Poly(arylene ethers)

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(Received 16 January 1987; accepted 8 June 1987)

Several new arylene ether homopolymers and copolymers have been prepared by the nucleophilic displacement of aromatic dihalides with aromatic potassium bisphenates. Polymer glass transition temperatures ranged from 114 to 310°C and a few of the polymers were semicrystalline. Two ethynyl-terminated poly(arylene ethers) were synthesized by reacting hydroxy-terminated oligomers with 4-ethynylbenzoyl chloride. Heat induced reaction of the acetylenic groups provided materials with good solvent resistance. The chemistry, physical and mechanical properties of the polymers are discussed.

(Keywords: poly(arylene ethers); bisphenols; activated dihalides; films; toughness; adhesive properties; melt viscosity; thermal properties)

INTRODUCTION

High performance thermoplastics are currently receiving considerable attention for potential use as structural resins on aerospace vehicles. These materials offer an attractive combination of chemical, physical and mechanical properties. Perhaps the most important advantage offered by the thermoplastics over new toughened thermosets in composite and adhesive applications is the potential of lower cost manufacturing. However, many problems must be resolved before thermoplastics find extensive use in aerospace structural applications.

Several poly(arylene ethers) (PAEs) such as Udel® (polysulphone), Kadel® (polyketone)[1], PEEK® [poly(ether ether ketone)][2] and Victrex® PES (polyethersulphone)[2] are commercially available. These materials are excellent high performance engineering thermoplastics and are used in a variety of applications such as coatings, adhesives, composites, moulded components, toughening agents and ultrafiltration membranes. The polyketone and poly(ether ether ketone) are semicrystalline polymers and exhibit good solvent resistance but require high moulding temperatures. Polysulphone and poly(ether sulphone) are amorphous materials with poor to moderate solvent resistance and require moderate moulding temperatures. The synthesis of PAEs involves the nucleophilic displacement of activated aromatic halides in polar solvents by alkali metal phenates or Friedel–Crafts processes. Nucelophilic displacement and Friedel–Crafts reactions leading to high molecular weight poly(arylene ethers) were initially reported in the late 1950s[3] and early 1960s[4], respectively. Since then numerous papers[5] and patents[6] have appeared.

The work presented here involves the preparation of PAEs, some with a new chemical structure, by the conventional aromatic nucleophilic displacement route. The chemistry, mechanical and physical properties of these polymers are presented. This work was performed as part of our programme on damage tolerant composites. The primary objective was to acquire basic informatin on structure–property relationships to permit the design of a thermoplastic with good overall properties for potential use in aerospace structural applications.

EXPERIMENTAL

1,3-Bis(4-chlorobenzoyl)benzene (1,3-CBB)

Anhydrous powdered aluminium chloride (160 g, 1.2 mol) was added to a cold (10–15°C) stirred solution of isophthaloyl chloride (101.5 g, 0.5 mol) in chlorobenzene (904 g, 8.0 mol) during ~ 10 min and the reaction mixture was stirred at this temperature for 1 h. The reaction mixture was then stirred for 16 h at room temperature, followed by heating to 70–80°C and stirred for an additional 3 h. The reaction mixture was precipitated in cold, aqueous hydrochloric acid and filtered to separate a white solid. The solid was washed with water twice and methanol once and dried at 100°C to yield 162 g of crude product (91% yield). The crude product was recrystallized twice from toluene to afford 1,3-bis(4-chlorobenzoyl)benzene as white crystals (m.p. 210.5–211.5°C, 85% yield). Elemental analyses calculated for $C_{20}H_{12}Cl_2O_2$: C, 67.63%; H, 3.40%; Cl, 19.96%. Found: C, 67.62%; H, 3.36%; Cl, 20.04%.

1,3-Bis(4-fluorobenzoyl)benzene (1,3-FBB)

Anhydrous powdered aluminium chloride (164.7 g, 1.24 mol) was added during ~5 min to a stirred solution of isophthaloyl chloride (101.5 g, 0.5 mol) in fluorobenzene (480.5 g, 5.0 mol). The reaction became exothermic, with the temperature increasing to ~60°C. After the exotherm subsided, the reaction was maintained at ~75°C for 4 h and then poured into cold, aqueous hydrochloric acid. The suspension was distilled to remove excess fluorobenzene and the residual solid was collected by filtration. The crude product was recrystallized from toluene to afford 1,3-bis(4-fluorobenzoyl)benzene as white crystals (m.p. 178–179°C, 81% yield). Elemental analysis calculated for $C_{20}H_{12}F_2O_2$: C, 74.53%; H, 3.75%; F, 11.79%. Found: C, 74.33%; H, 3.59%; F, 11.42%.

1,4-Bis(4-chlorobenzoyl)benzene (1,4-CBB)

Anhydrous powdered aluminium chloride (160 g,

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[*] NASA Contract NAS1-18000 with PRC Kentron Inc., Hampton, VA 23666, USA

0032-3861/88/020358-12$03.00

1.2 mol) was added to a stirred solution of terephthaloyl chloride (101.5 g, 0.5 mol) and chlorobenzene (738 g, 6.5 mol). After the exothermic reaction that raised the temperature to 30°C subsided, the solution was heated to 95°C and held for 3 h. Upon cooling, the solution was poured into cold, aqueous hydrochloric acid to precipitate a solid which was isolated by filtration. The cream coloured solid was thoroughly washed with methanol and dried at 100°C in air (90% crude yield). Recrystallization from *N*,*N*-dimethylacetamide (DMAc) afforded a yellow crystalline solid (m.p. 257–258°C) (lit.[7] m.p. 256°C).

Bis(4-chlorophenyl)ketone (4-CPK)

This monomer was obtained commercially (Aldrich Chemical Co., Milwaukee, WI, USA) and was recrystallized from ethanol to yield a white crystalline solid (m.p. 145–146°C).

Bis(4-chlorophenyl)sulphone (4-CPS)

This monomer was obtained commercially (Aldrich Chemical Co.) and was recrystallized from toluene to yield a white crystalline solid (m.p. 147–148°C).

Bis(4-fluorophenyl)sulphone (4-FPS)

This monomer was obtained commercially (Aldrich Chemical Co.) and was recrystallized from ethanol to yield a white crystalline solid (m.p. 98–99°C).

4,4'-Bis(4-fluorobenzoyl)diphenyl ether (4,4'-FBDE)

A solution of diphenyl ether (42.53 g, 0.25 mol) and 4-fluorobenzoyl chloride (79.28 g, 0.50 mol) in methylene chloride (100 ml) was added to a stirred slurry of anhydrous powdered aluminium chloride (83.3 g, 0.63 mol) in methylene chloride (200 ml) maintained at 10–15°C. The resulting solution was allowed to slowly warm to room temperature, stirred ~16 h, and subsequently poured into cold, aqueous hydrochloric acid to produce a gummy solid. The residual methylene chloride was boiled off and the resulting white solid was washed with dilute aqueous sodium bicarbonate and dried. Recrystallization from toluene afforded 4,4'-bis(4-fluorobenzoyl)diphenyl ether as a white crystalline solid (m.p. 213–214°C, 86% yield). Elemental analysis calculated for $C_{26}H_{16}F_2O_3$: C, 75.36%; H, 3.89%; F, 9.17%. Found: C, 75.62%; H, 3.89%; F, 9.08%.

4,4'-Bis(4-fluorobenzoyl)diphenyl methane (4,4'-FBDM)

Anhydrous powdered aluminium chloride (50.0 g, 0.375 mol) was added over a 2 min period to a mechanically stirred mixture of 4,4'-methylenedibenzoyl chloride (43.97 g, 0.15 mol) and fluorobenzene (141 ml, 1.5 mol). The mixture was stirred at room temperature for 1 h, then heated to 70–80°C for 4 h. The reaction mixture was allowed to cool to room temperature and poured into cold aqueous hydrochloric acid. The suspension was distilled to remove excess fluorobenzene. The residual solid was collected by filtration and washed with sodium bicarbonate solution. The crude solid, (61.4 g, 99% yield), was recrystallized from toluene to provide 39.6 g (64% yield) of 1,4-bis(4-fluorobenzoyl)diphenyl methane, m.p. 149.5–150.5°C, as a white solid. Elemental analysis calculated for $C_{27}H_{18}F_2O_2$: C, 78.63%; H, 4.40%; F, 9.21%. Found: C, 78.84%; H, 4.68%; F, 9.08%.

