Chemistry and properties of poly(arylene ether benzoxazole)s

J. G. Smith Jr, J. W. Connell* and P. M. Hergenrother
NASA Langley Research Centre, Hampton, VA 23665-5225, USA
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Novel poly(arylene ether benzoxazole)s were prepared by the aromatic nucleophilic displacement reaction of two new bis(hydroxyphenyl benzoxazole)s with activated aromatic difluorides. The bis(hydroxyphenyl benzoxazole)s were prepared from either 3,3′-dihydroxy-4,4′-diaminobiphenyl or 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane and phenyl-4-hydroxybenzoate. The polymerizations were carried out in either *N*,*N*-dimethylacetamide or diphenylsulphone, depending on the bis(hydroxyphenyl benzoxazole). The polymers had glass transition temperatures ranging from 204 to 275°C and inherent viscosities from 0.25 to 1.04 dl g^{-1}. Several of the polymers prepared from the 3,3′-dihydroxy-4,4′-diaminobiphenyl-derived bis(hydroxyphenyl benzoxazole) were semi-crystalline. Thermogravimetric analysis showed a 5% weight loss occurring at ≈450–500°C in air and ≈475–530°C in nitrogen. Thin films of the hexafluoroisopropylidene-containing polymers exhibited 23°C tensile strengths and moduli of 83–103 MPa and 1.9–2.4 GPa respectively, and high elongations. The chemistry and the physical and mechanical properties of these polymers are discussed.

(Keywords: aromatic polymer; poly(arylene ether benzoxazole); chemistry)

INTRODUCTION

High performance thermoplastics are currently under evaluation for potential use as structural resins for a variety of aerospace applications. Thermoplastic polymers have a unique combination of chemical, physical, and mechanical properties as well as the potential for low-cost composite fabrication. One class of high performance polymers that has received considerable attention is the poly(arylene ether)s (PAEs). They are generally prepared by the aromatic nucleophilic displacement of activated aromatic dihalides or dinitro compounds by alkali metal bisphenates in a polar aprotic solvent[1–4].

Prior work involving the incorporation of heterocyclic units within the backbone of PAEs has demonstrated certain advantages over PAEs without heterocyclic units, such as higher glass transition temperatures (T_g), tensile strengths and moduli. Heterocycles such as imides[5], phenylquinoxalines[6–8], imidazoles[9,10], 1,3,4-oxadiazoles[11], 1,2,4-triazoles[11], pyrazoles[12,13], benzimidazoles[14], and benzoxazoles[15,16] have been introduced into the backbone of PAEs via the aromatic nucleophilic displacement route.

Poly(benzoxazole)s (PBOs) were first synthesized in a two-step process which first involved reacting an aromatic diacid chloride with a bis(*o*-aminophenol) in solution to form a soluble poly(*o*-hydroxyamide). The second step was a thermal cyclodehydration to form the poly(benzoxazole)[17]. The most common synthetic method for PBOs involves a melt polymerization of bis(*o*-aminophenol)s with aromatic diphenyl esters[18]. The preparation of PBOs by the condensation of hydrochloride salts of bis(*o*-aminophenol)s with aromatic diacids in polyphosphoric acid has also been reported[19]. Another synthetic method involves the initial formation of poly(*o*-siloxyamide)s from the reaction of silylated derivatives of bis(*o*-aminophenol)s with aromatic diacid chlorides, followed by thermal cyclodehydration to form PBO[20].

The synthesis of PBOs via the aromatic nucleophilic displacement reaction offers distinct advantages over prior routes. These include easier synthesis and more versatility in the chemical structure. Concurrent with the present work, the synthesis of poly(arylene ether benzoxazole)s (PAEBs) from bis(fluorophenyl benzoxazole) compounds and aromatic bisphenols has been under investigation[15]. The work reported herein concerns the synthesis and the physical and mechanical properties of PAEBs prepared by the nucleophilic displacement reaction of activated aromatic difluorides with two new bis(hydroxyphenyl benzoxazole)s in the presence of potassium carbonate.

