0.80	252
P3	nil		1.09	240
P4	CO	SO_2	0.69	268
P5	CO		0.86	255
P6	CO	CO	1.30	253
P7	CO		0.61	235
P8	O	SO_2	0.34	240
P9	O		0.45	226
P10	O		0.46	213

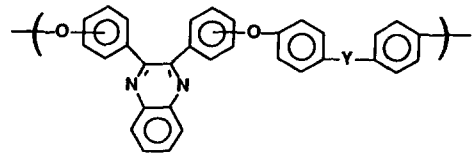
Polymer characterization is presented in *Table 1*. The inherent viscosities ranged from 0.34 to 1.30 dl g^{-1} and the T_gs ranged from 213 to 283°C. The PAEQs prepared from 6,6′-oxybis[2-(4-hydroxyphenyl)-3-phenylquinoxaline] (polymers P8–P10 in *Table 1*) exhibited the lowest inherent viscosities, presumably due to monomer purity. T.g.a. showed a 5% weight loss occurring at ~480°C in air and ~500°C in nitrogen.

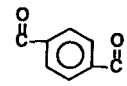
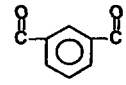
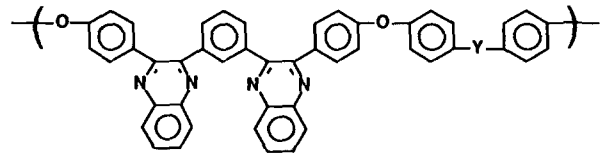
Polyphenylquinoxalines (PPQs) with identical chemical structures as P3 and P7 (*Table 1*) have been prepared via the conventional synthetic route[26]. Comparisons of the polymers prepared by the two different synthetic routes showed that they had identical T_gs and thermal stabilities, as measured by d.s.c. and t.g.a., respectively. However, differences in solubility were observed. For example, the PPQs prepared by the conventional route were soluble in chloroform, DMAc and *m*-cresol, whereas the PAEQs prepared via the nucleophilic displacement route with identical chemical structures were soluble in *m*-cresol and insoluble, but swollen, in DMAc and chloroform. These differences in solubility may be attributed to the presence of a small amount of crosslinking or a significantly different distribution of configurational isomers along the backbone of the PAEQs.

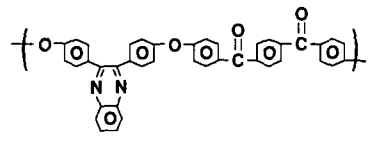
Polymers without configurational isomers. PAEQs without configurational isomers were prepared from activated aromatic difluoro compounds and bis(phenolquinoxaline)s by using potassium carbonate in DMAc (*Scheme 5*). All of these polymers precipitated during synthesis thereby limiting the molecular weight. The polymers were insoluble in other solvents such as NMP, 1,2-dichlorobenzene, sulpholane, diphenylsulphone and 3-methylanisole. Polymer characterization is presented in *Table 2*. The inherent viscosities ranged from 0.24 to 0.83 dl g^{-1} and the T_gs ranged from 179 to 240°C. A few of the polymers exhibited T_ms by d.s.c. which ranged from 365 to 388°C. A d.s.c. thermogram of a thin film of P13 (*Table 2*) cast from *m*-cresol is presented in *Figure 1*. The polymer exhibits a sharp transition indicative of an ordered $T_g \approx 208$°C and a broad endotherm indicative of a T_m peaking at 365°C on the first heat-up. After heating to 400°C and quenching, the polymer exhibits a $T_g \approx 208$°C and no T_m. WAXS analysis of this film indicated low levels of crystallinity.

Thin films of all of the polymers in *Table 2* cast from *m*-cresol were opaque and snapped when creased.

