Synthesis and properties of poly(arylene ether benzimidazole)s*

P. M. Hergenrother, J. G. Smith Jr† and J. W. Connell‡
NASA Langley Research Center, Hampton, VA 23681-0001, USA
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Poly(arylene ether benzimidazole)s were prepared by the aromatic nucleophilic displacement reaction of three new bis[(4-hydroxyphenyl)benzimidazole] compounds with activated aromatic difluoro compounds in *N*,*N*-dimethylacetamide at 155°C in the presence of anhydrous potassium carbonate. The polymers exhibited glass transition temperatures ranging from 264 to 352°C and inherent viscosities from 0.79 to 1.99 $\mathrm{dl\,g^{-1}}$. Unoriented thin films exhibited tensile strengths, moduli and elongations at break at 23°C of 121–157 MPa, 3.7–4.5 GPa and 6–18%, respectively. In most cases the films exhibited 50–60% retention of 23°C tensile properties when tested at 232°C. Based on preliminary evaluation, one polymer was prepared at several different controlled molecular weights and end-capped with a monofunctional benzimidazole compound. The polymer with a calculated number-average molecular weight of $\sim 9700\,\mathrm{g\,mol^{-1}}$ exhibited improved processability without significantly reducing thin-film properties. Composite specimens fabricated at 360°C under 1.4 MPa for 1 h exhibited good flexural and compressive propeties at 23°C and excellent retention of flexural strength and modulus at 232°C.

(Keywords: poly(arylene ether)s; polybenzimidazoles; high-temperature polymers; films; adhesives; composites)

INTRODUCTION

Aromatic polybenzimidazoles (PBIs) are heterocyclic polymers that exhibit high glass transition temperatures, good thermal stability, excellent chemical resistance and high mechanical properties[1]. In general, they are prepared via melt polymerization of aromatic bis(*o*-diamine)s with aromatic diacids or derivatives thereof[2]. Solution polymerization has been performed in polyphosphoric acid[3], sulfolane[4] and diphenylsulfone[4]. Other synthetic routes used to prepare PBIs include the alkoxide-catalysed reaction of aromatic bis(*o*-diamine)s with dinitriles[5] and the reaction of the bis(bisulfite adduct)s of aromatic dialdehydes with aromatic bis(*o*-diamine)s[6].

Commercially available PBI is prepared by melt polymerization of diphenyl isophthalate with 3,3′,4,4′-tetraaminobiphenyl[1]. The polymer was sold during the late 1960s under the name of Imidite 850 as an adhesive and laminating resin[7]. However, owing to its poor processability and relatively high cost, the material eventually disappeared from the marketplace. Currently, PBI can be obtained as a varnish, moulding resin (Celazole®) and fibre[8].

The utilization of high-performance thermoplastics as structural resins has undergone extensive investigation by the aerospace industry. These materials offer an attractive combination of chemical, physical and mechanical properties as well as the potential for low-cost composite fabrication. One class of high-performance thermoplastics that have received considerable attention are the poly(arylene ether)s (PAEs). These polymers are generally prepared by aromatic nucleophilic displacement[9] or electrophilic reactions[10,11]. Other routes used to prepare PAEs include oxidative coupling[12], Ullmann ether synthesis[13], Scholl reaction[14], nickel-catalysed coupling of aromatic chlorides[15] and ring opening of cyclic oligomers[16].

During the past 5 years, a significant effort has been devoted to PAEs containing heterocyclic units (PAEHs). The incorporation of heterocyclic units within PAEs has been observed generally to increase the glass transition temperature, tensile strength and modulus. Two different approaches have been employed to prepare PAEHs via the aromatic nucleophilic displacement reaction. One route concerns the reaction of aromatic difluoro heterocyclic compounds with alkali-metal bisphenates[17]. The heterocyclic ring sufficiently activates the fluoro groups for displacement. The other approach involves the reaction of alkali-metal salts of dihydroxy heterocyclic compounds with activated aromatic difluoro or dichloro compounds[18]. Both approaches afford high-molecular-weight polymers, with the latter route being less expensive and more versatile. Heterocyclic groups that have been incorporated into PAEs include imides[19], phenylquinoxalines[17,18,20], imidazoles[21–23], 1,3,4-oxadiazoles[24,25], 1,2,4-triazoles[24,25], benzoxazoles[26,27], pyrazoles[28,29], benzimidazoles[30,31], *N*-arylenebenzimidazoles[32] and benzothiazoles[25].

The work reported herein details the synthesis, and physical and mechanical properties of poly(arylene ether benzimidazole)s (PAEBIs) synthesized via the nucleophilic displacement reaction of activated aromatic difluorides with three new bis(hydroxyphenylbenzimid-

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† NASA Grant NAG1-448 with the University of Akron

‡ To whom correspondence should be addressed

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azole) monomers in the presence of anhydrous potassium carbonate. Based on results from preliminary evaluation of unoriented thin-film tensile properties, one particular PAEBI was scaled up and evaluated as an adhesive and composite matrix resin. In an attempt to stabilize melt flow and enhance processability, this polymer was prepared at several different controlled molecular weights and end-capped with a monohydroxybenzimidazole compound. The effect of molecular weight on various polymer properties is discussed.