EXPERIMENTAL

Starting materials

4,4′-Difluorodiphenylsulphone (Aldrich Chemical Co.) was recrystallized from ethanol to yield a white crystalline solid (m.p. 98–99°C). 4,4′-Difluorobenzophenone (Chemical Dynamics Corp.) was recrystallized from ethanol (m.p. 104–105°C). Bis[(4-fluorophenyl)phenyl] phosphine oxide (American Hoechst Corp.) was recrystallized from ligroin (m.p. 125–127°C). 1,3- and 1,4-bis(4-fluorobenzoyl)benzene (m.p. 178–179 and 215–217°C, respectively), 4,4′-bis(4-fluorobenzoyl)diphenyl ether (m.p. 213–214°C), 4,4′-bis(4-fluorobenzoyl)-diphenyl ketone (m.p. 291–295°C), 2,6-bis(4-fluoro-

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* To whom correspondence should be addressed

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benzoyl)naphthalene (m.p. 258–260°C), 3,3′-bis(4-fluorobenzoyl)biphenyl (m.p. 163.5–166.5°C), and 4,4′-bis(4-fluorobenzoyl)biphenyl (m.p. 264–265.5°C) were prepared as previously described[4]. 3,3′-Dihydroxy-4,4′-diaminobiphenyl (Chriskev Co.) was recrystallized from a mixture of *N*,*N*-dimethylacetamide (DMAc) and ethanol to yield a tan-coloured crystalline solid, m.p. 303–305°C. 2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane (m.p. 244–245°C) was used as received (Chriskev Co.). Phenyl-4-hydroxybenzoate (K and K Laboratories) was recrystallized from toluene (m.p. 174.5–176.5°C). Diphenylsulphone (Aldrich Chemical Co.) was recrystallized from methanol to yield a white crystalline solid (m.p. 126–128°C). High-purity grade *N*,*N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidinone (NMP) were used as received (Fluka Chem. Co.).

5,5′-Hexafluoroisopropylidyl-bis[2-(4-hydroxyphenyl)-benzoxazole]

A mixture of phenyl-4-hydroxybenzoate (51.03 g, 0.238 mol) and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (43.02 g, 0.119 mol) was slowly heated to 290°C and maintained at 290°C for 5 h under nitrogen. During this time, water and phenol were evolved and removed. The mixture was cooled to room temperature and the resulting solid was dissolved in ethanol and poured into water to afford 64.1 g (96% yield) of a yellow powder, m.p. by differential thermal analysis (d.t.a.), (heating rate 10°C min^{-1}) onset 305°C, peak 310°C. The powder was vacuum-sublimed at 320–340°C to afford a yellowish-green crystalline solid in 79% yield, m.p. (d.t.a.) 313°C. The analysis calculated for $C_{29}H_{16}H_2O_4F_6$ was (wt%): C, 61.06; H, 2.83; N, 4.91; F, 19.98. That found was (wt%): C, 61.17; H, 3.01; N, 4.86; F, 19.99.

6,6′-Bis[2-(4-hydroxyphenyl)benzoxazole]

A mixture of 3,3′-dihydroxy-4,4′-diaminobiphenyl (15.7 g, 0.073 mol), phenyl-4-hydroxybenzoate (31.2 g, 0.146 mol) and diphenylsulphone (50 g) was heated under nitrogen to 250°C and stirred at 250–260°C for 2 h. The cooled brown reaction mixture was boiled in methanol (400 ml) and then filtered, and the solid was subsequently air-dried. The resulting tan-coloured solid (52.2 g) was extracted with boiling ethanol (500 ml) to yield an insoluble tan-coloured solid (22 g, 72% crude yield). The solid was recrystallized twice from a mixture of DMAc (200 ml) and ethanol (300 ml) using charcoal to afford tan-coloured crystals (14.4 g, 47% yield). D.t.a. showed a sharp endotherm peaking at 393°C. The analysis calculated for $C_{29}H_{16}N_2O_4$ was (wt%): C, 74.28; H, 3.84; N, 6.66. That found was (wt%): C, 74.82; H, 3.86; N, 6.68.

Polymers

The following experimental procedures are representative of those used for the preparation of the PAEBs. Owing to solubility differences between the two bis(hydroxyphenyl benzoxazole) compounds, different polymerization conditions were used.

