Chemistry and properties of imide oligomers end-capped with phenylethynylphthalic anhydrides

P. M. Hergenrother* and J. G. Smith Jr
NASA Langley Research Center, Hampton, VA 23681-0001, USA
(Received 14 February 1994)

A series of phenylethynyl-terminated imide oligomers were prepared by the reaction of aromatic dianhydride(s) with a stoichiometric excess of aromatic diamine(s) at calculated number average molecular weights of 1500–9000 g mol^{-1} and end-capped with phenylethynylphthalic anhydrides in *N*-methyl-2-pyrrolidinone. Unoriented thin films cured in flowing air to 350°C exhibited tensile strengths and moduli of 105.5–139.3 MPa and 2.8–3.2 GPa at 23°C, respectively, with good retention of properties at 177°C. Stressed film specimens exhibited excellent resistance to a variety of solvents after a 2 week exposure period at ambient temperature. One phenylethynyl-terminated imide oligomer was selected for more extensive evaluation and gave high fracture toughness, adhesive and composite properties. The chemistry, physical and mechanical properties of these materials are discussed.

(Keywords: polyimide; oligomers; end-capping)

INTRODUCTION

Aromatic polyimides are thermally stable high performance polymers which are used in a variety of applications[1,2]. The polymers are usually prepared by the reaction of an aromatic diamine with an aromatic dianhydride in a polar aprotic solvent to form a poly(amide acid) precursor. The poly(amide acid) is then chemically or thermally cyclodehyrated to afford the corresponding polyimide[1,2]. In general, the polyimide is often difficult to process by compression or injection moulding owing to its infusible nature. The melt processability can usually be altered by the incorporation of more flexible units such as arylene ether segments within the polymer backbone, by controlling the molecular weight and by end-capping. However, certain properties such as the modulus and glass transition temperature (T_g) are compromised.

As a route to improving the compression mouldability of polyimides, imide oligomers terminated with reactive groups such as maleimide, nadimide, benzocyclobutene, ethynyl and others have been studied[2]. Of particular significance, a variety of imide oligomers and polymers containing phenylethynyl groups have been prepared[3–14]. The phenylethynyl group in these materials is located either pendent to the chain or at the chain ends. Upon thermal cure, the phenylethynyl group undergoes a complex reaction involving chain extension, branching and crosslinking to afford materials exhibiting a favourable combination of physical and mechanical properties. Phenylethynyl-terminated oligomers offer distinct advantages over ethynyl-terminated oligomers, such as a larger processing window and better thermo-oxidative stability of the cured polymer. Imide oligomers and polymers containing phenylethynyl groups have exhibited good processability by either solution casting or compression moulding. The work reported herein concerns the synthesis and preliminary evaluation of imide oligomers end-capped with 4-phenylethynylphthalic anhydride (PEPA) or 4-(4-phenylethynylphenoxy)phthalic anhydride (PEPOPA). This work was performed as part of a larger effort to develop high performance structural resins with an attractive combination of properties for aerospace applications.

EXPERIMENTAL

Starting materials

4-Bromophthalic anhydride (Ameribrom Corp.) was recrystallized from toluene (m.p. 104°C). 4-Bromophenol (Aldrich Chemical Co.) was sublimed prior to use. Phenylacetylene, triethylamine and sulfolane (all Aldrich Chemical Co.) were distilled prior to use. 3,4′-Oxydianiline (3,4′-ODA; Mitsui Petrochemical Ind., Ltd; m.p. 84°C) and 1,3-bis(3-aminophenoxy)benzene (APB; National Starch and Chemical Co.; m.p. 107–109°C) were used as-received. 4,4′-Oxydiphthalic anhydride (ODPA; Occidental Chemical Co.) was recrystallized from acetic anhydride/glacial acetic acid (m.p. 229°C). 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA; Occidental Chemical Co.; m.p. 305–308°C), 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA; Allco Chemical Corp.; m.p. 227°C), 3-aminophenyl-4′-phenylethynylbenzophenone (3-APEB; Daychem Chemical Co.; m.p. 137–139°C) and high purity *N*-methyl-2-pyrrolidinone (NMP; Fluka Chemical Co.) were used as-received.

---

*To whom correspondence should be addressed

0032-3861/94/22/4857-08

4-Phenylethynylphthalic anhydride (PEPA)

A mixture of triethylamine and benzene containing 4-bromophthalic anhydride (455.0 g, 2.004 mol), phenylacetylene (207.5 g, 2.0316 mol), cuprous iodide (0.21 g, 1.10 mmol), triphenylphosphine (1.68 g, 6.41 mmol) and bis(triphenylphosphine) palladium dichloride (0.20 g, 0.29 mmol) was heated at reflux under a nitrogen atmosphere for 24 h. The cooled reaction mixture was filtered to yield a rust coloured solid. The crude solid was washed several times in distilled water and dried under vacuum at 85°C for 3 h to afford 361.8 g (73% crude yield) of a light-tan powder, m.p. (by d.s.c., 20°C min^{-1}) peak at 152°C (sharp). The crude product was recrystallized from 1:1 toluene/hexane and dried under vacuum at 75°C for 3 h to afford 327.2 g (67% yield) of an orange crystalline solid, m.p. (d.s.c., 20°C min^{-1}) peak at 152°C (sharp).

Analysis calculated for $C_{16}H_8O_3$: C, 77.42%; H, 3.25%; found: C, 77.12%; H, 3.14%. Mass spectroscopy: (*m*/*e*) 248.0, calculated molecular weight: 248.24 g mol^{-1}.