EXPERIMENTAL

Starting materials

4,4′-Difluorobenzophenone (m.p. 104–105°C, Chemical Dynamics Corp.) was recrystallized from absolute ethanol. 4,4′-Difluorophenylsulfone (m.p. 98–99°C, Aldrich Chemical Co.) was recrystallized from absolute ethanol. 1,3-Bis(4-fluorobenzoyl)benzene and the 1,4 isomer (m.p. 178–179°C and 215–217°C, respectively) were prepared as previously described[33]. Phenyl-4-hydroxybenzoate (m.p. 174.5–176.5°C, K and K Laboratories) was recrystallized from toluene. Diphenylsulfone (m.p. 126–128°C, Aldrich Chemical Co.) was recrystallized from methanol, 3,3′,4,4′-Tetraaminobiphenyl (m.p. 180–183°C, Hoechst Celanese Corp.) was recrystallized from water containing sodium dithionite. 3,3′,4,4′-Tetraaminobenzophenone (m.p. 222–224°C, Burdick and Jackson) was recrystallized from water containing sodium dithionite. 3,3′,4,4′-Tetraaminodiphenyl ether was prepared as previously described (m.p. 151–154°C)[34]. 1,2-Diaminobenzene (m.p. 97°C, Aldrich Chemical Co.) was vacuum sublimed. *N*,*N*-Dimethylacetamide (DMAc, 99%, Fluka Chemical Co.) was used as received.

5,5′-Bis[2-(4-hydroxyphenyl)benzimidazole]

A mixture of 3,3′,4,4′-tetraaminobiphenyl (239.5 g, 1.1178 mol), phenyl-4-hydroxybenzoate (483.0 g, 2.2547 mol), diphenysulfone (1300 g) and toluene (350 ml) was heated under a nitrogen atmosphere for ~7 h at ~150°C (reflux condition). The water and/or phenol generated during the reaction were removed as an azeotrope with toluene and collected in a Dean–Stark trap. The toluene was subsequently removed and the temperature increased to ~280°C and maintained for ~1.5 h. Additional water and/or phenol generated during the reaction were removed via the Dean–Stark trap. During this time, the product precipitated from solution (even though the product precipitated from solution, the mixture was stirrable with a magnetic stirring bar). A vacuum (water aspirator) was subsequently applied and the temperature increased to ~300°C and maintained for 2–3 h. Additional phenol was recovered from the reaction mixture (along with diphenylsulfone) and collected in a receiver. When no additional phenol appeared to be liberated from the mixture (evident by more diphenylsulfone being recovered), the heat was removed and the mixture was allowed to cool to room temperature. The cooled yellowish brown reaction mixture was removed from the flask by washing with acetone (several times, ~600 ml each time). The tan solid was washed four times in acetone (~2 litres each time), recovered by filtration and air dried. The solid was subsequently dried at ~280°C for 3 h under vacuum and slowly cooled under vacuum to room temperature to afford a tannish brown powder (409.0 g, 87% yield). Via differential scanning calorimetry (d.s.c.) at a heating rate of $10°C\ min^{-1}$ the m.p. was determined as 389°C (broad). Analysis calculated for $C_{26}H_{18}N_4O_2$: C, 74.63%; H, 4.34%; N, 13.39%; found: C, 73.31%; H, 4.32%; N, 13.26%. The elemental analysis of this compound does not agree with the theoretical amount of carbon, presumably because of its hygroscopic nature.

5,5′-Carbonyl-bis[2-(4-hydroxyphenyl)benzimidazole]

The above compound was prepared in a similar fashion using 3,3′,4,4′-tetraaminobenzophenone. The yellow reaction mixture was washed successively in hot toluene and water and subsequently dried at 110°C to afford a 96% crude yield of a yellow powder, m.p. (d.t.a.) 387°C (broad). The yellow solid was dissolved in DMAc, treated with activated charcoal, filtered and poured into water to afford a yellow precipitate. The solid was dried under vacuum at 245°C to afford a 76% yield of brown solid, m.p. (d.t.a.) 346°C (broad). Analysis calculated for $C_{27}H_{18}N_4O_3$: C, 72.64%; H, 4.06%; N, 12.55%; found: C, 71.96%; H, 4.20%; N, 12.42%.

5,5′-Oxy-bis[2-(4-hydroxyphenyl)benzimidazole]

This compound was prepared in a similar fashion using 3,3′,4,4′-tetraaminodiphenyl ether. The dark reaction mixture was washed in hot toluene and dried at 110°C to afford a dark purple powder (~50% yield). The dark solid was extracted with acetone to afford a 30% yield of a tan solid, m.p. (d.t.a.) 317°C (broad). Analysis calculated for $C_{26}H_{18}N_4O_3$: C, 71.88%; H, 4.18%; N, 12.90%; found: C, 71.91%; H, 4.22%; N, 13.06%.

2-(4-Hydroxyphenyl)benzimidazole

A mixture of 1,2-diaminobenzene (25.17 g, 0.233 mol), phenyl-4-hydroxybenzoate (50.17 g, 0.234 mol), diphenylsulfone (121.15 g) and toluene (100 ml) was heated under a nitrogen atmosphere for 16 h at 150°C. The toluene was removed and the temperature increased to 260°C and maintained for 1.5 h. The warm reaction mixture was precipitated in toluene, washed in hot toluene, and subsequently dried at 110°C to afford 45.00 g (92% crude yield) of a reddish tan powder, m.p. (d.t.a.) 279°C (broad). The solid was recrystallized from 40% aqueous ethanol using charcoal to afford a light tan crystalline product (31.46 g, 64% yield), m.p. (d.t.a.) 280°C (sharp). Analysis calculated for $C_{13}H_{10}N_2O$: C, 74.27%; H, 4.79%; N, 13.32%; found: C, 74.21%; H, 4.75%; N, 13.21%.

Polymers

Poly(arylene ether benzimidazole)s (PAEBIs) were prepared by reacting stoichiometric quantities of the bis(hydroxyphenylbenzimidazole) monomer with an activated aromatic difluoride in the presence of pulverized anhydrous potassium carbonate in DMAc at 18% solids. Toluene was used as an azeotroping agent to remove the water generated. The reaction mixture was stirred at 155–160°C under a nitrogen atmosphere. Depending on the system, the reaction mixture became viscous after 1–3.5 h. The reaction mixture was diluted to ~10% solids with hot DMAc and maintained at 155–160°C. Once the mixture became viscous again (0.5–2 h), it was diluted with hot DMAc to ~7% solids and heating continued for 10–25 min. The reaction mixtures were decanted and the decantates were precipitated into water/acetic acid (10/1), washed successively in hot water and methanol, and subsequently dried at 110°C to afford the polymers in 75–99% yields. The lower yields are due to gel formation during the polymerization, which was removed by decantation.