Hexafluoroisopropylidene (6F)-containing PAEBs. 5,5′-Hexafluoroisopropylidyl-bis[2-(4-hydroxyphenyl)benzoxazole] (3.5738 g, 6.3 mmol), 4,4′-difluorobenzophenone (1.3670 g, 6.3 mmol), pulverized anhydrous potassium carbonate (2.3098 g, 16.7 mmol, 30% excess), dry DMAc (29 ml, 18% solids), and toluene (55 ml) were stirred under a nitrogen atmosphere at 130–140°C for 4 h, while water was removed via a Dean Stark trap. The toluene was subsequently removed and the mixture was stirred at 155°C overnight. The viscous brown solution was diluted with DMAc (20 ml) and precipitated in a water–acetic acid mixture (≈10:1). The polymer was collected, washed successively in water and methanol, and dried at 120°C to provide a cream-coloured polymer (4.4 g, 95% yield). The polymer exhibited a T_g of 244°C and an inherent viscosity (0.5% in NMP at 25°C) of 0.67 dl g^{-1}.

6,6′-Bis[2-(4-hydroxyphenyl)benzoxazole]-derived PAEBs. 6,6′-Bis[2-(4-hydroxyphenyl)benzoxazole] (2.3714 g, 5.6 mmol), 1,3-bis(4-fluorobenzoyl)benzene (1.8180 g, 5.6 mmol), pulverized anhydrous potassium carbonate (2.0378 g, 14.7 mmol, 30% excess), diphenylsulphone (16.99 g, 19% solids), and toluene (65 ml) were stirred under a nitrogen atmosphere at 140–150°C for 4 h, while water was removed via a Dean Stark trap. The toluene was subsequently removed and the mixture was heated to 180°C for 1 h, 230°C for 2 h, and 260°C for 1.5 h under nitrogen. The melt was cooled to 200°C, diluted with NMP (20 ml), and precipitated into an acetone–acetic acid mixture (≈10:1). The polymer was collected, washed successively in water and methanol, and dried at 120°C to afford a yellow polymer (3.80 g, 96% yield). The polymer exhibited a crystalline melt (T_m) by differential scanning calorimetry (d.s.c.) at 363°C on the first heat-up (no detectable T_g) and a T_g at 205°C on the second heat-up. The inherent viscosity of a 0.5% solution in concentrated sulphuric acid at 25°C was 1.04 dl g^{-1}.

Characterization

Differential thermal analysis (d.t.a.) was conducted using a DuPont 990 thermal analyzer at a heating rate of 10°C min^{-1}. Inherent viscosities (η_{inh}) were obtained on 0.5% solutions in NMP, DMAc, or sulphuric acid at 25°C. Differential scanning calorimetry (d.s.c.) was performed on a DuPont 990 thermal analyzer at a heating rate of 20°C min^{-1} with the T_g taken at the inflection point of the ΔT vs temperature curve. The T_m was taken at the minimum of the ΔT vs temperature curve. Thermogravimetric analysis (t.g.a.) was performed at a heating rate of 2.5°C min^{-1} on powder samples in air or nitrogen at a flow rate of 15 cm^3 min^{-1}. Wide angle X-ray diffraction (WAXS) data were obtained on powdered samples. The X-ray diffractometer was operated at 45 kV and 40 mA using copper radiation with a flat sample holder and a graphite monochromator. The intensities of one-second counts were taken every 0.01° (2θ) and recorded on hard disk for the angular range 10–40° (2θ). An external α-quartz standard was used in the goniometer alignment.

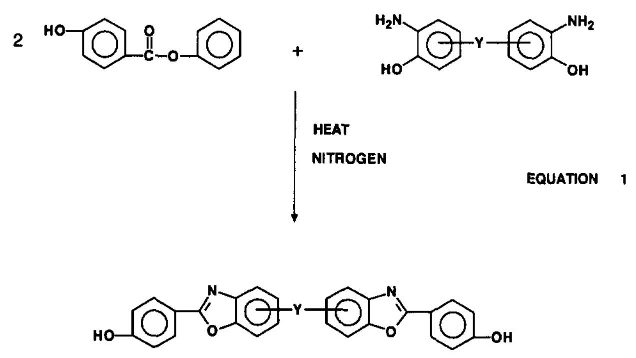
Films

NMP or DMAc solutions (15–20% solids) of the hexafluoroisopropylidene (6F)-containing polymers were centrifuged and the decantate was doctored onto clean, dry plate glass and dried to a tack-free form in a dry-air-purged chamber. The films on glass were dried at 100, 200 and 300°C for 1 h at each temperature in a forced-air oven. Thin-film tensile properties were determined according to ASTM D882.