4-(4-Bromophenoxy)phthalic anhydride

A mixture of 4-bromophenol (21.70 g, 0.125 mol), 4-fluorophthalic anhydride (22.90 g, 0.138 mol) and potassium fluoride (11.10 g, 0.19 mol) in sulfolane (142 g, 22% w/w) was heated at 165–170°C for 10.5 h under nitrogen. The cooled light brown mixture was poured into water to precipitate a solid that was collected by filtration. The crude solid was subsequently washed in water and dried under vacuum at 75°C to afford 35.1 g (88% crude yield) of a light orange powder, m.p. (d.s.c., 20°C min^{-1}) peak at 104°C (broad). The crude product was recrystallized from 2.6:1 cyclohexane/benzene to afford 27.0 g (67% yield) of a light orange powder, m.p. (d.s.c., 20°C min^{-1}) peak at 106°C (sharp).

Analysis calculated for $C_{14}H_7O_4Br$: C, 52.69%; H, 2.21%; Br, 25.04%; found: C, 52.09%; H, 2.23%; Br, 25.32%. Mass spectroscopy: (*m*/*e*) 319.9, calculated molecular weight: 319.12 g mol^{-1}.

4-(4-Phenylethynylphenoxy)phthalic anhydride (PEPOPA)

The preparation of PEPOPA was similar to that of PEPA using 4-(4-bromophenoxy)phthalic anhydride. The crude solid was dried under vacuum at 115°C for 3 h to afford a 33% yield of a brown powder, m.p. (d.s.c., 10°C min^{-1}) peak at 199°C (broad). The crude product was recrystallized from 1:1 toluene/hexane and dried at 105°C under vacuum for 2 h to afford a 29% yield of a light tan powder, m.p. (d.s.c., 20°C min^{-1}) peak at 202°C (broad).

Analysis calculated for $C_{22}H_{12}O_4$: C, 77.64%; H, 3.55%; found: C, 76.80%; H, 3.66%. Mass spectroscopy: (*m*/*e*) 339.9, calculated molecular weight: 340.34 g mol^{-1}.

N-*(4-Phenylethynylbenzoyl-4′-phenoxy-4″-phenyl)-4-phenylethynylphthalimide*

A mixture of PEPA (16.75 g, 0.068 mol) and 3-APEB (26.28 g, 0.068 mol) in glacial acetic acid (400 ml) was stirred at ambient temperature for ~24 h under a nitrogen atmosphere. The mixture was subsequently heated at reflux for ~24 h under a nitrogen atmosphere. As the reaction mixture cooled the product precipitated from solution. The crude solid was collected by filtration, washed in water and dried under vacuum at 100°C to afford 38.1 g (91% crude yield) of an off-white powder, m.p. (d.s.c., 20°C min^{-1}) peak at 167°C (broad). The crude product was recrystallized from glacial acetic acid to afford 35.8 g (86% yield) of an off-white powder, m.p. (d.s.c., 20°C min^{-1}) peak at 173°C (sharp).

Analysis calculated for $C_{43}H_{25}NO_4$: C, 83.35%; H, 4.07%; N, 2.26%; found: C, 82.81%; H, 4.06%; N, 1.95%.

Phenylethynyl-terminated imide oligomers

Imide oligomers of calculated number average molecular weights ($\bar{M}_n$) of 1500, 5000, 6000 and 9000 g mol^{-1} were prepared by reacting an excess of the appropriate diamine(s) with an appropriate quantity of the dianhydride(s) in NMP at 15–30% solids content. The phenylethynylphthalic anhydride end-capper was added at the beginning of the reaction. The reaction mixture was stirred for ~24 h at ambient temperature under a nitrogen atmosphere. A portion of the amide acid solution was used to cast unoriented thin films. Toluene was subsequently added to the remaining solution and the mixture heated to ~155°C for ~16 h under a nitrogen atmosphere. The water generated from the cyclodehydration of the amide acid to the imide was removed as an azeotrope with toluene. The imide oligomer generally precipitated from solution. The cooled reaction mixture was poured into water to precipitate a solid that was washed successively in hot water and methanol and subsequently dried at 240°C under vacuum for 4 h to afford the oligomers in >95% yields.

Films

NMP solutions (~15% solids) of the phenylethynyl-terminated amide acid oligomers 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 in flowing air at 100, 225 and 350°C for 1 h each. Thin film tensile properties were determined according to ASTM D882. Solvent resistance was determined on stressed (0.5 cm × 5.1 cm × 0.005 cm) film strips immersed in various solvents for 2 weeks at ambient temperature. The specimens were secured in a circular form by multiple wraps around a standard paper clip. Thin film tensile properties of stressed films exposed to various solvents for 1 week at ambient temperature were determined according to ASTM D882. A twisted configuration was applied to the secured specimens which induced a calculated stress of ~11.7 MPa based on uniform twists in the specimens.

Moulded specimens

Powdered imide oligomers (approximately 8.5 g) were compression moulded in a 3.2 cm^2 stainless steel mould by heating to a temperature of 350°C under 1.0–1.4 MPa and holding 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 fracture toughness (K_{Ic}, critical stress intensity factor) according to ASTM E399 using four specimens per test condition. Fracture energy (G_{Ic}, critical strain energy release rate) was calculated using the mathematical relationship, $G_{\text{Ic}} = (K_{\text{Ic}})^2/E$, where E is the tensile modulus of the material.

Adhesive specimens

Adhesive tape was prepared by applying multiple coats on 112 E glass (A-1100 finish) of a 16% solids (w/w) NMP solution of the amide acid oligomer ($\bar{M}_n = 9000\ \mathrm{g\ mol^{-1}}$) and subsequently stage-drying to 250°C after each coat. The volatile content of the adhesive tape was ~1%. Titanium (Ti)-to-Ti (6Al-4V) tensile shear specimens with a Pasa-Jell 107 (Products Research and Chemical Corp., Semco Division) surface treatment were fabricated in a press by heating to 350°C under 0.7 MPa and holding at 350°C under 0.7 MPa for 1 h. Tensile shear strengths were determined according to ASTM D1002 using four specimens per test condition.