Molecular-weight-controlled polymers

Controlled-molecular-weight PAEBIs were prepared by reacting an excess of 1,3-bis(4-fluorobenzoyl)benzene with 5,5′-bis[2-(4-hydroxyphenyl)benzimidazole] in the presence of pulverized anhydrous potassium carbonate in DMAc at 18% solids. 2-(4-Hydroxyphenyl)benzimidazole was used to end-cap the polymer and was added at the beginning of the reaction. The water generated during the reaction was removed as an azeotrope with toluene. The reaction mixture was stirred at 155–160°C under a nitrogen atmosphere. Depending on the stoichiometric imbalance, the reaction mixture became viscous after 1–3.5 h. The mixture was diluted to ~10% solids with hot DMAc and the reaction continued. Once the solution became viscous again, the mixture was diluted to ~7% solids with hot DMAc. The reaction solutions were decanted and the decantates were precipitated into water/acetic acid mixture (10/1), washed successively in hot water and methanol, and subsequently dried at 110°C to afford the polymers in 75–99% yields. The lower yields are due to gel formation during the polymerization, which was removed by decantation.

Films

DMAc solutions (7–15% solids) of the polymers were centrifuged, the decantate doctored onto clean, dry plate glass, and dried to a tack-free form in a low-humidity chamber. The films on glass were dried at 100, 200 and ~50°C above their respective glass transition temperatures (T_g) for 1 h at each temperature. Thin-film tensile properties were performed according to ASTM D882.

Moulded specimens

Powdered controlled-molecular-weight end-capped PAEBIs (approximately 10 g) were compression moulded in a 3.2 cm^2 stainless-steel mould by heating to 365°C under 2.4 MPa and held for ~1 h. Miniature compact tension specimens (1.6 cm × 1.6 cm × 0.95 cm thick) were machined from the mouldings and subsequently tested to determine their facture toughness (K_{Ic}, critical stress intensity factor) according to ASTM E399 using four specimens per test condition. G_{Ic} (critical strain energy release rate) was calculated using the mathematical relationship $G_{Ic}=(K_{Ic})^2/E$, where E is the modulus of the material.

Adhesive specimens

Adhesive tape was prepared by multiple coats of 112 E glass with an A-1100 finish secured on a frame with DMAc solutions of controlled-molecular-weight end-capped PAEBIs and subsequently dried to 200°C after each coat. Titanium (Ti)-to-Ti (6 Al–4 V) tensile shear specimens with a Pasa-Jell 107 (Products Research and Chemical Corp., Semco Division) surface treatment were fabricated in a press at 330°C under 1.7 MPa for 0.25 h. Tensile shear strengths were determined according to ASTM D1002 using four specimens per test condition.

Composite specimens

A 25% solids (w/w) solution of the controlled-molecular-weight end-capped PAEBI prepared from 5,5′-bis[2-(4-hydroxyphenyl)benzimidazole] and 1,3-bis(4-fluorobenzoyl)benzene in DMAc was used to coat unsized AS-4 (12K tow) carbon/graphite fibre on a drum winding prepreg machine. The polymer was prepared using a 7 mol% stoichiometric excess of the activated aromatic difluoride and end-capped with 2-(4-hydroxyphenyl)-benzimidazole in order to control the molecular weight and consequently improve melt flow behaviour. The polymer had a T_g of 266°C and an inherent viscosity of 0.55 dl g^{-1}. The solution used to prepare the prepreg had a Brookfield viscosity of 5350 cP at 26°C. The prepreg was initially dried to a tack-free state using heat lamps followed by stage drying to 200°C in a forced air oven. The prepregs had volatile contents of ~3.5% and calculated resin contents of 29–32%. Unidirectional laminates (7.6 cm × 7.6 cm × 10–20 ply) were fabricated in a stainless-steel mould by heating to 360°C under 1.4 MPa and holding for 1 h. The composite panels were ultrasonically scanned (C-scanned) to detect voids, cut into specimens, and tested for flexural properties according to ASTM D790 and compression properties according to ASTM D3410 Procedure B.

Molecular-weight characterization

Weight-average molecular weight ($\bar{M}_w$) measurements were conducted on an LDC/Milton Roy CMX-100 low-angle laser light scattering (l.a.l.l.s.) photometer operating at a wavelength of 633 nm. Specific refractive-index increments were obtained on a Chromatix KMX-16 laser differential refractometer set at 28°C. Gel permeation chromatography (g.p.c.) was performed on a Waters Associates high-performance liquid chromatograph having a bank of Microstyragel™ HT columns (10^3, 10^4, 10^5, 10^6 Å). The chromatograph was equipped with a Waters model 401 refractive-index detector set at 31°C. The analyses were conducted on polymer solutions in DMAc containing 0.0075 M LiBr at a flow rate of 1 ml min^{-1} and a sample size of 100 μl.