4,4'-Bis(4-fluorobenzoyl)diphenyl ketone (4,4'-FBDK)

Anhydrous powdered aluminium chloride (41.9 g, 0.315 mol) was added over a 2 min period to a mechanically stirred mixture of 4,4'-carbonyldibenzoyl chloride (38.65 g, 0.126 mol) and fluorobenzene (118.9 ml, 1.26 mol). The slurry was stirred at room temperature for 1 h then heated to 70–80°C for 4 h. The reaction mixture was allowed to cool to room temperature and poured into cold aqueous hydrochloric acid. The suspension was distilled to remove excess fluorobenzene. The residual solid was collected by filtration and washed with sodium bicarbonate solution. The crude solid was recrystallized from *N*,*N*-diemthylformamide (DMF) to provide 17.2 g (32% yield) of 1,4-bis(4-fluorobenzoyl)diphenyl ketone, m.p. 291–295°C, as a light yellow solid. Elemental analysis calculated for $C_{27}H_{16}F_2O_3$: C, 76.05%; H, 3.78%; F, 8.91%. Found: C, 76.56%; H, 3.65%; F, 8.73%.

2,6-Bis(4-fluorobenzoyl)naphthalene (2,6-FBN)

Anhydrous powdered aluminium chloride (51.2 g, 0.384 mol) was added during 15 min to a stirred suspension of 2,6-naphthalenedicarboxylic acid chloride (40.49 g, 0.16 mol) (prepared by treatment of 2,6-naphthalenedicarboxylic acid with thionyl chloride and recrystallizing from toluene, m.p. 189–190°C) in fluorobenzene (154 g, 1.60 mol) at 10°C. The suspension was stirred at room temperature for 1 h and at 80°C for 14 h. The organic material remained insoluble so sym-tetrachloroethane (100 ml) was added and the mixture reheated to 80°C for 4 h. The reaction mixture was poured into cold aqueous hydrochloric acid, the water decanted off and the residue washed several times with water. Methanol was added to the oily residue to precipitate a solid which was collected by filtration and dried. The crude solid was first recrystallized from toluene, then from DMF and dried under vacuum at 200°C to afford a light yellow solid (m.p. 258–260°C, 65% yield). Elemental analysis calculated for $C_{24}H_{14}F_2O_2$: C, 77.41%; H, 3.79%; F, 10.20%. Found: C, 77.68%; H, 4.00%; F, 10.32%.

2,6-Di(4-fluorobenzoyl)pyridine (2,6-FBP)

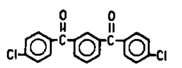
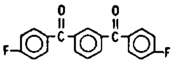
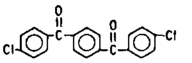
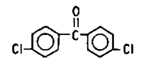
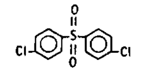
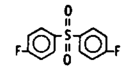
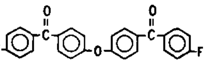
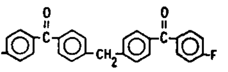
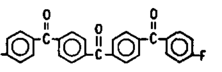
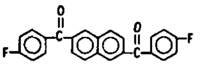
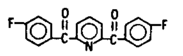
Anhydrous powdered aluminium chloride (116.7 g, 0.875 mol) was added during 30 min to a stirred solution of 2,6-pyridinedicarboxylic acid chloride (Aldrich Chemical Co.) (51.00 g, 0.25 mol) in fluorobenzene (200 g, 2.08 mol) at 5–10°C. The reaction mixture was stirred at room temperature for 1 h followed by heating at 80°C for 4 h. The mixture was added to cold aqueous hydrochloric acid and the excess fluorobenzene subsequently removed by distillation. The residual solid was collected by filtration, washed with water and sodium bicarbonate solution and allowed to dry. The crude solid (78.9 g) was recrystallized twice from toluene to obtain white crystals (m.p. 152–153; 52% yield). Elemental analysis calculated for $C_{19}H_{11}F_2NO_2$: C, 70.59%; H, 3.43%; F, 11.75%; N, 4.33%. Found: C, 70.36%; H, 3.81%; F, 11.48%; N, 4.13%.

The abbreviation for each dihalo monomer used in this study is shown in *Table 1*.

2,2-Bis(4-hydroxyphenyl)propane (BPA)

This monomer was obtained commercially (Aldrich Chemical Co.) and was recrystallized from toluene to

Table 1 Dihalide monomers

Compound	Abbreviation	Recrystallization solvent	Melting point (°C)
	1,3-CBB	Toluene	210.5–211.5
	1,3-FBB	Toluene	178–179
	1,4-CBB	DMAc	257–258
	4-CPK	Ethanol	145–146
	4-CPS	Toluene	147–148
	4-FPS	Ethanol	98–99
	4,4'-FBDE	Toluene	213–214
	4,4'-FBDM	Toluene	149.5–150.5
	4,4'-FBDK	DMF	291–295
	2,6-FBN	Toluene, DMF	258–260
	2,6-FBP	Toluene	152–153

yield a white crystalline solid (m.p. 156–157°C).

1-Methyl-1-phenyl bis(4-hydroxyphenyl)methane (MPHPM)

This monomer was supplied by Mitsui Petrochemical Co., Iwakuni, Japan, and was recrystallized from toluene to yield a white crystalline solid (m.p. 186–187°C).

Bis(3-hydroxyphenyl)methane (3-HPM)

A cold solution of concentrated sulphuric acid (88 ml, 1.58 mol) in ice water (900 ml) was added to bis(3-aminophenyl)methane (39.65 g, 0.20 mol). While the suspension was maintained at 0°C, a solution of sodium nitrite (27.95 g, 0.41 mol) in water (68 ml) was slowly added with stirring. The reaction vessel was maintained in an ice-bath for an additional ~30 min. Afterwards, the entire reaction mixture was slowly added to a boiling mixture of sulphuric acid (270 ml) and water (200 ml). A black oil separated, which was dissolved in a small amount of methylene chloride and dried over magnesium sulphate. The dark oil was vacuum distilled and a yellow solid was recovered. Recrystallization from toluene afforded bis(3-hydroxyphenyl)methane as light yellow needles (m.p. 101–103°C, 30% yield) (lit.[8] m.p. 102–103°C).

Bis(4-hydroxyphenyl)methane (4-HPM)

This monomer was obtained commercially (Aldrich Chemical Co.) and was recrystallized from water to yield a white crystalline solid (m.p. 158–159.5°C).

9,9-Bis(4-hydroxyphenyl)fluorene (9,9-HPF)

9-Fluorenone (135.15 g, 0.75 mol) was reacted with phenol (282.34 g, 3.0 mol) in the presence of a small amount (~2 g) of 3-mercaptopropionic acid at ~50°C with stirring while hydrogen chloride gas was bubbled into the mixture. After 4 h at ~50°C, the reaction mixture became light amber and viscous. The reaction was terminated when a light green solid formed and the mixture became too viscous to stir. The solid was steam distilled and subsequently air dried at ~100°C. This crude product was recrystallized twice from toluene to yield an off-white solid (m.p. 222–223.5°C, ~40% yield) (lit.[9] m.p. 223–224°C).

9,9-Bis(3-methyl-4-hydroxyphenyl)fluorene (9,9-MHPF)

This monomer was prepared by a procedure similar to that for 9,9-HPF using *o*-cresol in place of phenol. The crude product was recrystallized from toluene to afford a light-tan coloured solid (m.p. 214.5–216.5°C, ~55% yield). Elemental analysis calculated for $C_{27}H_{22}O_2$: C, 85.68%; H, 5.86%. Found: C, 85.87%; H, 5.81%.