RESULTS AND DISCUSSION

Bis(hydroxyphenyl benzoxazole)s

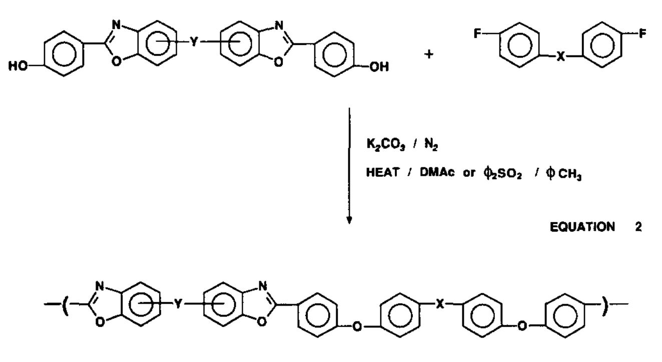
Novel bis(hydroxyphenyl benzoxazole)s were prepared from the reaction of phenyl-4-hydroxybenzoate with bis(*o*-aminophenol)s [equation (1)] in ≈50–75% yield after purification. The hexafluoroisopropylidene (6F)-containing benzoxazole monomer was prepared from 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane and phenyl-4-hydroxybenzoate. The 6F-containing bis(hydroxyphenyl benzoxazole) was soluble in a variety of organic solvents, thereby making isolation from the reaction media (diphenylsulphone) and subsequent recrystallization difficult. It was therefore prepared in the melt and subsequently purified by vacuum sublimination.



Y = 6,6' nil or 5,5'C(CF$_3$)$_2$

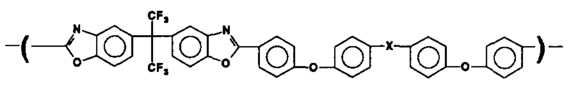
The 6,6'-bis[2-(4-hydroxyphenyl)benzoxazole] was prepared from 3,3'-dihydroxy-4,4'-diaminobiphenyl and phenyl-4-hydroxybenzoate [equation (1)] in diphenylsulphone at 250°C. The compound was obtained in ≈50% yield after recrystallization from a mixture of DMAc and ethanol. This one-step synthesis worked well and can be performed using a variety of aromatic bis(*o*-aminophenol)s.

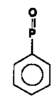
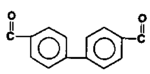
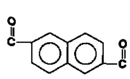
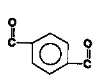
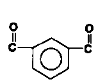
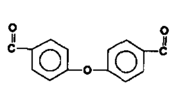
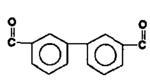
Polymers



Y = 6,6' nil or 5,5'C(CF$_3$)$_2$
X = See Tables 1 and 2

Table 1 Polymer characterization: 6F-containing PAEBs

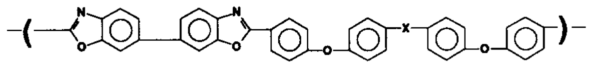


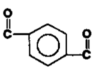
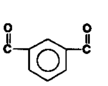
X	η_{inh} (dl g^{-1})[a]	T_g[b] (°C)	Temperature (°C)[c] at 5% wt loss in Air	Temperature (°C)[c] at 5% wt loss in N$_2$
SO_2	0.86	275	500	507
	0.25	250	483	519
	0.72[d]	247	494	530
	0.67[d]	244	499	529
	0.49	243	488	525
	0.92[d]	239	489	524
	0.40	217	492	517
	0.62	211	478	528
	0.41	204	488	526

[a] Measured on 0.5% solution in DMAc at 25°C unless otherwise noted
[b] By d.s.c. at 20°C min^{-1}
[c] By t.g.a. at 2.5°C min^{-1}
[d] On 0.5% solution in NMP at 25°C