Other characterization

Differential thermal analysis (d.t.a.) was performed using a DuPont 990 thermal analyser at a heating rate of 10°C min^{-1}. Differential scanning calorimetry (d.s.c.) was conducted on a DuPont 990 thermal analyser at a heating rate of 20°C min^{-1} with the glass transition temperature (T_g) taken as the inflection point of the ΔT vs. temperature curve. Dynamic thermogravimetric analyses (t.g.a.) were performed on a Perkin–Elmer instrument on powder samples (pre-dried for 0.5 h at 180°C) at a heating rate of 2.5°C min^{-1} in air and nitrogen at a flow rate of 15 cm^3 min^{-1}. Isothermal gravimetric analyses (i.t.g.a.) were performed on a Perkin–Elmer instrument on powder samples, in air at 316°C. Inherent viscosities (η_{inh}) were obtained on 0.5% solutions in DMAc at 25°C. Brookfield viscosity was obtained on a Brookfield LVT Synchro-Lectric viscometer at 26°C using spindle LV3 at 1.5, 3.0, 6 and 12 r.p.m. Wide-angle X-ray scattering (WAXS) was obtained on as-isolated polymer powders and films. The X-ray diffractometer was operated at 45 kV and 40 mA using copper radiation with a flat sample holder and graphite monochromator. The intensity of 1 s 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. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

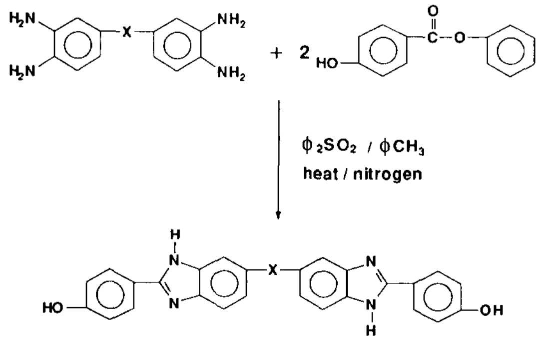
RESULTS AND DISCUSSION

Bis(hydroxyphenylbenzimidazole) compounds

Novel bis[2-(4-hydroxyphenyl)benzimidazole]s were prepared by the reaction of aromatic bis(*o*-diamine)s and phenyl-4-hydroxybenzoate in diphenylsulfone (*Scheme 1*). Initially all of the bis[2-(4-hydroxyphenyl)-benzimidazole]s were recrystallized prior to use in polymer synthesis. It was subsequently determined, using 5,5′-bis[2-(4-hydroxyphenyl)benzimidazole], that simply washing the crude product in acetone was sufficient to obtain polymer-grade material. This greatly improved the yield to ~87% for this compound. The other two bis[2-(4-hydroxyphenyl)benzimidazole]s were obtained in 30–76% yield after recrystallization. Although purification by acetone washing was not attempted for these two compounds, it seems reasonable to assume that this method would produce similar improvements in yields. Elemental analyses for the bis[2-(4-hydroxyphenyl)-benzimidazole]s generally agreed well with theoretical values, with the exception of carbon analysis for the bisphenol containing the nil and carbonyl linkage. This may be due to the hygroscopic nature of the bis[2-(4-hydroxyphenyl)benzimidazole]s. Although broad melting points were observed for these compounds, they provided high-molecular weight polymers as evident by the inherent viscosity data (*Table 1*). Prior to use in polymer synthesis, all of the bis[2-(4-hydroxyphenyl)-benzimidazole]s were dried under vacuum at 250°C for 1 h. The end-capping agent, 2-(4-hydroxyphenyl)-benzimidazole, was prepared from 1,2-diaminobenzene and phenyl-4-hydroxybenzoate and obtained in 64% yield after recrystallization from ethanol and water.

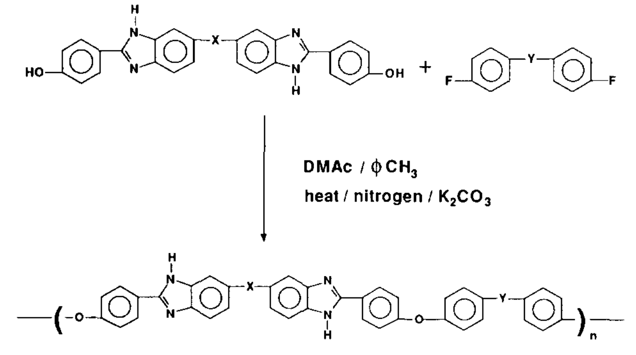
Poly(arylene ether benzimidazole)s

High-molecular-weight polymers were prepared as depicted in *Scheme 2* by the nucleophilic displacement reaction of activated aromatic difluorides and alkali-metal bisphenates of the bis[2-(4-hydroxyphenyl)benzimidazole]s in DMAc at 155°C under a nitrogen atmosphere. Typically, the polymerizations proceeded rapidly, as evident from the increase in solution viscosity of the reaction mixture within 1–3.5 h. Isolated yields of DMAc-soluble polymer were generally >90%.



X = nil, CO, O

Scheme 1



X and Y = See Table 1

Scheme 2

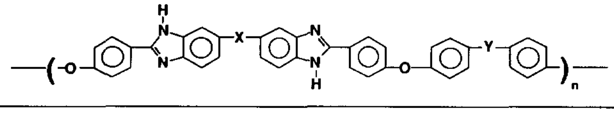
The polymers prepared using exact stoichiometry and stoichiometric imbalances of 1.5 and 3 mol% formed extremely viscous reaction solutions and various amounts of insoluble material (gel). Formation of insoluble gel is presumably due to hot spots in the reaction medium, which form as a result of inefficient heat transfer in the viscous solutions.

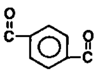
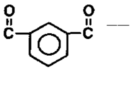
Polymer characterization is presented in *Table 1*. Glass transition temperatures for the as-isolated PAEBI powders ranged from 264 to 352°C and the inherent viscosities ranged from 0.79 to 1.99 dl g^{-1}. The general trend for the T_g values within a series of polymers of comparable molecular weights was sulfone > carbonyl > terephthaloyl > isophthaloyl. This trend has been seen in PAEHs containing other heterocyclic units, such as imidazole[21,22], 1,3,4-oxadiazole[24] and *N*-arylene-benzimidazole[32]. T.g.a. performed on polymers pre-dried to 180°C for 0.5 h showed no weight loss before 300°C, with 5% weight loss occurring at ~450°C in air and ~475°C in nitrogen. The three PAEBIs prepared from 1,3-bis(4-fluorobenzoyl)benzene and the bis[2-(4-hydroxyphenyl)benzimidazole]s were isothermally aged at 316°C for 100 h. The trend for isothermal stability based on weight retention was carbonyl (94.6%) > nil (92.5%) > ether (88.9%).