9,9-Bis(3,5-dimethyl-4-hydroxyphenyl)fluorene (9,9-DMHPE)

This monomer was prepared by a procedure similar to that for 9,9-HPF using 2,6-dimethylphenol instead of phenol. The crude product was recrystallized first from an ethanol–water mixture and then from ethanol to afford a white crystalline solid (m.p. 275–277°C, ~50% yield). Elemental analysis calculated for $C_{29}H_{26}O_2$: C, 84.68%; H, 6.45%. Found: C, 84.91%; H, 6.34%.

1,4-Bis[(4-hydroxyphenyl)-2-propyl]benzene (HPB)

This monomer was supplied by Shell Development Co., Houston, TX, USA, and was recrystallized from toluene to yield a white crystalline solid (m.p. 190–191°C).

1,4-Bis[(4-hydroxy-3,5-dimethylphenyl)-2-propyl]benzene (HDMPB)

This monomer was supplied by Shell Development Co. and was recrystallized from an ethanol–water mixture to yield a white crystalline solid (m.p. 157–158°C).

4,4'-Bis(4-hydroxyphenyl)diphenyl methane (HPDPM)

This monomer was obtained commercially (Applied Silicone Organics, Inc., Bound Brook, NJ, USA) and was recrystallized from mixed xylenes to afford a yellow crystalline solid (m.p. 296–297.5°C).

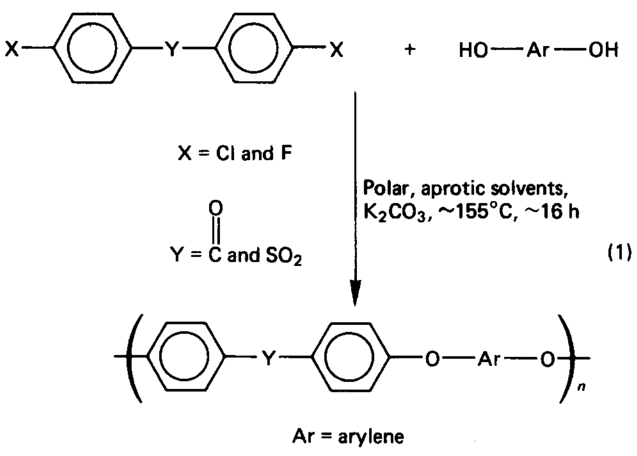
The abbreviation for each bisphenol used in this study is shown in *Table 2*.

4-Ethynylbenzoyl chloride (4-EBC)

This monomer was prepared by a previously reported procedure[10] (m.p. 76–77°C).

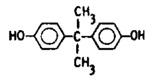
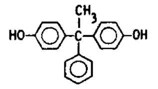
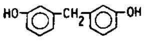
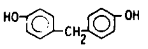
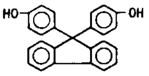
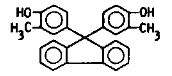
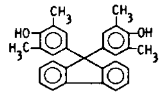
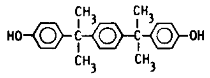
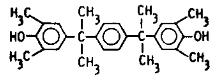
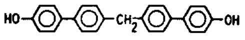
Polymers

The PAEs were prepared as shown in the representative reaction in equation (1) by nucleophilic aromatic substitution using a stoichiometric ratio of monomers, a slight excess of potassium carbonate and DMAc as solvent at 20–25% solids content.



(1)

Table 2 Bisphenols

Compound	Abbreviation	Recrystallization solvent	M.P. (°C)
	BPA	Toluene	156–157
	MPHPM	Toluene	186–187
	3-HPM	Toluene	101–103
	4-HPM	Water	158–159.5
	9,9-HPF	Toluene	222–223.5
	9,9-MHPF	Toluene	214.5–216.5
	9,9-DMHPF	Ethanol/water, ethanol	275–277
	HPB	Toluene	190–191
	HDMPB	Ethanol/water	157–158
	HPDPM	Xylenes	296–297.5

Toluene was used to azeotrope the water formed and the reaction was stirred at ~155°C overnight under a nitrogen atmosphere. The following examples are representative of the synthetic procedure used for polymer preparation. Polymers are represented using the abbreviations of the monomers used in polymer preparation.

(*1,3-CBB/BPA*). 1,3-Bis(4-chlorobenzoyl)benzene (26.642 g, 0.075 mol), 1,1-dimethyl bis(4-hydroxyphenyl)methane (17.122 g, 0.075 mol), and potassium carbonate (25 g, 0.18 mol) in DMAc (175 ml) and toluene (75 ml) were stirred under a Dean–Stark trap in a nitrogen atmosphere. Toluene was used to azeotrope the water formed and the reaction was heated to ~155°C during ~3 h and held at ~155°C for ~16 h. The reaction was allowed to cool to ~80°C, filtered through a sintered glass funnel and neutralized with a 50:50 mixture of acetic acid–DMAc. The polymer solution was poured into water in a blender to precipitate the polymer which was washed successively with water and methanol and subsequently boiled in methanol. An alternative work-up avoided the filtration step by pouring the reaction solution slowly into water containing acetic acid in a blender. The resulting precipitate was successively washed with water and methanol and subsequently boiled in methanol. Drying in air at 100°C for 4 h afforded an off-white polymer in >95% yield. Characterization of the PAEs is presented in *Tables 3–6*.

(*1:1; 1,3-CBB:1,4-CBB/4-HPM random copolymer*). 1,3-Bis(4-chlorobenzoyl)benzene (1.7761 g, 0.005 mol), 1,4-bis(4-chlorobenzoyl)benzene (1.7761 g, 0.005 mol), bis(4-hydroxyphenyl)methane (2.0024 g, 0.01 mol) and potassium carbonate (3.04 g, 0.022 mol) in DMAc (25 ml) and toluene (35 ml) were stirred under a Dean–Stark trap in a nitrogen atmosphere. Toluene was used to azeotrope the water formed and the reaction was heated to ~155°C during ~3 h and held at ~155°C for ~16 h. The dark red reaction mixture was allowed to cool to ~70°C and the polymer precipitated. The reaction mixture was poured into 15% aqueous acetic acid in a blender. The polymer was washed with water and methanol and subsequently boiled in methanol. Drying in air at 100°C for 4 h afforded an off-white polymer in >95% yield. Characterization of arylene ether copolymers is presented in *Table 7*.

Two ethynyl-terminated PAEs were prepared by a

Table 3 Characterization of bisphenol-A based PAEs

Polymer					
Dihalide	Bisphenol	$\eta_{inh}{}^{a}$ (dl/g)	T_g $(T_m)^b$ (°C)	$\bar{M}_n^c$ (g/mol)	Film^d
1,3-CBB	BPA	0.57	152	28 100	Clear, tough, flexible
1,4-CBB	BPA	0.68	166^e	26 950	Clear, tough, flexible
1,3-FBB	BPA	1.23	155	–	Clear, tough, flexible
4,4′-FBDE	BPA	1.41	162	–	Clear, tough, flexible
4,4′-FBDK	BPA	0.32^f	155 (283)	–	Brittle film
4,4′-FBDM	BPA	1.36	155	–	Clear, tough, flexible
2,6-FBN	BPA	1.05^f	185 (220)	–	Clear, tough, flexible
2,6-FBP	BPA	0.17	132	–	Brittle film
4-CPK	BPA	0.59	155	–	Clear, tough, flexible

^{a}Inherent viscosity, 0.5% solution in chloroform at 25°C
^{b}Differential scanning calorimetry at a heating rate of 20°C/min
^{c}Number-average molecular weight by membrane osmometry using chloroform solvent
^{d}Cast from chloroform solution or melt pressed
^{e}Ref. 5a reported a T_g of 165°C
^{f}Inherent viscosity, 0.5% solution in *m*-cresol at 25°C (dissolved hot)

Table 4 Characterization of bis(3- and 4-hydroxyphenyl)methane based PAEs

Polymer					
Dihalide	Bisphenol	η_{inh}^{a} (dl/g)	T_g $(T_m)^b$ (°C)	$\bar{M}_n{}^c$ (g/mol)	Film^d
1,3-CBB	3-HPM	0.39	114	23 150	Clear, tough, flexible
1,4-CBB	3-HPM	0.79	122	27 850	Clear, tough, flexible
4,4'-FBDE	3-HPM	Insoluble	123	–	Clear, tough, flexible
1,3-CBB	4-HPM	0.71	145	–	Clear, tough, flexible
1,4-CBB	4-HPM	0.16^e	120 (275)	–	Opaque, brittle
4,4-FBDE	4-HPM	Insoluble	128 (275)	–	Opaque, brittle