Composite specimens

A 30% solids (w/w) NMP solution of amide acid oligomer ($\bar{M}_n = 9000\ \mathrm{g\ mol^{-1}}$, inherent viscosity, $\eta_{inh} = 0.46\ \mathrm{dl\ g^{-1}}$) with a Brookfield viscosity of 5.2 Pa s at 27°C was used to coat unsized IM-7 carbon/graphite fibre on a tape machine to afford unidirectional prepreg with a volatile content of 7–9%. Unidirectional laminates were fabricated in a stainless steel mould by heating to 350°C under 1.4 MPa and holding for 1 h. The composite panels were ultrasonically scanned (C-scanned), cut into specimens, and tested for flexural properties according to ASTM D790 and short beam shear strength according to ASTM D2344.

Other characterization

Inherent viscosities (η_{inh}) were obtained on 0.5% solutions in NMP or *m*-cresol at 25°C. D.s.c. was conducted on a Shimadzu DSC-50 thermal analyser at a heating rate of 20°C min^{-1} with the melting point taken at the minimum of the endothermic peak (T_m) and with the glass transition temperature (T_g) taken at the inflection point of the ΔT *versus* temperature curve. Dynamic thermogravimetric analyses (t.g.a.) were performed on a Seiko 200/220 instrument on powder samples at a heating rate of 2.5°C min^{-1} in air. Brookfield viscosity was obtained on a Brookfield LVT Synchro-Lectric viscometer at 27°C. Mass spectroscopy was performed on a Finnigan 4500 GC/MS instrument operating in the solid probe mode. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

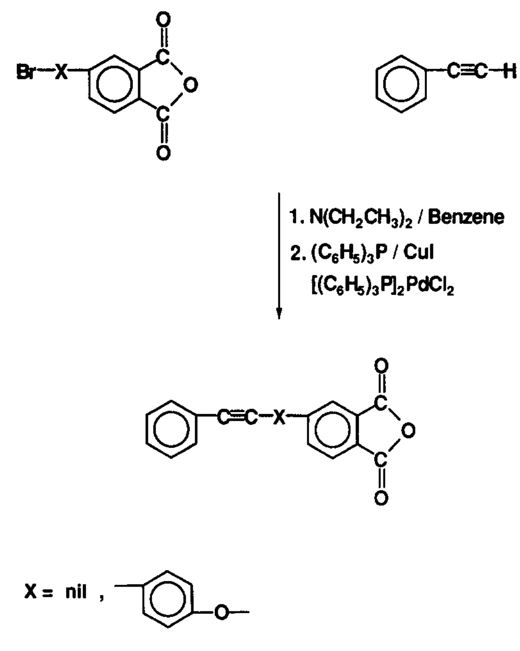
RESULTS AND DISCUSSION

Phenylethynyl anhydrides

PEPA was obtained in one step from the palladium-catalysed reaction of 4-bromophthalic anhydride and phenylacetylene in 67% yield after recrystallization (*Scheme 1*). D.s.c. measurements (heating rate 20°C min^{-1}) showed that the exothermic onset and peak maximum due to the reaction of the phenylethynyl group occurred at ~350 and 404°C, respectively. PEPOPA was prepared in two steps from 4-fluorophthalic anhydride in ~20% overall yield. It is postulated that the yield can be improved significantly by optimization of the reaction conditions. D.s.c. measurements (heating rate 20°C min^{-1}) showed that the exothermic onset and peak maximum due to the reaction of the phenylethynyl group occurred at 388 and 421°C, respectively. As a comparison, 3-(3-phenylethynylphenoxy)aniline exhibited a lower exothermic onset and a lower peak maximum than 3-phenylethynylaniline[8].

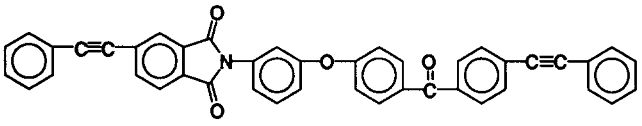
Model compound

A model compound (chemical structure in *Table 1*) containing two phenylethynyl groups was prepared from 3-APEB and PEPA in 86% yield. As the heating rate of samples in the d.s.c. was increased from 2 to 50°C min^{-1}, the exothermic onset and peak temperatures due to the reaction of the phenylethynyl group increased as shown in *Table 1*. The exothermic peak temperature increased from 351°C (at a heating rate of 2°C min^{-1}) to 424°C (at a heating rate of 50°C min^{-1}) as shown in *Figure 1*.



Scheme 1

Table 1 Exothermic onset and peak maxima for *N*-(4-phenylethynylbenzoyl-4′-phenoxy-4″-phenyl)-4-phenylethynylphthalimide



Heating rate[a] (°C min^{-1})	Exothermic temperatures (°C)	
	Onset	Peak maximum
2	325	351
5	329	372
10	359	383
20	361	405
50	363	424

[a] Determined by d.s.c.

Phenylethynyl-terminated imide oligomers

Phenylethynyl-terminated amide acid oligomers with calculated $\bar{M}_n$s of 1500–9000 g mol^{-1} were prepared by the reaction of an aromatic dianhydride(s) with a stoichiometric excess of an aromatic diamine(s) and end-capped with phenylethynylphthalic anhydrides in NMP (*Scheme 2*). The η_{inh} of the amide acid oligomers ranged from 0.13 to 0.53 dl g^{-1} (*Table 2*). The amide acid oligomers were subsequently thermally cyclodehydrated to the corresponding phenylethynyl-terminated imide oligomers in solution. The water by-product was removed by azeotropic distillation with toluene. During the imidization process, the imide oligomers precipitated