Hexafluoroisopropylidene (6F)-containing PAEBs. Poly(arylene ether benzoxazole)s were prepared by the nucleophilic displacement reaction of activated aromatic difluorides with the potassium bisphenate of 5,5'-hexafluoroisopropylidyl-bis[2-(4-hydroxyphenyl)benzoxazole] in DMAc under a nitrogen atmosphere as depicted in equation (2). The PAEBs prepared were low to high molecular weight, as evident from their inherent viscosities, which ranged from 0.25 to 0.86 dl g^{-1} (*Table 1*). The low inherent viscosity (0.25 dl g^{-1}) of the phosphine oxide-containing PAEB was surprising, since high molecular weight PAEs have been prepared from the reaction of this same batch of bis[(4-fluorophenyl)-phenyl] phosphine oxide with various other bisphenols [e.g. 2,2-bis(4-hydroxyphenyl)propane] in our laboratory. Certain bisphenols containing heterocyclic units have failed to form high molecular weight PAE when reacted with bis[(4-fluorophenyl)phenyl] phosphine oxide in DMAc at ≈155°C. For example, high molecular weight poly(arylene ether imidazole)s containing phosphine oxide were not formed[9]. However, high reaction temperatures in diphenylsulphone appear to favour the formation of high molecular weight PAEs from the reaction of bisphenols containing heterocylic units and bis[(4-fluorophenyl)phenyl] phosphine oxide. For example, high molecular weight poly(arylene ether 1,3,4-oxadiazole)s containing phosphine oxide were prepared in diphenylsulphone at ≈210°C[11], whereas only low molecular weight polymer was obtained in DMAc at ≈155°C. The reaction of 5,5'-hexafluoroisopropyidyl-bis[2-(4-hydroxyphenyl)benzoxazole] with bis[(4-fluorophenyl)phenyl] phosphine oxide was not attempted in diphenylsulphone. In spite of the low inherent viscosities of some of these PAEBs, solvent-free, creasable films were obtained for all the polymers. The polymers

Table 2 Polymer characterization: 6,6′-bis[2-(4-hydroxyphenyl)-benzoxazole]-derived PAEBs



X	η_{inh} $(dl\,g^{-1})^a$	T_g $(T_m)^b$ (°C)	Temperature (°C)^c at 5% wt loss in	
			Air	N_2
 $C{=}O$	0.50	239 (415)	449	505
SO_2	0.40	237	470	477
	0.40	227 (395,436)	446	501
	1.04	205 (363)	475	530

[a] Measured on 0.5% solution in H_2SO_4 at 25°C
[b] By d.s.c. at 20°C min^{-1}
[c] By t.g.a. at 2.5°C min^{-1}

(*Table 1*) where X is carbonyl, terephthaloyl, or bis(4-benzoyl) gave cloudy solutions in DMAc at 25°C, but cleared when heated to 35°C. These polymers gave clear solutions in NMP at 25°C.

The T_gs ranged from 204 to 275°C and followed the trend for other PAEs, with the exception of the phenylphosphine oxide-containing polymer. The T_g of this polymer was lower than expected, owing presumably to its low molecular weight. In previous work[9] with poly(arylene ether imidazole)s the T_g trend was phenylphosphine oxide > sulphone > benzophenone > terephthaloyl > isophthaloyl. The 6F-containing polymers were amorphous, as evidenced by d.s.c. and wide angle X-ray diffraction. T.g.a. of the polymers showed no weight loss below 300°C in air or nitrogen, and a 5% weight loss at ≈485°C in air and 525°C in nitrogen (*Table 1*).

6,6′-Bis[2-(4-hydroxyphenyl)benzoxazole]-derived PAEBs. The PAEBs were prepared by the nucleophilic displacement reaction of activated aromatic difluorides with the potassium bisphenate of 6,6′-bis[2-(4-hydroxyphenyl)benzoxazole]. The polymerizations were carried out in diphenylsulphone because of the insolubility of the polymers in DMAc or NMP. Previously reported PAEBs prepared from 6,6′-bis[2-(4-fluorophenyl)benzoxazole] and bisphenols containing bulky substituents, such as fluorene, were soluble in NMP[15]. The 6,6′-bis-[2-(4-hydroxyphenyl)benzoxazole]-derived polymers reported here were insoluble in NMP, DMAc, *m*-cresol and chlorinated solvents, but they were soluble in concentrated sulphuric acid. Polymers of moderate to high molecular weight were obtained, as evidenced by inherent viscosities of 0.40 to 1.01 dl g^{-1} (*Table 2*).