Table 2 Polymer characterization



Polymer	Isomer	Y	η_{inh} (dl g^{-1})	T_g(T_m) (°C)
P11	4,4′-	SO_2	0.54	240
P12	4,4′-	CO	0.58	209
P13	4,4′-		0.83	208 (365)
P14	4,4′-		0.50	179
P15	3,3′-	CO	0.52	179 (377)
				
P16	–	SO_2	0.25	235 (388)



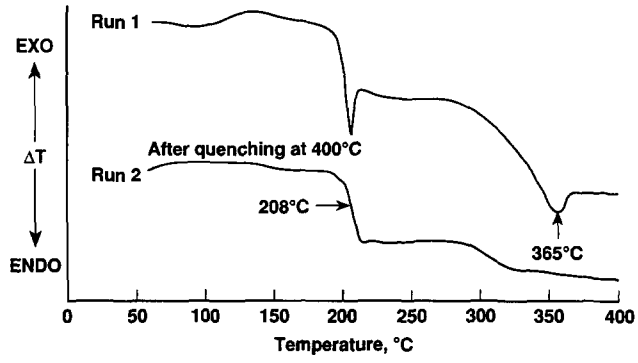


Figure 1 Differential scanning calorimetric curve of film in static air (heating rate, 20°C min^{-1}; sample size, 6.7 mg; sensitivity 0.5 mcal s^{-1} in^{-1})

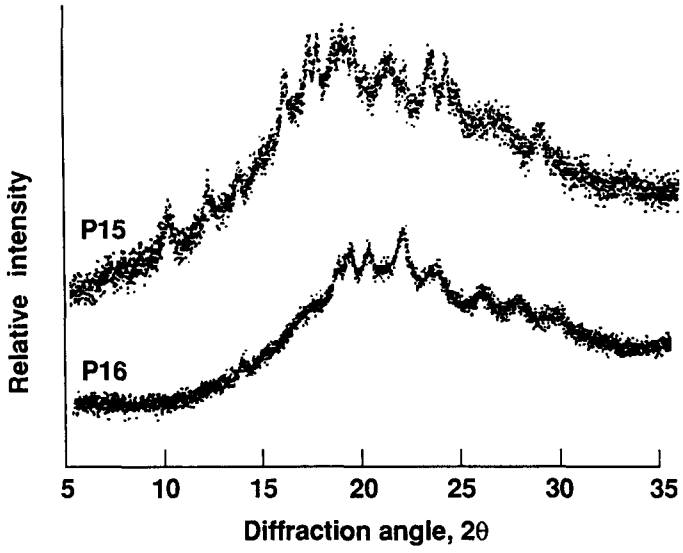


Figure 2 Wide-angle X-ray diffractogram of thin films (see *Table 2* for chemical structures)

Table 3 Thin film properties

Polymer	Test temperature (°C)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)
P3	23	98.6	2.9	7.1
	177	48.9	2.1	67.2
P7	23	94.4	2.8	9.9
	177	46.9	2.0	25.3
P13	23	89.6	2.8	3.5

However, a T_m was detected in only three of the films. WAXS analysis of thin films of P11–P14 showed a broad, poorly defined peak indicative of low levels of crystallinity. Attempts to further induce crystallinity in these films by annealing at elevated temperature were unsuccessful. Thin films of P15 and P16 (*Table 2*) exhibited sharper better defined peaks by X-ray diffraction and may possess higher levels of crystallinity (*Figure 2*). T.g.a. of these polymers indicated a 5% weight loss occurring at ~480°C in air and ~500°C in nitrogen.

Thin films

Thin films of PAEQs with configurational isomers cast from *m*-cresol solutions were flexible and creasable with representative properties presented in *Table 3*. The films from the PAEQs without configurational isomers were opaque and brittle. Thin-film mechanical properties were obtained for one of the polymers. The tensile strengths and moduli of the PAEQs with configurational isomers were similar to those of PPQs prepared via the conventional route[7].

CONCLUSIONS

A series of two different types of PAEQs were prepared by the aromatic nucleophilic displacement reaction of bis(phenolquinoxaline)s with activated aromatic difluoro compounds. The PAEQs that did not contain configurational isomers exhibited low levels of crystallinity.

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