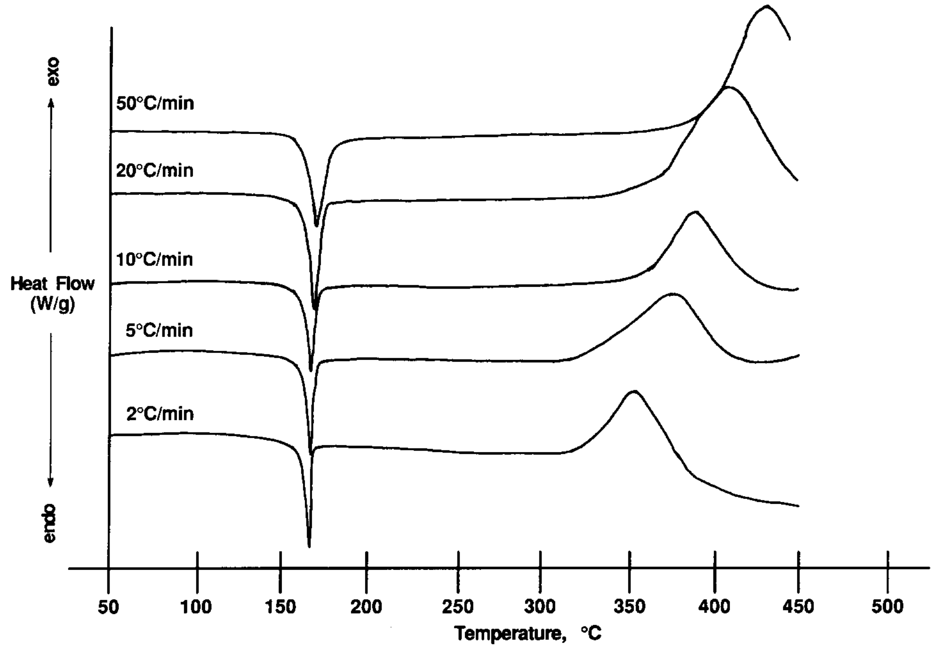
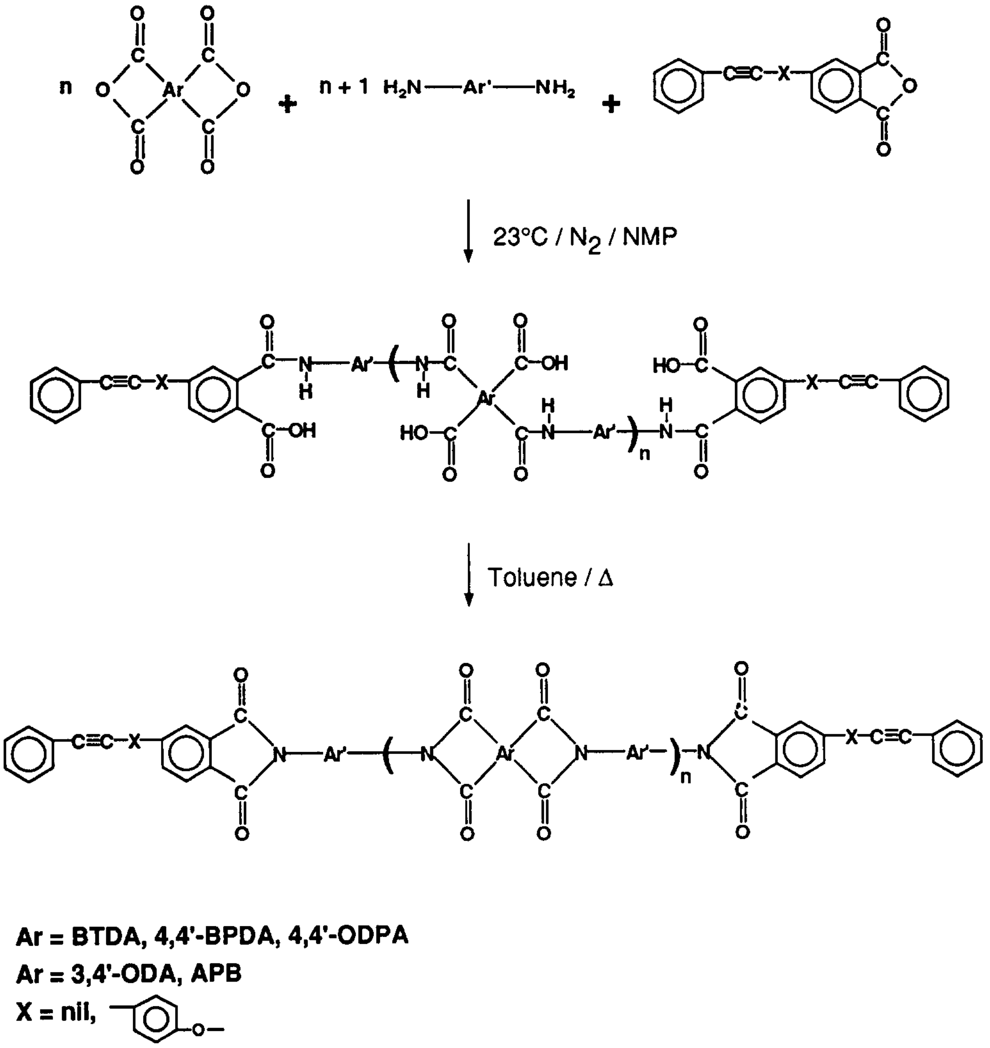


Figure 1 Differential scanning calorimetric curves of *N*-(4-phenylethynylbenzoyl-4′-phenoxy-4″-phenyl)-4-phenylethynylphthalimide



Scheme 2

Table 2 Oligomer and polymer characterization

Imide[a]	$\bar{M}_n$ ($g\,mol^{-1}$)	η_{inh} ($dl\,g^{-1}$)[b]		T_g (T_m) (°C)		Temp. of 5% weight loss (°C)	
		Amide acid	Imide	Imide[c]	C-Imide[d]	Imide[c]	C-Imide[d]
1	9000	0.47	0.27*	222 (291, 326)	243	489	516
1	5000	0.31	0.19*	211 (268, 329)	237	508	513
2	9000	0.47	0.43	232 (277)	256	493	515
3	9000	0.43	0.38	229	263	487	521
3	6000	0.32	0.33	220	267	505	528
3	5000	0.29	0.28	221	250	513	512
4	9000	0.49	0.36*	225 (323)	264	486	494
5	9000	0.53	–	217 (279, 325)	246	487	502
6	5000	0.27	0.28*	210 (286)	249	505	503
7	1500	0.13	–	262 (351)	275	451	470