$^{a-d}$See *Table 3*

^{e}Inherent viscosity, 0.5% solution in *m*-cresol at 25°C (dissolved hot)

Table 5 Characterization of 9,9-bis(4-hydroxyphenyl)fluorene based PAEs

Polymer					
Dihalide	Bisphenol	η_{inh}^{a} (dl/g)	T_g $(T_m)^b$ (°C)	$\bar{M}_n{}^c$ (g/mol)	Film^d
1,3-CBB	9,9-HPF	0.95	223	28 300	Clear, tough, flexible
1,4-CBB	9,9-HPF	1.27	243	39 850	Clear, tough, flexible
2,6-FBP	9,9-HPF	0.29	223	–	Clear, brittle
2,6-FBN	9,9-HPF	1.29	252	–	Clear, tough, flexible
4-CPK	9,9-HPF	1.02	252^f	33 800	Clear, tough, flexible
4-CPS	9,9-HPF	0.67^e	280^g	–	Clear, brittle
4,4'-FBDE	9,9-HPF	Insoluble	231 (430)	–	Clear, tough, flexible
1,3-CBB	9,9-MHPF	0.55	217	–	Clear, tough, flexible
1,3-FBB	9,9-MHPF	1.20	218	–	Clear, tough, flexible
1,3-CBB	9,9-DMHPF	0.32	229	–	Clear, brittle
1,3-FBB	9,9-DMHPF	1.24	257	–	Clear, tough, flexible
4-CPS	9,9-DMHPF	0.37	294	–	Clear, brittle
4-FPS	9,9-DMHPF	0.64	310	–	Clear, brittle

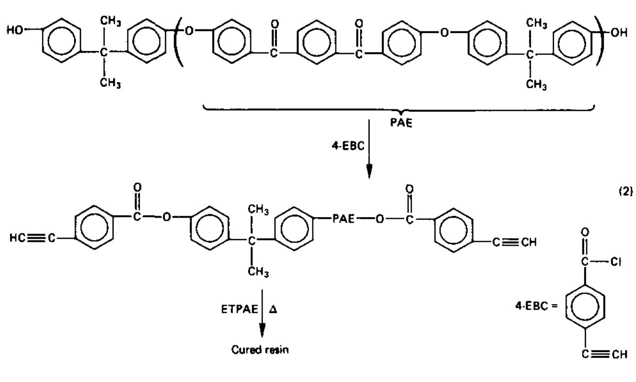
$^{a-d}$See *Table 3*

^{e}Inherent viscosity, 0.5% solution in *m*-cresol at 30°C

^{f}Ref. 5b reported polymer softening temperature of 240°C

^{g}Ref. 5b reported polymer softening temperature of 270°C

previously reported procedure[11]. Hydroxy-terminated PAEs with controlled molecular weight were prepared by offsetting the monomer stoichiometry followed by reaction with 4-ethynylbenzoyl chloride as shown in equation (2).



The following example is representative of the synthetic procedure used to prepare ethynyl-terminated PAEs.

(*Ethynyl-terminated 1,3-CBB/BPA*). 1,3-Bis(4-chlorobenzoyl)benzene (11.563 g, 0.0325 mol), 1,1-dimethyl bis(4-hydroxyphenyl)methane (7.990 g, 0.035 mol), and potassium carbonate (10.65 g, 0.077 mol) were stirred in a mixture of DMAc (55 ml) and toluene (30 ml) under a Dean–Stark trap in a nitrogen atmosphere. Toluene was used to azeotrope the water formed and the reaction was heated to ~155°C during ~3 h and held at 155°C for 16 h. The reaction was cooled to room temperature and filtered through a sintered glass funnel. 4-Ethynylbenzoyl chloride (1.5 g, 0.009 mol) and triethylamine (5 ml) were added and the solution was stirred at room temperature for 2 h. The solution was poured into dilute acetic acid in a blender and the precipitate was successively washed with water and methanol. Drying in air at 100°C afforded an off-white polymer in >90% yield. An alternative approach involved precipitation of the hydroxy-terminated PAE by pouring the reaction mixture into water containing acetic acid in a blender. The precipitate was washed successively with water and methanol and subsequently boiled in

Table 6 Characterization of other PAEs

Polymer				
Dihalide	Bisphenol	η_{inh}^{a} (dl/g)	T_g $(T_m)^b$ (°C)	Film^c
1,3-CBB	HPDPM	0.71	184	Clear, tough, flexible
1,4-CBB	HPDPM	1.07	195	Clear, tough, flexible
1,3-CBB	HPB	0.45	150	Clear, flexible
1,4-CBB	HPB	1.28	168 (207)	Clear, tough, flexible
2,6-FBN	HPB	1.08	185	Clear, tough, flexible
1,3-FBB	HDMPB	1.93	191	Clear, tough, flexible
1,3-CBB	MPHPM	0.59	172	Clear, tough, flexible
1,4-CBB	MPHPM	1.26	189	Clear, tough, flexible

^{a,b}See *Table 3*

^{c}Cast from chloroform solution or melt pressed

Table 7 Characterization of arylene ether copolymers

Polymer		η_{inh}[a]	T_g (T_m)[b]	
Dihalide	Bisphenol	(dl/g)	(°C)	Film[c]
1,3-CBB/1,4-CBB (1:1)	4-HPM (Random)	Insoluble	152	Clear, tough, flexible
1,3-CBB/1,4-CBB (1:1)	4-HPM (Block DP≈4)	Insoluble	150	Clear, tough, flexible
1,3-CBB/1,4-CBB (1:3)	4-HPM (Random)	Insoluble	150 (280)	Clear, tough, flexible
1,3-CBB/1,4-CBB (3:1)	4-HPM (Random)	0.78	145	Clear, tough, flexible
1,4-CBB	BPA/4-HPM (4:1) (Random)	0.62	162	Clear, tough, flexible
4,4'-FBDE	BPA/9,9-HPF (1:1) (Random)	Insoluble	198	Translucent, tough, flexible

[a,b] See *Table 3*

[c] Cast from chloroform solution or melt pressed

Table 8 Characterization of ethynyl-terminated PAEs

Polymer		η_{inh}[a]	T_g[b] (°C)		$\bar{M}_n$[d]	
Dihalide	Bisphenol	(dl/g)	Initial	Cured[c]	(g/mol)	Film[e]
1,3-CBB	BPA	0.24	140	160	8500	Clear, moderately tough, flexible
1,3-CBB	9,9-HPF	0.15	198	233	~4000	Clear, slightly tough, flexible

[a] Inherent viscosity, 0.5% solution in chloroform at 25°C

[b] Differential scanning calorimetry at a heating rate of 20°C/min

[c] After heating to 300°C

[d] Number-average molecular weight by membrane osmometry using chloroform solvent

[e] Solution cast and thermally cured

methanol. After drying at ~100°C, the hydroxy-terminated PAE was dissolved in methylene chloride or dry DMAc and subsequently reacted with 4-ethynylbenzoyl chloride and triethylamine. Characterization of the ethynyl-terminated PAEs is given in *Table 8*.

Films

Chloroform or DMAc solutions (10–20% solids) of the various polymers were centrifuged, the decantate doctored onto plate glass and dried at 45°C to a tack-free form in a dust-proof chamber. The films on glass were stage-dried ~6 h in air to 250°C and held at 250°C for 0.5 h. Mechanical tests were performed according to ASTM D882 on four specimens per test condition. Small-area films of the insoluble polymers were prepared by melt pressing using an induction heater. The polymer powder was placed between two pieces of Kapton®, heated under pressure and held at the desired temperature for 2 min. Kapton was then peeled away from the experimental film. Films of ~1 in^2 were readily prepared in this manner.