Since PBIs are known to absorb water because of hydrogen bonding with the benzimidazole ring, it was of interest to investigate the moisture absorption characteristics of the PAEBIs. The moisture absorption of as-isolated polymer powders and thin films were determined at room temperature (~23°C) and 96% relative humidity. The samples were dried under vacuum at ~250°C for 4 h, cooled under vacuum and placed in a desiccator over $CaCl_2$ to cool prior to weighing. The as-isolated polymer powders were exposed to 96% relative humidity for up to 5000 h, with data recorded at various intervals (*Table 2*). The general trend for moisture absorption based on percentage weight gain of the various polymers containing the three bis[2-(4-hydroxyphenyl)benzimidazole]s was carbonyl ⩾ nil > ether (*Table 2*). Sulfone-containing PAEBIs absorbed the greatest amount of water (up to ~8%), while other bridging groups of the activated difluoride were in the 3–6% range.

The moisture uptake of polymer films (1.3 cm × 1.3 cm × ~0.0038 cm) was also determined for up to 500 h at 96% relative humidity (*Table 3*). The trend for the films was similar to that for the powders. The PAEBI films absorbed 3.5–4.5% water by weight. In most cases, the percentage weight loss of these polymers at 300°C

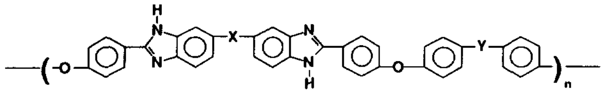
Table 1 Polymer characterization

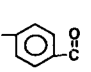
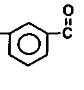


Y	X	η_{inh}[a] (dl g^{-1})	T_g[b] (°C)	Temperature of 5% weight loss[c] (°C) Air	N$_2$
SO$_2$	nil	1.87	352	441	456
	O	1.42	322	435	451
	CO	0.93	ND[d]	422	433
CO	nil	1.11	307	466	502
	O	1.34	294	442	489
	CO	0.93	ND	433	451
	nil	1.19	295	469	520
	O	1.23	282	469	490
	CO	0.79	276	444	478
	nil	1.99	276	476	515
	O	1.79	269	454	499
	CO	1.93	264	467	489

[a] Inherent viscosity measured in DMAc on 0.5% (w/v) solutions at 25°C
[b] Glass transition temperature determined by d.s.c. at a heating rate of 20°C min^{-1}
[c] T.g.a. measured on powdered samples at a heating rate of 2.5°C min^{-1} after preheating sample to 180°C and holding for 0.5 h before analysis
[d] ND = not detected

Table 2 Polymer powder moisture uptake[a]



Y	X	η_{inh}[b] (dl g^{-1})	75 h (%)	500 h (%)	5000 h (%)
SO$_2$	nil	1.87	5.9	6.3	6.8
	O	1.42	2.8	4.5	4.0
	CO	0.93	4.9	6.0	8.1
CO	nil	1.11	4.3	4.6	3.6
	O	1.34	2.6	3.6	3.9
	CO	0.93	4.0	4.6	5.0
	nil	1.19	4.5	4.9	4.9
	O	1.23	2.1	2.7	2.8
	CO	0.79	3.0	3.8	3.8
	nil	1.99	4.0	4.9	5.2
	O	1.79	2.6	3.3	3.3
	CO	1.43	2.7	3.5	3.8

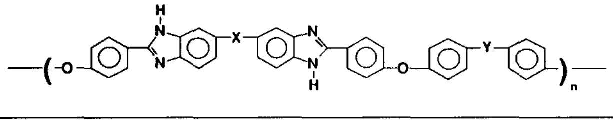
[a] Moisture uptake determined on powders at ~23°C and 96% relative humidity. Samples heated under vacuum at 245°C for 4 h, cooled under vacuum and subsequently placed in desiccator prior to obtaining initial weight
[b] Inherent viscosity measured in DMAc on 0.5% (w/v) solutions at 25°C

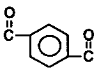
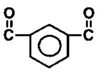
by t.g.a. correlates well with the percentage weight increase observed after 500 h exposure to 96% relative humidity. In comparison, films of poly(arylene ether imidazole)s absorbed ~3–3.5% water by weight[21] and unmodified fibres of commercial PBI absorb ~16% by weight of water[35].

PAEBI films after stage drying to ~50°C above their respective T_g values were insoluble and did not exhibit swelling in DMAc. In addition, the T_g values of the dried films were observed to increase ~7–20°C over that of the as-isolated polymer powders depending on drying temperatures. This increase in T_g may be attributed to either thermally induced crosslinking or molecular ordering.

Unoriented thin-film tensile properties are presented in *Table 4*. Tensile strengths, moduli and elongations at break were in the ranges of 121.4–157.2 MPa, 3.7–4.5 GPa and 6–18%, respectively, at 23°C. In most cases the films exhibited 50–60% retention of room-temperature strengths and moduli when tested at 232°C. For comparative purposes, commercial PBI film ($[\eta]=0.75$ dl g^{-1}), which had been annealed to induce ordering, exhibited tensile strength, tensile modulus and elongation at break of 186.2 MPa, 3.8 GPa and 24%, respectively,

Table 3 Polymer film moisture uptake[a]



Y	X	η_{inh} (dl g^{-1})	T_g (°C)	Weight increase after 500 h exposure[b] (%)	T.g.a. weight loss (%) at 300°C[c]
SO_2	nil	1.87	ND[d]	4.5	5.6
	O	1.42	ND	3.5	4.7
CO	nil	1.11	ND	5.3	4.2
	O	1.34	ND	3.8	4.6
	nil	1.19	ND	3.1	4.2
	O	1.23	301	4.0	3.2
	nil	1.99	309	4.2	3.7
	O	1.79	279	0.9	2.6
	CO	1.43	289	3.2	3.6