[a] Imide-1, ODPA/3,4'-ODA/PEPA; imide-2, 3:1 ODPA:BPDA/3,4'-ODA/PEPA; imide-3, 1:1 ODPA:BPDA/3,4'-ODA/PEPA; imide-4, 1:3 ODPA:BPDA/3,4'-ODA/PEPA; imide-5, ODPA/3,4'-ODA/PEPOPA; imide-6, BPDA/(.85)3,4'-ODA:(.15)APB/PEPA; imide-7, BTDA/3:1 3,4'-ODA:APB/PEPA

[b] Inherent viscosity determined on 0.5% (w/v) NMP solution at 25°C or, for those marked by asterisk, on 0.5% (w/v) *m*-cresol solution at 25°C

[c] T_g and T_m of as-isolated oligomers by d.s.c. at a heating rate of $20°C\,min^{-1}$

[d] Powdered samples after hold at 350°C for 1 h in static air

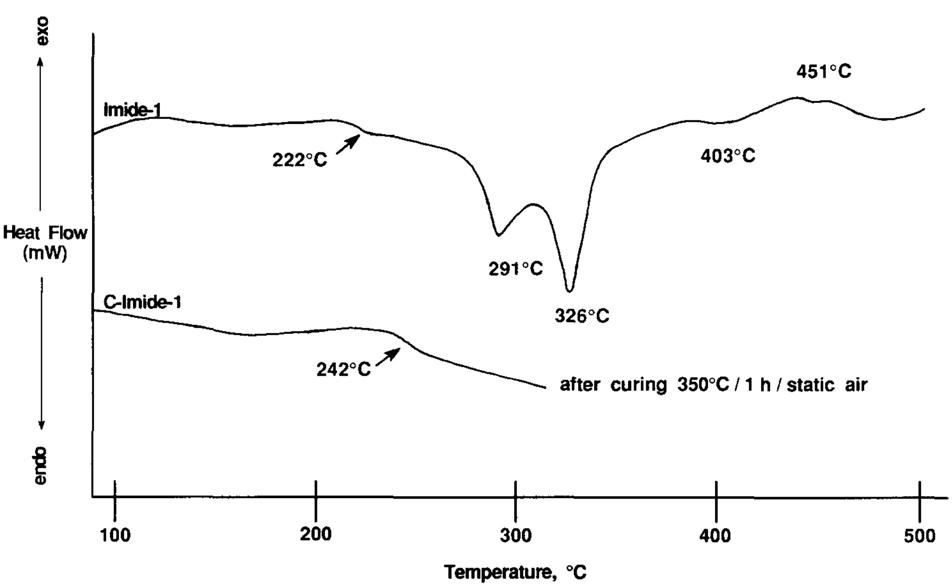


Figure 2 Differential scanning calorimetric curves of imide-1

from solution with the exception of imide-2 and imide-3 (*Table 2*). The imide-2 and imide-3 oligomers which were prepared from a 3:1 and a 1:1 molar ratio of ODPA:BPDA, respectively, were readily soluble in NMP at room temperature and had η_{inh} ranging from 0.28 to $0.43\,dl\,g^{-1}$ (*Table 2*). Imide-1, imide-4 and imide-6 oligomers were soluble in hot *m*-cresol and had η_{inh} ranging from 0.19 to $0.36\,dl\,g^{-1}$ while the imide-5 and imide-7 oligomers were only partially soluble in *m*-cresol.

The T_gs of the as-isolated powders of the imide oligomers ranged from 210 to 262°C (*Table 2*). The d.s.c. thermograms of several of the as-isolated powders of the imide oligomers contained melting exotherms (T_ms) which disappeared upon curing. On the initial d.s.c. scan to 500°C (heating rate $20°C\,min^{-1}$), the initial T_g for the imide-1 oligomer was 222°C. The exothermic onset and peak due to the reaction of the phenylethynyl group occurred at 403 and 451°C, respectively (*Figure 2*). Under actual processing conditions the imide oligomers were observed to be fully cured after a hold at 350°C for 1 h in static air or under vacuum. The imide-1 oligomer cured for 1 h at 350°C in a sealed d.s.c. pan had a T_g of 242°C (*Figure 2*). After the initial cure, the sample was post-cured at 375°C for 1 h which resulted in no change in the T_g. However, a post-cure at 400°C for 1 h (after an initial cure at 350°C for 1 h) resulted in an increase of ~20°C in the final T_g.

The effect of heating rate upon the thermal transitions of the imide oligomers was evaluated with d.s.c. (*Table 3*). As the heating rate was increased from 5 to $50°C\,min^{-1}$ for the imide-6 oligomer, the initial T_g, T_ms and the exothermic onset and peak temperatures increased. The initial T_g increased from 203 to 218°C and the exothermic onset increased from 358 to 413°C when the heating rate was increased from 5 to $50°C\,min^{-1}$. A similar change in the exothermic onset was observed for *N*-(4-phenylethynylbenzoyl-4'-phenoxy-4''-phenyl)-4-phenylethynylphthalimide as previously discussed. The

T_g of the imide-6 oligomer cured at 350°C for 1 h in a sealed d.s.c. pan decreased from 263 to 249°C when the heating rate was increased from 5 to 20°C min^{-1}.

The cured imide oligomers, designated as C-imides, exhibited T_gs ranging from 237 to 275°C (*Table 2*) after curing at 350°C for 1 h in a sealed d.s.c. pan. The T_g for C-imide oligomers of similar $\bar{M}_n$ increased with increasing BPDA content. The C-imides from the 5000 g mol^{-1} imide oligomers exhibited T_gs lower than those of the corresponding 9000 g mol^{-1} materials (*Table 2*). Similar behaviour has been observed for other C-imide oligomers[9]. The temperature of 5% weight loss in air as determined by t.g.a. was ~490°C for the as-isolated imide oligomers and ~507°C for the C-imides.