Moulded specimens

The polymers were compression moulded in a 1.26 in square stainless steel mould using a hydraulic press equipped with electrically heated platens. The temperature and pressure used depended on the particular polymer sample and varied accordingly. Four compact tension specimens approximately 0.63 x 0.63 x 0.32 in thick were cut from the 1.26 in square mouldings and tested according to a known procedure[12].

Adhesive specimens

Standard tensile shear specimens (bond area 1.26 in wide x 0.5 in overlap) were fabricated from the PAEs and ETPAEs using titanium (6A1-4V) adherends having a Pasa Jell 107 (Products Research and Chemical Corp., Semco Div.) surface treatment. The substrate was primed with a dilute dioxane solution (~5% solids) of the polymer and dried. Unformulated tapes (12 ml thick) were prepared by multiple brush coating of dioxane solutions (20% solids) of each polymer onto 112 E-glass with an A-1100 finish. The final drying cycle was 100°C *in vacuo* for 18 h. Process conditions to fabricate tensile shear specimens are presented in the text. After fabrication, tensile shear specimens were tested according to ASTM D1002.

Composite specimens

Carbon/graphite fabric (F3T 584) was solution coated with a methylene chloride solution (30% solids) of the 1,3-CBB/BPA polymer (η_{inh} = 0.43 dl/g) and dried for 0.5 h at 110°C. Eight plies of the prepreg (volatile content <0.3%) were stacked and cured in an autoclave for 3 h at 177°C under 80 psi. The composite (4 in x 6 in x 0.128 in thick, calculated resin content 41%) was cut into flexural and short-beam shear specimens and tested according to ASTM D790 and D2344, respectively.

Characterization

Inherent viscosities were obtained on 0.5% solutions in chloroform or *m*-cresol at 25°C. Number-average molecular weights ($\bar{M}_n$) were measured by Arro Laboratories, Inc., Joliet, IL, USA, using a membrane osmometer and chloroform solvent. Gel permeation (size exclusion) chromatography (g.p.c.) was performed in chloroform at a flow rate of 1 ml/min using an ultra-Styragel column bank (10^6, 10^5, 10^4, 10^3 Å) and u.v. detector (254 nm). Differential scanning calorimetry (d.s.c.) was performed at a heating rate of 20°C/min with the apparent glass transition temperature (T_g) taken at the inflection point of the ΔT versus temperature curve. Torsional braid analyses (t.b.a.) were conducted at a heating rate of 3°C/min in a nitrogen atmosphere over the temperature range −100 to 300°C. The T_g values were taken at the peak of the damping curves. Thermogravimetric analyses (t.g.a.) were conducted at a heating rate of 2.5°C/min in flowing air and nitrogen. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, USA. Polymer melt viscosity was measured using a Rheometrics System IV rheometer with a parallel plate configuration with the top plate operating in an oscillating mode at different frequencies (0.1 to 100 radians/s) at a temperature > 50°C higher than the T_g of the polymer.

Wide-angle X-ray scattering (WAXS) data was obtained on powder or thin film specimens of the PAEs. With the X-ray diffractometer operated at 45 kV and 40 mA, using copper radiation with a flat sample holder and a graphite monochromator, the intensity of one second counts taken every 0.01 degrees (2θ) was recorded on hard disc for the angular range: 10–40° (2θ). An external α-quartz standard was used in goniometer alignment.

RESULTS AND DISCUSSION

Synthesis

High molecular weight arylene ether homopolymers and copolymers were prepared by the reaction of activated aromatic dihalides and potassium bisphenates in DMAc (or DMSO) at 155°C. Polymer characterization is presented in *Tables 3–7*. The aromatic dihalide reactivity is dependent on both the activating group and the halide to be displaced. It has been reported [5a] that the fluoro group is more easily displaced than the chloro group, and this was seen in our work by the higher inherent viscosities for the polymers prepared from the activated difluoro monomers. However, several high molecular weight poly(arylene ethers) were obtained from the less expensive activated dichloro monomers. The bisphenate reactivity is also important in polymer formation and has been reported to be directly related to the basicity or nucleophilicity[5a].

High molecular weight PAEs were readily formed, except in a few cases. These exceptions were presumably due to reactivity or precipitation due to crystallization prior to the formation of high molecular weight polymer. These exceptions are discussed below. High molecular weight polymers were not obtained from the reaction of 2,6-FBP with BPA or 9,9-HPF. Two preparations of the 2,6-FBP/BPA polymer (see *Table 3*) gave materials with inherent viscosities of only 0.17 and 0.16 dl/g. The 2,6-FBP/9,9-HPF polymer (see *Table 5*) was also of low molecular weight ($\eta_{inh}=0.29$ dl/g). The inability to obtain high molecular weight from 2,6-FBP was surprising since this monomer was of high purity, as indicated by sharp melting, elemental analysis, proton nuclear magnetic spectroscopy and mass spectroscopy. High molecular weight 2,6-FBP/BPA polymer ($\eta_{inh}=0.61$ dl/g) has recently been reported by others[13] using essentially the same polymerization conditions. This difference may be attributed to any one of several factors, such as heating rate, final reaction temperature and time, purity, particle size and quantity of potassium carbonate and the mode of addition of potassium carbonate or the activated dihalide monomer.

In three cases, crystalline polymers (4,4′-FPDK/BPA in *Table 3* and 1,4-CBB/4-HPM and 4,4-FBDE/4-HPM in *Table 4*) precipitated from the DMAc solution at 155°C prior to the formation of high molecular weight. Higher boiling solvents such as *N*-methylpyrrolidinone and diphenylsulphone were also used in the synthesis of these polymers but high molecular polymer may not have formed. High molecular weight was judged by the integrity (flexibility) of melt-pressed films since the polymer was insoluble in common organic solvents, including boiling *m*-cresol. However, the integrity of the film is severely influenced by the degree of crystallinity (more crystalline, more brittle) and therefore this screening test is not a valid indication of high molecular weight polymer.

The 1,3-CBB/9,9-DMHPF polymer in *Table 5* had an inherent viscosity of only 0.32 dl/g. However, the same polymer was prepared in high molecular weight form ($\eta_{inh}=1.24$ dl/g) using the more reactive fluoro monomer (1,3-FBB). The 4-CPS/9,9-DMHPF polymer in *Table 5* was also of low molecular weight ($\eta_{inh}=0.37$ dl/g), presumably due to the lower reactivity of the sterically hindered 9,9-DMHPF. Relatively high molecular weight polymer $\eta_{inh}=0.67$ dl/g) was obtained from the reaction of 4-CPS with the sterically unhindered 9,9-HPF. The 4-CPK/9,9-HPF polymer in *Table 5* was obtained in high molecular weight form ($\eta_{inh}=1.02$ dl/g) whereas problems were encountered in preparing high molecular weight polymer from the reaction of 4-CPK and BPA. In the first attempt, a relatively high molecular weight 4-CPK/BPA polymer ($\eta_{inh}=0.58$ dl/g, see *Table 3*) was obtained. In five additional attempts using monomers from the same source and identical reaction conditions, only low molecular weight polymers were obtained. Low molecular weight polymer ($\eta_{inh}=0.37$ dl/g, see *Table 5*) was obtained from the reaction of 4-CPS and 9,9-DMHPF whereas higher molecular weight polymer ($\eta_{inh}=0.64$ dl/g) was formed using the more reactive difluoro monomer (4-FPS).

Bulky cardo groups such as the fluorene group in polymer backbones can cause a significant increase in the T_g while providing good solubility. This was observed with the PAEs shown in *Table 5*. The effect of methyl substituents *ortho* to the ether connecting group on T_g is evident in comparing the polymers indicated by 1,3-CBB/HPF (no methyl groups), 1,3-FBB/9,9-MHPF (one methyl group) and 1,3-FBB/9,9-DMHPF (two methyl groups) in *Table 5*. The polymer with no methyl substituents, one methyl group *ortho* to the ether oxygen and two methyl groups both *ortho* to the ether oxygen had T_g values of 223, 218 and 257°C, respectively. It was surprising to observe that the T_g for the 1,3-FBB/9,9-MHPF polymer was lower than that of the 1,3-CBB/9,9-HPF polymer. Normally the T_g of the 1,3-FBB/9,9-MHPF polymer would be expected to be in between the T_g values of the 1,3-CBB/9,9-HPF and the 1,3-FBB/9,9-DMHPF polymers. The highest T_g obtained in our work for a linear soluble PAE (4-FPS/9,9-DMHPF in *Table 5*) was 310°C.