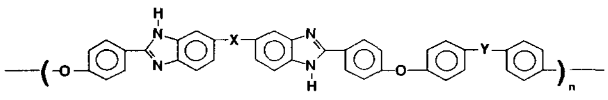
[a] Films held at ~23°C and 96% relative humidity

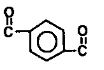
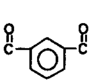
[b] Film samples (1.3 cm × 1.3 cm) were dried at 250°C for 4 h in vacuum prior to analysis, avg. after 500 h

[c] Film samples analysed by t.g.a. at a heating rate of 2.5°C min^{-1}

[d] ND = not detected

Table 4 Unoriented thin-film properties[a]



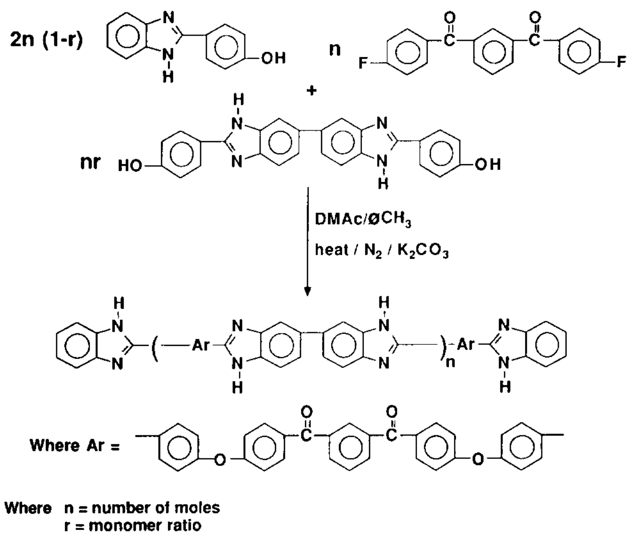
Y	X	η_{inh} (dl g^{-1})	Test temp. (°C)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
SO_2	nil	1.87	23	155.2	4.5	9
			232	102.8	2.6	7
	O	1.42	23	129.7	3.9	8
			232	84.8	2.2	9
CO	nil	1.11	23	157.2	4.5	12
			232	97.2	2.3	20
	O	1.34	23	135.9	4.0	7
			232	77.9	2.0	13
	nil	1.19	23	139.3	4.2	14
			232	80.0	2.2	18
	O	1.23	23	121.4	3.7	18
			232	71.0	1.9	33
	nil	1.99	23	125.5	4.1	14
			232	85.5	2.8	7
	O	1.79	23	126.9	4.1	6
			232	57.2	2.2	6
	CO	1.43	23	135.2	4.2	6
			232	70.3	2.4	4

[a] Films dried at 100, 200 and ~50°C above their respective T_g in flowing air

at room temperature[1]. PAEBIs prepared from 5,5′-carbonyl-bis[2-(4-hydroxyphenyl)benzimidazole] and activated aromatic difluorides containing the carbonyl, sulfonyl or terephthaloyl linkage provided brittle films, even though the inherent viscosities indicated high-molecular-weight polymers. WAXS analyses of these films showed low-intensity reflections due to orientation and/or low levels of crystallinity.

Controlled-molecular-weight end-capped poly(arylene ether benzimidazole)s

Based on preliminary evaluation of physical and mechanical properties, the PAEBI prepared from 1,3-bis(4-fluorobenzoyl)benzene and 5,5′-bis[2-(4-hydroxyphenyl)benzimidazole] was chosen for scale-up and further evaluation. As part of a study to determine the effect of molecular weight on mechanical properties, controlled-molecular-weight end-capped polymers were prepared from 1,3-bis(4-fluorobenzoyl)benzene, 5,5′-bis[2-(4-hydroxyphenyl)benzimidazole] and 2-(4-hydroxyphenyl)benzimidazole (*Scheme 3*) using stoichiometric imbalances of 1.5, 3, 5 and 7 mol%. The effect of molecular weight on some physical and mechanical properties is presented in *Table 5*. Inherent viscosities of the controlled-molecular-weight end-capped polymers ranged from 0.55 to 1.65 dl g^{-1} and the T_g values ranged from 266 to 274°C. The polymer prepared with no stoichiometric imbalance exhibited an inherent viscosity of 1.99 dl g^{-1} and a T_g of 276°C. When polymerizations were performed at exact stoichiometry or using stoichiometric imbalances of 1.5 and 3 mol%, the reaction solution became extremely viscous, resulting in difficult stirring and subsequent hot spots that led to some gel formation. The amount of gel formation was observed to decrease with increasing stoichiometric imbalance (i.e. decreasing solution viscosity). No gel was detected in the polymer prepared using stoichiometric imbalances of 5 and 7 mol% under similar reaction conditions. The temperature of 5% weight loss by t.g.a. for the various controlled-molecular-weight end-capped polymers was ~470°C in air and ~500°C in nitrogen (*Table 5*). The temperature of 5% weight loss by t.g.a. in nitrogen decreased from 515 to 472°C for the polymer prepared using a stoichiometric imbalance of 7 mol%. The temperature of 5% weight loss by t.g.a. in air was unaffected by the stoichiometric imbalance.