The imide oligomer prepared from 3,4′-ODA and ODPA was end-capped with either PEPA (imide-1) or PEPOPA (imide-5) to assess the effect of the incorporation of a phenoxy linkage in the end-capper. The oligomers exhibited similar physical (i.e. η_{inh}, crystallinity, cure onset and peak exotherm, cured T_g) and unoriented thin film tensile properties (*Tables 2* and *4*). However, the PEPOPA-end-capped material (imide-5) had an initial T_g ~5°C lower than the PEPA-terminated material (imide-1). A more pronounced effect was evident in comparing the physical (i.e. Brookfield viscosity, crystallinity, cure onset and peak exotherm, cured T_g) and mechanical properties for imide oligomers end-capped with 3-phenylethynylaniline and 3-(3-phenylethynylphenoxy)aniline[8].

Table 3 Effect of d.s.c. heating rate on imide-6 thermal properties

Heating rate (°C min^{-1})	T_g (°C)	T_m (°C)	Exothermic onset (°C)
5	203	277, 340	358
10	205	279, 344	359
20	209	283, 348	395
50	218	288, 345	413

Films

Unoriented thin films cast from NMP solutions of the amide acid oligomers and cured in flowing air to 350°C were fingernail creasable. The T_gs of the films ranged from 247 to 274°C (*Table 4*) and were typically greater than those of the imide oligomer powders cured in a sealed d.s.c. pan (*Table 2*). Our work has shown that the T_g and certain other properties such as modulus of phenylethynyl-containing oligomers are enhanced by curing in air as compared to curing in a mould or under vacuum where air exposure is limited. The average tensile strength, modulus and elongation to break were 124.1 MPa, 3.0 GPa and 45% at 23°C, and 72.4 MPa, 2.3 GPa and 53% at 177°C, respectively (*Table 4*). The high elongation to break of these materials was more typical of a linear thermoplastic than a thermoset and suggests the presence of linear segments as opposed to a highly crosslinked material. Similar behaviour has been observed for films of imide oligomers end-capped with either 3- or 4-amino-4′-phenylethynylbenzophenone cured under the same conditions[10]. As a comparison, films from imide oligomers end-capped with either 3- or 4-(4-aminophenoxy)-4′-phenylethynylbenzophenone had tensile strengths and moduli ranging from 133.1 to 135.1 MPa and 3.1 to 3.9 GPa, respectively, and elongations to break of < 10% at 23°C[9]. The tensile strength, modulus and elongation to break at 23°C for a phthalic anhydride-endcapped polymer from ODPA and 3,4′-ODA with $\bar{M}_n$ of 9250 g mol^{-1} (5 mol% offset) were 114.5 MPa, 3.0 GPa and 8%, respectively[15]. A film from imide-7 (*Table 4*) prepared by compression moulding at 360°C under 0.34 MPa for 1 h, had tensile strength, modulus and elongation to break at 23°C of 105.5 MPa, 2.8 GPa and 5%, respectively.

Table 4 Unoriented thin film tensile properties

Imide	Calcd $\bar{M}_n$ (g mol^{-1})	T_g[a] (°C)	Test temp. (°C)	Strength (MPa)	Modulus (GPa)	Elongation at break (%)
1	9000	251	23	119.3	2.8	38
			177	64.8	2.2	60
1	5000	258	23	106.9	3.2	5
			177	64.1	2.2	17
2	9000	259	23	117.9	2.9	38
			177	69.0	2.3	38
3	9000	262	23	139.3	3.0	69
			177	73.8	2.4	70
3	6000	268	23	123.4	2.9	40
			177	74.5	2.4	63
3	5000	267	23	132.4	3.0	40
			177	71.7	2.2	56
4	9000	272	23	122.7	3.1	41
			177	79.3	2.4	35
5	9000	247	23	116.5	2.8	35
			177	59.3	2.0	56
6	5000	270	23	129.6	3.1	32
			177	84.1	2.3	83
7	1500	274	23	105.5	2.8	5

[a] Determined by d.s.c. at 20°C min^{-1} on film samples cured at 100, 225 and 350°C for 1 h each in flowing air

Unoriented stressed thin films of imides-1 to 4 with a calculated $\bar{M}_n$ of 9000 g mol^{-1} and imide-3 with a calculated $\bar{M}_n$ of 6000 g mol^{-1} were immersed in toluene, methyl ethyl ketone (MEK), hydraulic fluid, jet fuel, ethylene glycol and methylene chloride at ambient temperature for 2 weeks (*Table 5*). The film specimens were secured in a circular form by multiple wraps around a standard paper clip. All the film specimens exhibited excellent solvent resistance except in methylene chloride. The methylene chloride exposed films deformed after a 1 day soak. The imide-3 film exhibited slight crazing after a 2 day exposure to MEK, with similar effects observed for the imide-1 film after the 2 week exposure to MEK. Solvent uptake by weight of the film specimens decreased in the following order: methylene chloride ($\sim$12%) > MEK ($\sim$1.4%) $\approx$ ethylene glycol ($\sim$1%) > hydraulic fluid (< 1%) $\approx$ toluene (< 1%) > jet fuel (< 0.5%). Similar solvent effects have been observed for films from other phenylethynyl-terminated imide oligomers[8].