The 2,6-FBN and 4,4′-FBDE/9,9-HPF polymers in *Table 5* and the 4,4′-FBDE/1:1 BPA:9,9-HPF random copolymer in *Table 7* precipitated from the stirred DMAc reaction mixture at 155°C in high molecular weight forms. The 4,4′-FBDE/9,9-HPF formed a cake on the bottom of the flask which had a honeycomb-type structure. The polymer was extremely tough and had to

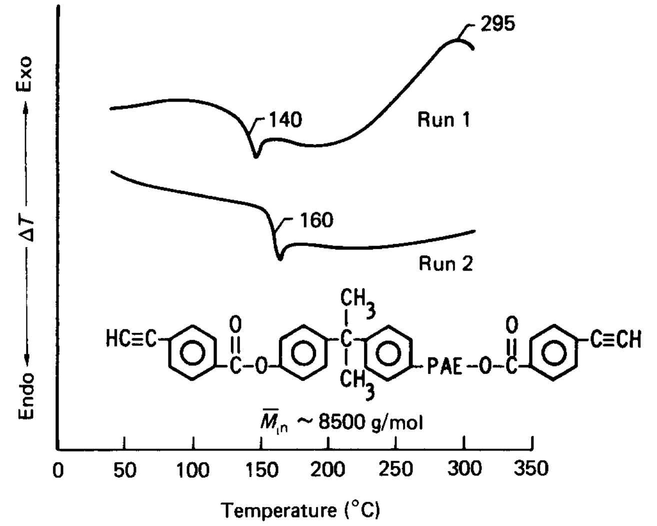


Figure 1 Differential scanning calorimetry. Heating rate: 20°C/min. Atmosphere: static air

be broken into smaller pieces and ground in a Wiley mill to obtain small particle size to effect thorough washing. This polymer was insoluble in warm chloroform, hot DMAc and hot *m*-cresol. Wide-angle X-ray diffractometry showed a low degree of crystalline order. Thermally annealed samples displayed weak endotherms at 430°C in their d.s.c. curves. The copolymer from 4,4′-FBDE and a 1:1 mixture of BPA and 9,9-HPF (see *Table 7*) formed a translucent film. However, wide-angle X-ray diffractometry did not show distinct crystalline order.

PAEs from more unusual bisphenols are listed in *Table 6*. The 1,3-CBB, 1,4-CBB and 2,6-FBN/HPB polymers exhibited T_g values which were about the same as for the corresponding BPA polymers (see *Table 3*). The incorporation of two *para* connected biphenyl moieties (from HPDM) within the polymer repeat unit resulted in a significant increase in T_g relative to the corresponding BPA polymers (see *Table 3*). However, it was surprising that the all *para* 1,4-CBB/HPDPM polymer failed to display any crystallinity. The effect of methyl substituents *ortho* to the ether oxygen on the T_g is again evident. The 1,3-FBB/HDMPB polymer (although of high molecular weight) had a T_g 41 degrees higher than the corresponding unsubstituted 1,3-CBB/HPB polymer. The effect of a bulky pendant phenyl group on T_g is evident in the 1,3-CBB and 1,4-CBB/MPHPM polymers. These polymers had T_g values ~20 degrees higher than the corresponding BPA polymers (see *Table 3*).

Several insoluble arylene ether copolymers, as presented in *Table 7*, were prepared in high molecular weight forms, as evidenced primarily from qualitative film flexibility measurements. Some of these copolymers were synthesized in an attempt to obtain high molecular weight materials in DMAc at 155°C with the intention that subsequent thermal inducement could lead to crystallinity and, accordingly, good solvent resistance. Only one copolymer, 1:3 1,3-CBB–1,4-CBB/4-HPM (random), was readily amenable to crystallization (evidenced by X-ray diffraction and d.s.c.) by thermal inducement at a temperature of ~240°C and without the benefit of hot drawing. The film of this polymer was crystalline and transparent (crystalline regions not large enough to scatter light). Only cursory thermal annealing studies were performed on these polymers. More detailed work may show that crystallinity can be thermally induced into some of the copolymers. The 4,4′-FBDE/1:1 BPA:9,9-HPF random copolymer exhibited a weak endotherm at 300°C in its d.s.c. curve. The intensity of this endothermic peak could be altered slightly by the thermal history. Even after quenching, the peak was evident with no prior exotherm detected due to crystallization. Wide-angle X-ray diffractograms of this polymer having a moderately intense d.s.c. endotherm at 300°C showed no formal order or crystallinity. The nature of this d.s.c. peak remains a mystery.

The ethynyl (acetylenic) group on molecules can serve as a latent reactive group to provide chain extension and crosslinking. Attractive features of acetylene-terminated oligomers include excellent shelf-life, moderate cure temperatures, no volatile evolution and a cured resin with attractive properties. As a result, the ethynyl group has been used to terminate many different types of oligomers[14]. The curing of oligomers and polymers terminated with the ethynyl group results in an increase in solvent resistance but a corresponding decrease in fracture energy[15].

Two ethynyl terminated poly(arylene ethers) (ETPAEs) were prepared and characterized as shown in *Table 8*. The 1,3-CBB/BPA ETPAE was limited to a $\bar{M}_n$ $= 8500$ g/mol. As expected, the inherent viscosity and initial T_g are lower than those of the higher molecular weight linear polymer ($\eta_{inh} = 0.24$ dl/g vs. 0.57 dl/g and $T_g = 140$°C vs. 152°C). As shown in the d.s.c. curves in *Figure 1*, this polymer displayed an exothermic peak at 295°C due to reaction of the ethynyl groups. After heating to 300°C and cooling, the same sample had a T_g of 160°C and was insoluble. A film of the polymer was relatively tough and flexible. The 1,3-CBB/9,9-HPF ETPAE was limited to an $\bar{M}_n \approx 4000$ g/mol and had an initial T_g of 198°C and a T_g of 233°C after heating to 300°C. This material also formed a clear, relatively flexible film.

Wide-angle X-ray diffraction

Besides the wide-angle X-ray diffraction results previously mentioned in the preceding section, diffractograms were obtained on several PAEs thought to display crystallinity.

The wide-angle X-ray diffractogram of the 1,4-CBB/4-HPM low molecular weight polymer is compared to that of commercially available PEEK shown in *Figure 2*. The diffractograms are essentially identical for peak positions but peak intensities are greater for the 1,4-CBB/4-HPM polymer. Apparently this polymer can achieve a higher degree of crystallinity than PEEK due to its lower molecular weight. Furthermore, substitution of the methylene group for a carbonyl or ether group does not appear to change the overall chain packing.