The T_gs ranged from 205 to 239°C and were lower than those of the corresponding 6F-containing PAEBs. The T_g of the sulphone-containing polymer was lower than that of the carbonyl-containing polymer, owing presumably to its lower molecular weight. Several of the polymers were semi-crystalline, with T_ms of 363 to 436°C (*Figure 1*). One polymer exhibited two endotherms (*Figure 1*), which was probably due to a kinetically controlled T_m at the lower temperature (395°C) and a thermodynamically controlled T_m at the higher temperature (436°C). When this polymer was heated to 410°C and quenched and the d.s.c. sample was rerun, no T_m was observed at 395°C and the intensity of the T_m at 436°C increased. The polymer containing a sulphone bridging group did not exhibit a T_m. When the semi-crystalline polymers were heated above their respective T_ms and cooled, they became amorphous and the crystallinity could not be regained through annealing at various temperatures between 300 and 350°C for several hours. Since the $T_m - T_g$ difference was large, the polymers were expected to recrystallize readily from their melts. Transient crystallinity has been observed in PAEs[4]. In one case a PAEB exhibited a relatively high T_m (436°C) and some thermal degradation may have occurred during the d.s.c. run, thereby preventing or inhibiting recrystallization. The X-ray diffraction patterns for several of the as-isolated polymer powders are presented in *Figure 2*.

The 6,6′-bis[2-(4-hydroxyphenyl)benzoxazole]-derived polymers exhibited 5% weight loss by t.g.a. at slightly lower temperatures than did the 6F-containing PAEBs. No weight loss was observed up to 300°C in air or nitrogen, and a 5% weight loss as low as 446°C in air and 477°C in nitrogen (*Table 2*). These polymers were expected to exhibit higher temperatures of 5% weight loss by t.g.a. than the 6F-containing PAEBs. However, the benzoxazole isomers are different (5,5′ *versus* 6,6′), and this may account for the difference in the t.g.a. results.

Films

Unoriented thin film properties for 6F-containing PAEBs are presented in *Table 3*. Tensile strengths and moduli ranged from 84.8 to 102 MPa and 1.94 to 2.40 GPa respectively at 23°C. The 6F-containing PAEBs were extremely ductile; films that exhibited high elongations (>15%) were not pulled to the breaking point. The room temperature tensile strengths and moduli of the 6F-containing PAEBs were comparable with those