Scheme 3

The molecular-weight-controlled end-capped PAEBI prepared using a stoichiometric imbalance of 7 mol% (η_{inh} = 0.55 dl g^{-1}) was analysed by l.a.l.l.s. and g.p.c. to obtain molecular-weight information. The analyses were performed in DMAc containing 0.0075 M LiBr to suppress aggregate formation. Weight-average molecular weights of ~68 000 and ~87 000 g mol^{-1} were obtained by l.a.l.l.s. and g.p.c., respectively. A number-average molecular weight of ~19 000 g mol^{-1} was obtained by g.p.c. The calculated number-average molecular weight for this polymer is ~9700 g mol^{-1}. Polymers that have strong intermolecular association such as hydrogen bonding tend to aggregate in solution and consequently appear to be of higher molecular weight when analysed by g.p.c. and l.a.l.l.s. This would explain the discrepancy between the theoretical and experimentally determined number-average molecular weights. Difficult filtering of the higher-molecular-weight PAEBI solutions, presumably due to the formation of larger aggregates, precluded their analysis.

The controlled-molecular-weight end-capped polymers formed tough creasable films with unoriented thin-film tensile properties presented in *Table 5*. Thin-film tensile properties measured at 23 and 232°C were unaffected for polymers prepared with stoichiometric imbalances up to 7 mol%. The retention of tensile properties for the polymer prepared using a stoichiometric imbalance of 7 mol% is impressive since this polymer has a calculated number-average molecular weight of ~9700 g mol^{-1}. The T_g values for the films after drying in flowing air increased ~10°C over that of the as-isolated polymer powders.

Mouldings of the molecular-weight-controlled end-capped polymers were prepared by heating to 365°C for 1 h under 2.4 MPa. The mouldings were subsequently machined into compact tension specimens and tested for fracture toughness. As the calculated number-average molecular weight of the polymers decreased to ~9700 g mol^{-1}, the fracture toughness (G_{Ic}) dropped from ~1000 to ~475 J m^{-2} (*Table 5*).

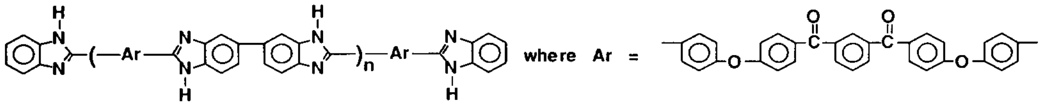
Table 5 Characterization of molecular-weight-controlled PAEBI

Property	Stoichiometric imbalance (mol%) 0	1.5	3	5	7
$\bar{M}_n$ (calculated)	–	46 367	23 008	13 665	9 661
η_{inh} (dl g^{-1})	1.99	1.65	1.42	0.84	0.55
T_g (°C) (powder)	276	274	274	269	266
T_g (°C) (film)	284	287	284	291	273
Temp. of 5% wt loss (air/N$_2$) (°C)	476/515	467/511	467/507	477/510	470/472
Tensile strength (MPa), 23/232°C	125/85	125/81	129/83	118/65.5	114/71
Tensile modulus (GPa), 23/232°C	4.1/2.8	3.6/2.6	4.0/2.8	3.5/2.3	3.6/2.6
Elongation at break (%), 23/232°C	14/7	12/5	30/12	13/8	22/10
G_{Ic} (J m^{-2})	–	860	1 000	–	475

Films of the end-capped PAEBI prepared at 5 mol% stoichiometric imbalance that were dried up to 330°C in air prior to exposure exhibited excellent solvent resistance as shown in *Table 6*. After 167 h (1 week) of submersion in methylene chloride, hydraulic fluid (Skydrol) and jet fuel (Hyjet IV) at ambient temperature, essentially no major change was observed in the tensile properties of the films except for the higher elongation and lower tensile modulus at 232°C of the methylene chloride exposed films. The thin-film tensile properties of the unexposed film are included in *Table 6* for comparative purposes.

In order to assess the effect of film drying atmosphere on physical and mechanical properties, thin films were prepared from the same batch of polymer and dried separately under flowing air and nitrogen (*Table 7*). The T_g of the film dried under nitrogen was 5°C lower than that of the air-dried film, presumably due to more crosslinking in air. In addition, the film dried under nitrogen was lighter in colour (yellow) than the air-dried film (amber). Film dried under a nitrogen atmosphere under similar thermal conditions exhibited essentially the same unoriented thin-film tensile properties at room temperature as air-dried film. The air-dried film exhibited higher tensile strength and modulus at 232°C, but lower elongation. Presumably these results are due to a higher degree of crosslinking upon drying the film in flowing air.

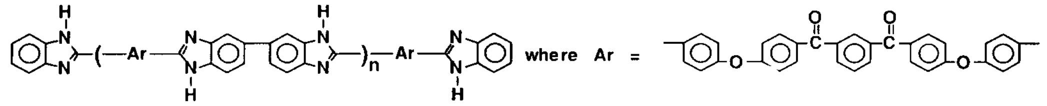
Table 6 Effect of solvent exposure on 5% offset end-capped PAEBI film[a]



Solvent	Test temperature (°C)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
Control	23	117.9	3.46	13
	232	65.5	2.27	8
CH_2Cl_2	23	113.1	3.43	20
	232	64.1	1.71	38
Hydraulic fluid	23	122.1	3.40	15
	232	71.7	2.53	7
Jet fuel	23	117.2	3.62	10
	232	67.6	2.34	8

[a] Films approximately 2.0 mil (50 μm) thick dried to 330°C in air prior to exposure. Immersed in solvent for 167 h at room temperature. Thickness measured before/after exposure revealed no detectable swelling

Table 7 Effect of drying atmosphere on films[a]

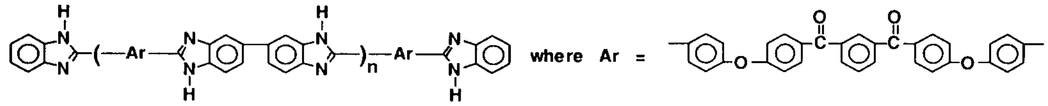


Property	Air	Nitrogen
Colour	Amber	Yellow
T_g (°C) (film)[b]	284	279
DMAc solubility	Insoluble	Insoluble
Tensile strength (MPa), 23/232°C	125.5/82.9	129.6/59.2
Tensile modulus (GPa), 23/232°C	4.1/2.8	4.2/2.1
Elongation at break (%), 23/232°C	47/12	40/96