Table 5 Weight uptake (per cent) of stressed film specimens[a]

	Imide				
Solvent	1	2	3 (9 K)	3 (6 K)	4
Toluene	0.54	1.06	0.43	0.40	0.44
MEK	0.44	1.38	1.59	0.80	1.09
Hydraulic fluid	0.55	0.93	0.79	0.67	0.42
Jet fuel	0.00	0.48	0.00	0.41	0.34
Ethylene glycol	0.54	1.40	0.91	0.37	0.97
Methylene chloride	11.23	12.37	12.50	11.07	9.29

[a] Soaked in solvent for 2 weeks at ambient temperature

Table 6 Unoriented thin film tensile properties of imide-1 after 1 week exposure of stressed films[a]

Solvent	Test temp. (°C)	Strength (MPa)	Modulus (GPa)	Elongation at break (%)
Unstressed	23	119.4	2.8	38
	177	64.9	2.2	60
Control (stressed)	23	113.2	3.0	16
	177	66.9	2.1	77
Jet fuel	23	140.1	2.9	66
	177	66.9	2.0	83
Hydraulic fluid	23	114.5	2.8	23
	177	69.0	2.0	79
MEK	23	112.5	2.8	31
	177	64.9	2.0	81
Toluene	23	124.2	3.0	53
	177	68.3	2.0	65
Ethylene glycol	23	117.3	3.0	26
	177	63.5	2.0	56
Water boil	23	118.7	2.8	12
	177	60.7	2.0	38

[a] Soaked in solvent for 1 week at ambient temperature

Table 7 Preliminary Ti-to-Ti tensile shear properties of imide-1

Exposure	Test temp. (°C)	Strength (MPa)	Cohesive failure (%)
Control	23	49.0	100
	177	29.7	100
Jet fuel[a]	23	49.7	95
	177	31.1	90
Hydraulic fluid[a]	23	50.4	95
	177	30.4	75
Water boil[b]	23	45.5	85
	177	23.5	55
1000 h at 177°C in air[c]	23	49.0	90
	177	33.1	90

[a] Unstressed samples soaked in solvent for 72 h at ambient temperature
[b] Unstressed samples soaked in solvent for 72 h
[c] Unstressed samples aged in flowing air

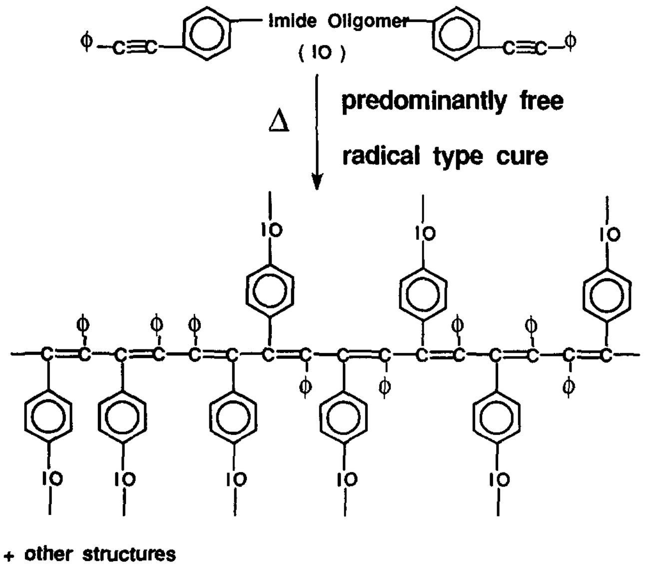
Unoriented stressed thin films from imide-1 with a calculated $\bar{M}_n$ of 9000 g mol^{-1} cured in flowing air to 350°C were soaked in several solvents at ambient temperature and in boiling water. A twisted configuration was applied to the secured specimens which induced a calculated stress of $\sim$11.7 MPa based on uniform twists in the specimens. After a 1 week soak in the solvents, no significant changes in the thin film tensile properties were observed at 23 and 177°C (*Table 6*).

Mouldings

The fracture toughness (K_{Ic}, critical stress intensity factor) of imide-1 ($\bar{M}_n = 9000$ g mol^{-1}) specimens compression moulded at 350°C under 1.4 MPa for 1 h was 3388 Pa m$^{1/2}$. The fracture energy (G_{Ic}, critical strain energy release rate) was 4025 J m^{-2}. Flash from the moulding of imide-1 exhibited a T_g of 239°C while the T_gs of the cured powder and film were 243 and 251°C, respectively. The T_g of the cured film was greater than that of either the cured powder or moulding for reasons mentioned previously, pertaining to air exposure. The K_{Ic} of imide-6 ($\bar{M}_n = 5000$ g mol^{-1}) specimens compression moulded at 350°C under 1.0 MPa for 1 h was 3878 Pa m$^{1/2}$ and the G_{Ic} was 4795 J m^{-2}. Flash from the moulding of imide-6 exhibited a T_g of 253°C. The T_gs of the cured powder and film were 249 and 270°C, respectively. The high fracture energies, like the high elongations of film specimens, were more typical of a thermoplastic material.

Adhesives

Titanium (Ti)-to-Ti tensile shear specimens of imide-1 ($\bar{M}_n = 9000$ g mol^{-1}) that were fabricated at 350°C under 0.7 MPa for 1 h had strengths of 49.0 MPa at 23°C and 29.6 MPa at 177°C (*Table 7*). Unstressed lap shear specimens exposed to hydraulic fluid and jet fuel for 72 h at ambient temperature exhibited no change in shear strengths at 23 and 177°C. After a 72 h water boil, the



Scheme 3

strength decreased by $\sim$10% at 23°C and by $\sim$20% at 177°C due to more adhesive type failure at both temperatures. The strength at 23°C was unaffected for unstressed lap shear specimens aged at 177°C for 1000 h in flowing air; however, the strength at 177°C increased slightly. Similar adhesive properties were observed for the same imide backbone end-capped with 3-APEB[9].

Composites

Carbon fibre-reinforced unidirectional composites of imide-1 ($\bar{M}_n = 9000\ \mathrm{g\,mol^{-1}}$) were fabricated at 350°C under 1.4 MPa for 1 h from solution-coated IM-7 carbon graphite fibre. The composites gave flexural strength and modulus of 2137 MPa and 140.1 GPa at 23°C and 1241 MPa and 124.8 GPa at 177°C, respectively. The short beam shear strength was 113.1 MPa at 23°C and 52.4 MPa at 177°C. The fibre volume fraction of the panels was $\sim$66% with <1% void content, as determined by image analysis of polished cross-sections of composite specimens.