As precipitated from the reaction mixtures, the 1,4-CBB/HPB (see *Table 6*) and the 2,6-FBN/BPA (see *Table 3*) polymers exhibited moderate to strong endotherms at 207 and 220°C respectively, unusually close to their respective T_g at 168 and 185°C. In addition, wide-angle X-ray diffractograms (*Figure 3*) suggested crystallinity or high order. It was thought that these polymers may be liquid crystalline but their chemical structure, melt flow behaviour and appearance under cross-polarized light did not support this assumption. This phenomenenon is apparently due to unstable or transient crystalline or highly ordered states formed under the polymerization

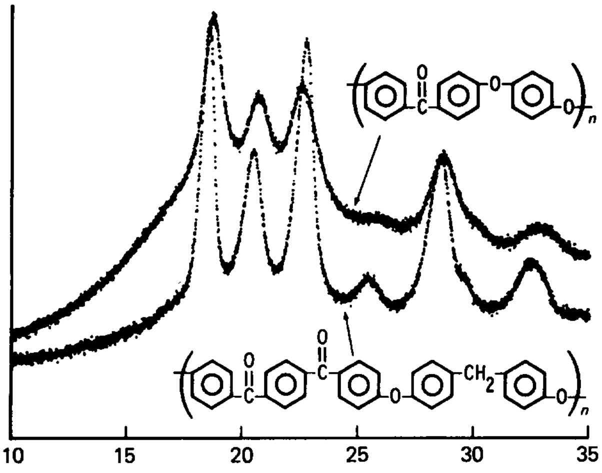


Figure 2 X-ray diffractograms

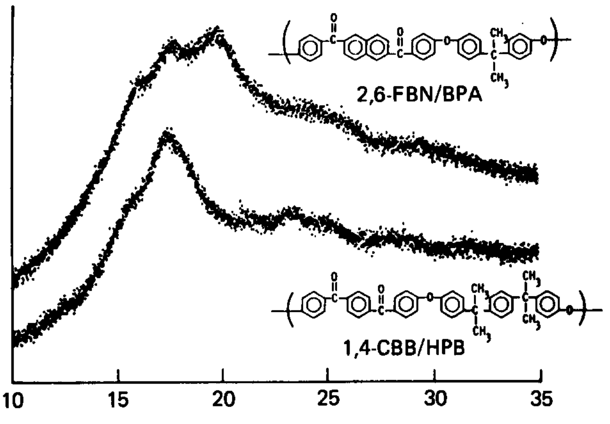


Figure 3 X-ray diffractograms

conditions. When either polymer was heated to a temperature above its respective endotherm and cooled, crystallinity was lost and could not be regained by annealing. In addition, crystallinity could not be recovered by inducement in DMAc.

Gel permeation chromatography

Many of the polymers reported herein were analysed by gel permeation chromatography to obtain molecular weight distributions. Most of the polymers have Gaussian distributions with a small low molecular weight peak presumably due to a small amount of cyclic oligomers. A typical example is the top chromatogram in *Figure 4* of 1,3-CBB/BPA. The middle chromatogram is of 1,3-CBB/4-HPM and has a broader distribution of molecular weight but also has the small low molecular weight peak at about the same relative intensity. The bottom chromatogram is of the 1,3-CBB/3-HPM polymer and is different from any others obtained. The high molecular weight peak is Gaussian, as expected, but there are two peaks at longer retention times which are associated with cyclic oligomers. The peak at 42.24 min is more intense than the corresponding peak on the previous curves (42.10 and 42.20 min). Furthermore, there is a sharp and intense peak at a higher retention time of 43.29 min (lower molecular weight) that is not present in the other chromatograms. This polymer has a repeat unit containing three *meta* linked benzene rings. It is possible to build an essentially strain-free cyclic model of this repeat unit which presumably forms during synthesis and gives rise to the sharp peak at long retention times.

Melt viscosity measurements

The melt viscosity of several PAEs was measured at different temperatures and frequencies (shear rates). *Figure 5* shows the melt viscosity curves for several poly(arylene ethers) measured at various run temperatures (T_0) under different frequencies or shear rates constructed using time–temperature superposition of data. The T_0 varied from 60 to 129°C above the apparent T_g because a few polymers (e.g. 1,3-CBB/MPHPM and 1,3-CBB/9,9-HPF) required higher temperatures to obtain melt viscosity measurements with this particular rheometer. In spite of this variation in T_0, certain conclusions can be drawn. As the substituent on the bisphenol portion of the molecule changed from

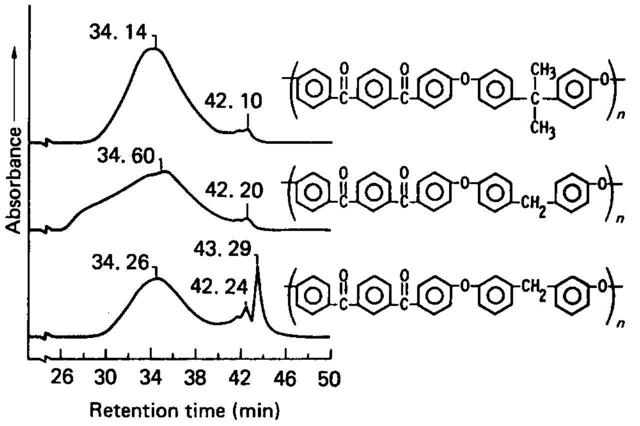


Figure 4 Gel permeation chromatography. Solvent: chloroform. Column: 10^6, 10^5, 10^4, 10^3 Å ultra-Styragel. Flow: 1 ml/min (475 psi). Detector: 254 nm

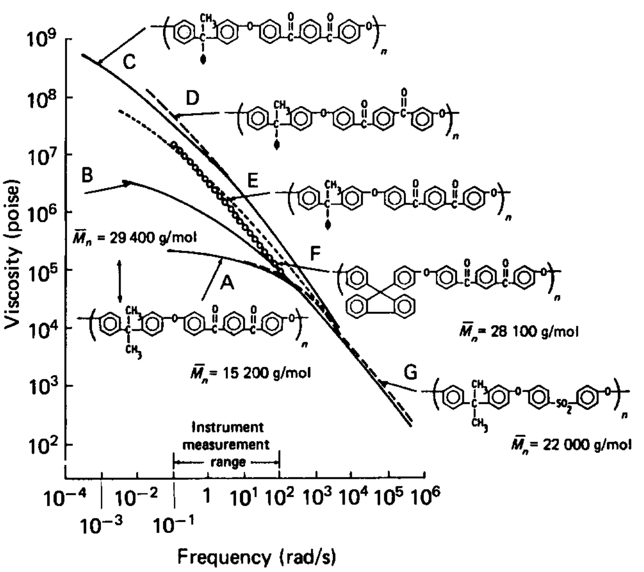


Figure 5 Melt viscosity of thermoplastics. A, $\eta_{inh} = 0.43$ dl/g, $T_g = 152$°C, $T_0 = 230$°C. B, $\eta_{inh} = 0.61$ dl/g, $T_g = 152$°C, $T_0 = 230$°C. C, $\eta_{inh} = 0.59$ dl/g, $T_g = 172$°C, $T_0 = 230$°C. D, $\eta_{inh} = 1.26$ dl/g, $T_g = 189$°C, $T_0 = 310$°C. E, $\eta_{inh} = 0.59$ dl/g, $T_g = 172$°C, $T_0 = 250$°C. F, $\eta_{inh} = 0.95$ dl/g, $T_g = 223$°C, $T_0 = 350$°C. G, $\eta_{inh} = 0.44$ dl/g, $T_g = 190$°C, $T_0 = 240$°C

methyl to phenyl to 9,9-fluorene, the melt viscosity increased significantly. It should be noted that the melt viscosities of the 1,3-CBB/BPA, 1,3-CBB/MPHPM and 1,3-CBB/9,9-HPF polymers were determined at temperatures of 78, 58 and 127 degrees above the respective apparent T_g values. $\bar{M}_n$ values of two of these polymers (1,3-CBB/BPA and 1,3-CBB/9,9-HPF) were similar whereas the inherent viscosity of the 1,3-CBB/MPHPM ($\eta_{inh} = 0.59$ dl/g) was similar to the 1,3-CBB/BPA polymer ($\eta_{inh} = 0.61$ dl/g). This tends to eliminate differences in melt viscosity due to variations in molecular weight. The effect of molecular weight was evidenced in the melt viscosity of two different molecular versions of the 1,3-CBB/BPA polymer ($\bar{M}_n = 29\,400$ and 15 200 g/mol). The lower molecular weight polymer had a melt viscosity essentially one decade lower than the higher molecular weight version. Another lower molecular version of this polymer ($\bar{M}_n = 13\,500$ g/mol) exhibited a melt viscosity curve only slightly lower than the polymer with $\bar{M}_n$ of 15 200 g/mol. No characterization was performed on the samples after the melt viscosity measurements to determine if the molecular weight changed during the run.