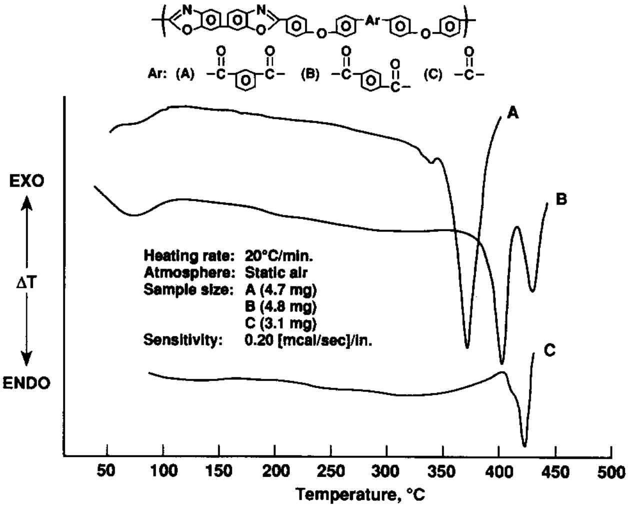


Figure 1 Differential scanning calorimetric curves of as-isolated PAEB powders

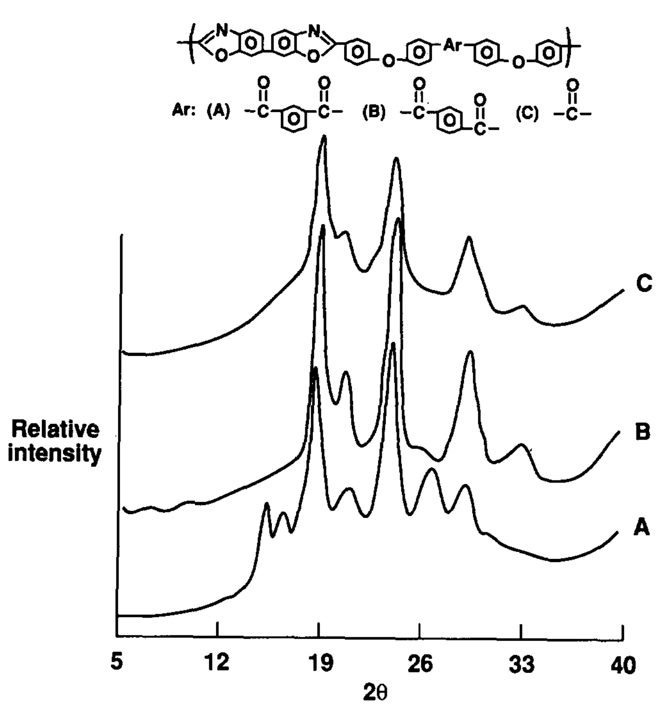
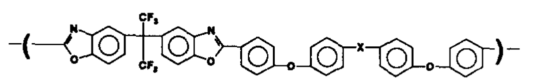
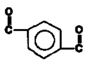
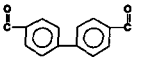
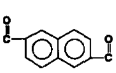
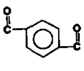
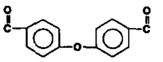


Figure 2 Wide angle X-ray diffractograms of as-isolated PAEB powders

Table 3 Properties of unoriented thin films of 6F-containing PAEBs



X	η_{inh} (dl g^{-1})^a	Temperature (°C)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)^b
	0.40	23	93	2.40	>15
		93	65	2.00	>15
		150	38	1.81	>15
	0.72^c	23	91	1.85	>15
		150	43	1.50	>15
	0.49	23	102	1.94	>15
		93	70	1.77	>15
		150	45	1.65	>15
	0.92^c	23	88	2.10	9.0
		93	52	1.62	>15
		150	34	1.44	>15
	0.62	23	85	1.99	>15
		93	59	1.81	>15
		150	34	1.55	>15
 $\overset{\overset{O}{\|}}{C}$	0.67^c	23	90	2.19	10.9
		150	39	1.60	>15

[a] Measured on 0.5% solution in DMAc unless otherwise noted

[b] Where values >15 are quoted, the specimen was not pulled to the break point

[c] On 0.5% solution in NMP

previously reported[15]. Owing to the relatively low retention of thin film tensile properties at 150°C, further evaluation of these polymers in adhesive or composite form was not undertaken.

The 6,6′-bis[2-(4-hydroxyphenyl)benzoxazole]-derived polymers could not be cast as films, since they were soluble only in concentrated sulphuric acid. However, polymer films could be prepared by melt-pressing polymer powder under ≈7 MPa at temperatures above the T_m of the polymers. A thin film (~130 μm thick) of the polymer prepared from 6,6′-bis[2-(4-hydroxyphenyl)-benzoxazole] and 1,3-bis(4-fluorobenzoyl)benzene was melt-pressed at 400°C under 6.2 MPa for 1 min. The amorphous film was tough and flexible, but because of the noticeable variation in thickness and uniformity, it exhibited lower than expected tensile properties at room temperature.

CONCLUSIONS

Several new PAEBs were prepared by the nucleophilic displacement reaction of activated aromatic difluorides with two novel bis(hydroxyphenyl benzoxazole)s, using potassium carbonate. The 6F-containing PAEBs exhibited better solubility and higher T_gs than did the 6,6′-bis-[2-(4-hydroxyphenyl)benzoxazole]-derived polymers. Several of the 6,6′-bis[2-(4-hydroxyphenyl)benzoxazole]-derived polymers exhibited crystallinity by d.s.c. and WAXS. Unorientated thin film properties of the 6F-containing PAEBs were comparable with those of other 6F-containing PAEBs, previously reported.

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