Proposed cured structures

The high fracture energies and high unoriented thin film elongations from cured imide oligomers were more typical of high molecular weight linear polymers than a thermoset material. The thermal curing of imide oligomers terminated with phenylethynyl groups appears to be extremely complex and most likely proceeds predominantly by a free-radical process. Presumably, a polyene initially begins to form, but probably concurrent with its formation, branching and crosslinking also occur. Trimerization of the phenylethynyl groups is sterically unfavourable. A simplistic view of the type of chemical structures expected is presented in *Scheme 3*. The imide oligomer (IO) in *Scheme 3* has a calculated $\bar{M}_n$ of 5000–9000 $\mathrm{g\,mol^{-1}}$, therefore, relatively long segments are between the attachment points. The basic backbone might be irregular, with pendent phenyl groups located not only on every other carbon atom but also on adjacent carbon atoms. The oligomer probably extends randomly along a relatively short polyene backbone. Similar conclusions were drawn based on the heats of polymerization of several phenylethynyl-containing compounds[16].

The proposed structures are speculative, with little experimental work performed to identify the nature of the cured product. The curing of the phenylethynyl groups would be expected to be significantly different from that of the ethynyl groups ($\mathrm{HC{\equiv}C{-}}$) primarily because of the large steric impact of the phenyl groups. Information generated from studies on the curing of model compounds would not be directly applicable to the curing of the oligomers because of the gross difference in phenylethynyl group density and molecular mobility or diffusivity. Much effort can be spent on trying to elucidate the nature of the cured product without reaping a significant performance benefit. The important point is that the curing of these oligomers is reproducible from the standpoint of providing materials with an excellent combination of properties that includes high toughness, high strength, moderate modulus and good solvent resistance.

CONCLUSIONS

Several new imide oligomers end-capped with 4-phenylethynylphthalic anhydride and 4-(4-phenylethynylphenoxy)-phthalic anhydride were prepared, with calculated $\bar{M}_n$s of 1500–9000 $\mathrm{g\,mol^{-1}}$. All of the oligomers formed tough, creasable films with high elongations to break. Unoriented stressed thin film specimens exhibited excellent solvent resistance. Titanium tensile shear specimens fabricated from a phenylethynyl-terminated imide oligomer displayed high strengths at 23 and 177°C. Preliminary composite properties of a cured phenylethynyl-terminated imide oligomer were high, with moderate retention of properties at 177°C.

ACKNOWLEDGEMENTS

The composite work was performed by Dr Steve Wilkinson who was associated with the College of William and Mary, Williamsburg, Virginia and is now employed by Air Products and Chemicals, Allentown, Pennsylvania.

During this work J. G. Smith was in receipt of NASA grant NAG1-1251 with Virginia Commonwealth University.

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

REFERENCES

1 Wilson, D., Stenzenberger, H. D. and Hergenrother, P. M. 'Polyimides', Blackie, Glasgow, 1990

2 Sroog, C. E. *Prog. Polym. Sci.* 1991, **16**, 561

3 Harris, F. W., Padaki, S. M. and Vavaprath, S. *Am. Chem. Soc. Div. Polym. Chem., Polym. Prepr.* 1980, **21** (1), 3

4 Harris, F. W., Sridhav, K. and Das, S. *Am. Chem. Soc. Div. Polym. Chem., Polym. Prepr.* 1984, **25** (1), 110

5 Harris, F. W., Pamidimukkala, A., Gupta, R., Das, S., Wu, T. and Mock, G. *Am. Chem. Soc. Div. Polym. Chem., Polym. Prepr.* 1983, **24** (2), 324

6 Harris, F. W., Pamidimukkala, A., Gupta, R., Das, S., Wu, T. and Mock, G. *J. Macromol. Sci.—Chem. A* 1984, **21** (8/9), 1117

7 Hino, S., Sato, S. and Suzuki, O. Jpn Kokai Tokkyo Koho JP 63, 196, 564, 1988; *Chem. Abstr.* 1989, **110**, 115573w

8 Paul, C. W., Schultz, R. A. and Fenelli, S. P. in 'Advances in Polyimide Science and Technology' (Eds C. Feger, M. M. Khoyasteh and M. S. Htoo), Technomic, Lancaster, PA, 1993, p. 220

9 Bryant, R. G., Jensen, B. J. and Hergenrother, P. M. *Am. Chem. Soc. Div. Polym. Chem., Polym. Prepr.* 1993, **34** (1), 566

10 Havens, S. J., Bryant, R. G., Jensen, B. J. and Hergenrother, P. M. *Am. Chem. Soc. Div. Polym. Chem., Polym. Prepr.* 1994, **35** (1), 553

11 Smith, J. G. Jr and Hergenrother, P. M. *Am. Chem. Soc. Div. Polym. Chem., Polym. Prepr.* 1994, **35** (1), 353

12 Jensen, B. J., Hergenrother, P. M. and Nwokogu, G. *Polymer* 1993, **34** (3), 630

13 Meyer, G. W., Jayaraman, S. and McGrath, J. E. *Am. Chem. Soc. Div. Polym. Chem., Polym. Prepr.* 1993, **34** (2), 540

14 Meyer, G. W., Glass, T. E., Grubbs, H. J. and McGrath, J. E. *Am. Chem. Soc. Div. Polym. Chem., Polym. Prepr.* 1994, **35** (1), 549

15 Dezern, J. F. and Croall, C. I. paper presented at Recent Advances in Polyimides and Other High Performance Polymers, Am. Chem. Soc. Div. Polym. Chem., Sparks, NV, 18–21 January 1993

16 Sastri, S. B., Keller, T. M., Jones, K. M. and Armistead, J. P. *Macromolecules* 1993, **26**, 6171