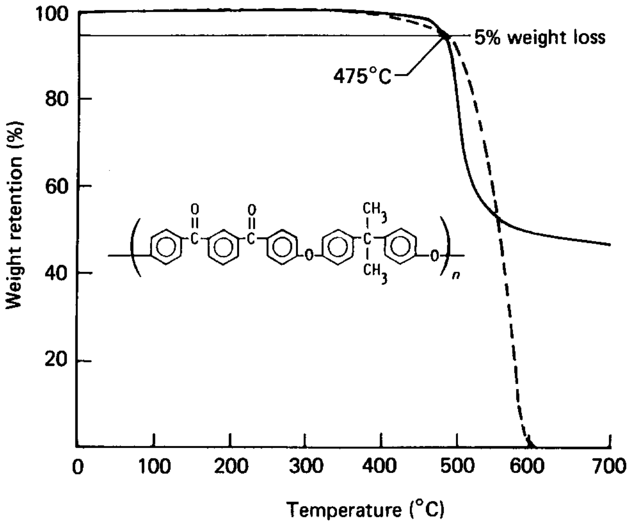


Figure 6 Thermogravimetric analysis. ---, Air; ——, nitrogen

Table 9 Thermogravimetric analysis

Polymer		Temperature (°C) at % weight loss			
		Air		Nitrogen	
Dihalide	Bisphenol	5%	10%	5%	10%
1,3-CBB	BPA	475	505	475	490
1,4-CBB	BPA	455	490	–	–
1,3-CBB	9,9-HPF	482	504	534	549
1,4-CBB	9,9-HPF	456	479	424	431
1,3-CBB	HPDPM	430	467	485	507
4,4'-FBDE	9,9-HPF	413	435	438	469

Thermogravimetric analysis

A representative thermogravimetric analysis curve for the 1,3-CBB/BPA polymer is presented in *Figure 6*. *Table 9* contains the temperature for 5 and 10% weight loss for several polymers. In general, the PAEs exhibited good thermal stability with no weight loss in air below 350°C. Typically, 10% weight loss occurred at ~425 to 500°C in air and ~430 to 550°C in nitrogen.

Mechanical properties

Mechanical properties of films, compact tension specimens and tensile shear adhesive specimens were obtained. Film properties of representative linear PAEs are presented in *Table 10*. Strength and modulus for each of the polymers were good and elongation for the 1,3- and 1,4-CBB/BPA polymers at both 25 and 93°C were excellent. The entire 3 in gauge length for these film specimens elongated and stress crazed, turning opaque. The high elongations are due to crazing which serves as an energy absorption mechanism. These films also exhibited strain hardening (higher strengths with increased strain).

Representative PAEs were compression moulded in a stainless steel mould to provide compact tension specimens for fracture toughness measurements. Fracture toughness for these PAEs, Udel P-1700 and Ultem 1000 are presented in *Table 11*. Fracture toughness values for the 1,3- and 1,4-CBB/BPA polymers are significantly higher than those for the commercial thermoplastics. The failed surface of the 1,3- and 1,4-CBB/BPA specimens was highly crazed and pitted due to yielding, absorbing energy by creating a larger surface area. Even the low molecular weight 1,3-CBB/BPA polymer ($\bar{M}_n = 15\,200$ g/mol) was tougher than the commercial polymers. Both the 1,3-CBB/9,9-HPF and 1,3-CBB/9,9-MHPF polymers had

Table 10 Film properties of PAEs

Polymer							
Dihalide	Bisphenol	$\eta_{inh}{}^a$ (dl/g)	$T_g{}^b$ (°C)	Test temp. (°C)	Tensile strength (Ksi)	Tensile modulus (Ksi)	Elongation (%)
1,3-CBB	BPA	0.57	153	25	12.7	381	136
				93	7.6	340	124
1,4-CBB	BPA	0.68	166	25	12.7	390	145
				93	8.1	349	128
1,3-CBB	9,9-HPF	0.80	220	25	13.5	378	4.6
				93	10.0	349	3.5
				150	6.9	307	2.6
1,3-CBB	HPB	0.45	150	25	9.9	401	2.5
				93	7.1	338	2.6
1,4-CBB	HPB	0.63	165	25	10.2	356	6.9
				93	8.7	334	4.6

[a,b] See *Table 3*

Table 11 Fracture toughness of thermoplastics

Polymer					
Dihalide	Bisphenol	η_{inh}^a (dl/g)	$\bar{M}_n^c$ (g/mol)	Fracture toughness K_{Ic} (psi $\sqrt{in}$)	Fracture energy, G_{Ic} (in-lb/in^2)
1,3-CBB	BPA	0.57	28 100	3700	36
		0.43	15 200	3400	30
1,4-CBB	PBA	0.68	26 950	3800	37
1,3-CBB	9,9-HPF	0.95	28 300	2400	15
1,3-CBB	9,9-MHPF	0.55	–	1950	–
1,4-CBB	HPB	0.63	–	3400	32
Udel® P-1700		0.44	22 000	2600	19
Ultem® 1000		0.49	19 000	3150	23

[a,c] See *Table 3*

Table 12 Adhesive properties of PAEs and ETPAEs

	Tensile shear strength (psi) (failure mode)[a]			
Test condition	1,3-CBB/BPA[b]	ET 1,3-CBB/BPA[c] ($\bar{M}_n = 8500$)	1,3-CBB/9,9-HPF[d]	ET 1,3-CBB/9,9-HPF[e] ($\bar{M}_n \approx 4000$)
Room temp.	5300 (coh)	5700 (coh)	5450 (coh)	4300 (mixed)
93°C	3900 (coh)	4500 (coh)	4550 (coh)	4200 (mixed)
150°C	–	–	3500 (coh)	3800 (mixed)
Room temp. after 72 h H_2 boil	2900 (40% adh)	3900 (coh)	–	–
93°C after 72 h H_2O boil	2400 (40% adh)	–	–	–
Room temp. after 72 h hydraulic fluid	1300 (60% adh)	5400 (coh)	1800 (adh)	4400 (mixed)
93°C after 72 h hydraulic fluid	700 (>80% adh)	4200 (coh)		

[a] Ti/Ti Pasa-Jell 107 surface treatment, 112-A1100 E glass
[b] Room temp.→204°C/50 psi, hold 10 min
[c] Room temp.→177°C/contact pressure, hold 10 min; 50 psi, hold 20 min; 177°C→232°C/50 psi, hold 0.5 h
[d] Room temp.→280°C/100 psi, hold 10 min
[e] Room temp.→250°C/100 psi, hold 0.5 h

Table 13 Preliminary carbon/graphite fabric composite properties of 1,3-CBB/BPA polymer

Test condition	Flexural strength (Ksi)	Flexural modulus (Msi)	Short beam shear strength (Ksi)
25	75.8	7.5	4.1
93	64.3	6.9	3.6

lower fracture toughness than the commercial materials.

The Ti/Ti tensile shear strength for four PAEs was obtained under a variety of test conditions as presented in *Table 12*. The adhesive properties of the ethynyl-terminated 1,3-CBB/BPA polymer were significantly better than those of the corresponding linear polymer after exposure to hydraulic fluid. The ethynyl-terminated 1,3-CBB/9,9-HPF specimens exhibited lower adhesive strengths at room temperature than the linear 1,3-CBB/9,9-HPF polymer, presumably because they were more brittle. However, the ethynyl-terminated 1,3-CBB/9,9-HPF exhibited higher strengths at 150°C than the linear polymer and was unaffected by hydraulic fluid soak.

Preliminary flexural and short-beam shear strengths of carbon/graphite fabric composites of the 1,3-CBB/BPA polymer are reported in *Table 13*. All of the tested specimens exhibited ductile deformation under the bending load and, accordingly, poor and improper failure modes. Based on past experience, the modulus of the 1,3-CBB/BPA polymer (381 Ksi at 25°C) should have been sufficient for translation into better composite properties. Other composites will be fabricated to verify these results.

CONCLUSIONS

A variety of new high molecular weight, amorphous and semicrystalline PAEs were readily prepared which exhibited excellent processability and good mechanical properties. In addition, ethynyl-terminated PAEs were synthesized which exhibited excellent processability, high adhesive properties and good resistance to hydraulic fluid.

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