[a] 3% stoichiometric imbalance, $\bar{M}_n$ (calculated) ~23000 g mol^{-1}, η_{inh} (DMAc, 25°C, 0.5%) = 1.42 dl g^{-1}, T_g (powder) = 274°C

[b] Film cure cycle: 50, 100, 150, 200, 250 for 0.5 h each and 330°C for ~1 h

Table 8 Unoriented thin-film properties after isothermally ageing at 200°C in flowing air[a]



Property	Time (h)		
	0	500	1000
T_g (°C)	274	272	272
Tensile strength (MPa), 23°C	122.8	133.8	127.6
Tensile modulus (GPa), 23°C	3.7	3.6	3.2
Elongation at break (%), 23°C	12	10	9

[a] 7% stoichiometric imbalance, η_{inh} = 0.46 dl g^{-1}, T_g (powder) = 265°C

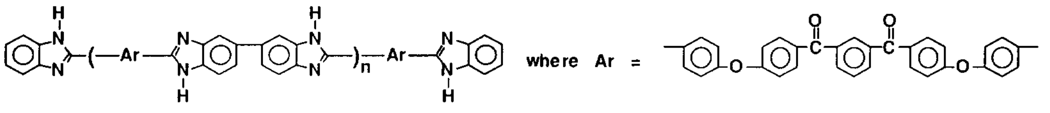
Table 9 Preliminary Ti-to-Ti tensile shear properties after isothermally ageing at 200°C in flowing air[a]

	Exposure time (h)					
	0		500		1000	
Test temperature (°C)	Shear strength (MPa)	Failure mode[b] (%)	Shear strength (MPa)	Failure mode (%)	Shear strength (MPa)	Failure mode (%)
23	22.31	~90 Adh	23.15	~100 Adh	21.21	~100 Adh
177	15.41	~90 Adh	16.82	~90 Adh	17.67	~90 Adh
200	13.92	~80 Adh	17.18	~750 Adh	16.57	~80 Adh
232	11.37	~50 Adh	13.30	~70 Coh	16.11	~70 Coh

[a] 7 mol% molecular-weight-controlled end-capped PAEBI, $\eta_{\text{inh}} = 0.52$ dl g^{-1}, $T_g = 265$°C. Specimens bonded at 1.7 MPa/330°C/0.25 h

[b] Adh, adhesive; Coh, cohesive

Table 10 Preliminary properties of carbon fibre (AS-4) unidirectional composites[a]



Test temp. (°C)	Flexural strength (MPa)	Flexural modulus (GPa)	Resin content[b] (%)
23	1910	135.8	31
23	1607	102.8	35
200	1290	107.6	35
232	1124	100.0	35

[a] 7% stoichiometric imbalance, fabricated at 360°C/1.4 MPa/1 h

[b] Resin content determined by acid digestion using concentrated sulfuric acid and 30% hydrogen peroxide

Unstressed film specimens from the 7 mol% offset PAEBI ($\eta_{\text{inh}} = 0.46$ dl g^{-1}) were aged in flowing air at 200°C for up to 1000 h. The tensile strength of the films measured at 23°C remained unaffected after 1000 h ageing. However, the tensile modulus and elongation at break measured at 23°C decreased ~20% (*Table 8*).

Preliminary titanium adhesive properties are presented in *Table 9*. Ti-to-Ti lap shear specimens from the 7 mol% stoichiometric offset PAEBI were fabricated at 330°C for 0.25 h under 1.7 MPa. The tensile shear strengths of the unaged specimens were lower than anticipated and the failure modes predominantly adhesive. Unstressed tensile shear specimens were aged at 200°C in flowing air for 500 and 1000 h. The tensile shear strengths were unaffected by the isothermal ageing. An increase in shear strength was observed for specimens tested at elevated temperatures (200 and 232°C). The adhesive failures may be an indication of the incompatibility between these polymers and the surface treatment. Adhesive properties for a 3 mol% stoichiometric offset PAEBI were also determined. These tensile shear specimens were fabricated under similar conditions as described above and exhibited similar tensile shear strengths, with good retention of strengths at 232°C. The failure mode for the 3 mol% system was more cohesive as compared to the 7 mol% version. Further work is under way to improve the adhesive properties.

Preliminary carbon-fibre-reinforced unidirectional composite properties for the PAEBI prepared at a 7 mol% stoichiometric offset are presented in *Table 10*. The panels were fabricated at 360°C for 1 h under 1.4 MPa and were void-free as indicated by C-scan. Specimens from the panel that contained 31% resin by weight gave the highest room-temperature flexural properties. Composite specimens from panels with 35% resin content by weight exhibited a reduction in flexural properties at room temperature due to higher resin content. However, the relative retention of room-temperature flexural strength (70%) and modulus (97%) up to 232°C is notable. Compression tests (IITRI) were also performed on composite specimens. Compression strength and modulus measured at room temperature were 1.15 and 115.8 GPa, respectively. Poisson's ratio was 0.318.

CONCLUSIONS

A series of poly(arylene ether benzimidazole)s were prepared by the aromatic nucleophilic displacement reaction of bis(hydroxyphenylbenzimidazole)s with activated aromatic difluorides. The polymers exhibited high unoriented thin-film tensile properties up to 232°C. The thin-film tensile properties of a controlled-molecular-weight end-capped PAEBI were unaffected by solvent exposure. Controlled-molecular-weight end-capped PAEBI exhibited improved processability without reduction in tensile strength or modulus. Adhesive specimens exhibited moderate strengths at room temperature with good retention of strengths to 232°C. Composite specimens processed under 1.4 MPa exhibited good flexural and compressive properties at room temperature and excellent retention of flexural strength and modulus at 232°C.

The use of tradenames of manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

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