Synthesis and characterization of imide oligomers end-capped with 4-(phenylethynyl)phthalic anhydrides

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A new series of phenylethynyl end-capped imide oligomers was synthesized and analysed for thermal stability, thermo-oxidative stability, glass transition temperature (T_g), cure temperatures and adhesive strength. Thus, 4-(phenylethynyl)phthalic anhydride (PEPA) and four substituted PEPAs containing electron-withdrawing groups were synthesized and used as end-capping agents for oligomers of 1,4-diaminobenzene and 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride. The oligomers underwent an exothermic reaction above 350°C to afford an insoluble network. The cure reaction was apparently promoted by electron-withdrawing groups as the oligomers end-capped with the substituted PEPAs started to cure at lower temperatures. Their rate of cure was also faster, as evidenced by the faster rise in their T_gs. The cured resins had T_gs as high as 405°C and displayed good thermo-oxidative stability at 371°C. A cured sample of a PEPA end-capped oligomer with a calculated molecular weight of 4200 g mol^{-1} displayed moderate high-temperature adhesive strength.

(Keywords: polyimide oligomers; curing)

INTRODUCTION

The overall objective of this ongoing project is to develop a polymer that can be used in high temperature composite and adhesive applications. The targeted properties for this material are: a glass transition temperature (T_g) of 400°C, low pressure processability at 0.34 MPa, and long-term thermo-oxidative stability at 371°C. Previous attempts to prepare such materials have involved the polymerization of monomeric reactants during processing, i.e. the so-called PMR approach. For example, Blatz[1] developed a high temperature adhesive based on 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), 1,4-diaminobenzene (*p*-PDA) and 4,4′-oxydianiline (ODA), which approaches these goals. The adhesive displays a titanium–titanium (Ti–Ti) lap shear strength of 24.18 MPa at 23°C and 15.55 MPa at 315°C when bonded at 1.379 MPa. FM® X680 (American Cyanamid) has similar high temperature capabilities. This adhesive has a Ti–Ti lap shear strength[2] of 17.72 MPa at 29°C and 12.07 MPa at 338°C when bonded at 0.6895 MPa. However, volatiles are evolved in both systems and may result in voids in the bondline. Our approach to developing an adhesive with the desired properties involves the use of polyimide oligomers that are end-capped with reactive functional groups. The oligomers are processed above their T_gs and then cured at higher temperatures by thermally polymerizing the end groups.

The design of the candidate materials in this study began with the selection of the polyimide backbone. Since polyimides prepared from 6FDA and *p*-PDA have been reported[3,4] to display outstanding thermo-oxidative stability, 6FDA/*p*-PDA oligomers were chosen for initial evaluation. Since such oligomers were expected to display T_gs above 250°C, an end-capping group was sought that would undergo a crosslinking reaction above 300°C. Previous work in this laboratory[5,6] with polyimide oligomers end-capped with 3-(phenylethynyl)aniline (PEA) showed that the phenylethynyl group cures above this temperature to afford a thermally stable network. Thus, this group was to be incorporated in the initial end-capping agents.

Paul *et al.*[7,8] also later prepared polyimide oligomers end-capped with PEA and substituted PEAs. Substitution of the pendent phenyl ring with trifluoromethyl group (*meta*) or a fluorine atom (*para*) did not significantly alter the cure temperature of model compounds, but did reduce their thermo-oxidative stability at 400°C. Insertion of a phenoxide linkage between the phenylethynyl group and the aniline ring reduced the cure temperature by 60°C, lowered the T_g of the cured resin and the solution viscosity, and almost doubled the tensile elongation.

Takekoshi and Terry[9] prepared polyimide oligomers end-capped with PEA and 4-(phenylethynyl)phthalic anhydride (PEPA). The PEPA end-capped systems were found to display higher thermo-oxidative stabilities than the PEA end-capped systems. In order to learn more about the thermal curing of these materials, the

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thermal polymerization of two model compounds, i.e. *N*-[3-(phenylethynyl)phenyl]phthalimide and *N*-phenyl-4-(phenylethynyl)phthalimide, was investigated. The PEA derivative was found to undergo a second-order reaction upon heating, while the PEPA underwent a first-order reaction. The curing for the PEA derivative was also slower than that of the PEPA derivative. The mass spectra of the model compounds after curing indicated that they decomposed via benzyl radicals or cations. It was proposed that electron-withdrawing groups attached to the phenyl ring of PEPA might destabilize the benzyl intermediates formed during the thermal depolymerization of the cured materials. Thus, the thermal stability of the cured resins might be increased. In order to test this hypothesis, PEPA end-caps substituted with electron-withdrawing groups were prepared and evaluated in this study.

The initial objective of this research was to synthesize 4-[4-(trifluoromethyl)phenylethynyl]phthalic anhydride (TPEPA), 4-(4-cyanophenylethynyl)phthalic anhydride (CPEPA), 4-(4-benzoylphenylethynyl)phthalic anhydride (BPEPA), and 4-(2,3,4,5-pentafluorophenylethynyl)phthalic anhydride (FPEPA). These compounds and PEPA were to be used to end-cap 6FDA/*p*-PDA oligomers. The oligomers were to be thermally cured, and the thermo-oxidative stability of the cured resins determined.

EXPERIMENTAL

Instrumentation

Intrinsic viscosities were determined in a Cannon-Fenske viscometer at $30\pm0.1°C$. Differential scanning calorimetry (d.s.c.) was performed on a Dupont 9900 thermal analyser system. Thermogravimetric analysis (t.g.a.) was performed on a Dupont Model 1090 thermal analyser equipped with a Dupont Model 951 t.g.a. Dynamic mechanical thermal analyses (d.m.t.a.) were obtained in a nitrogen atmosphere using a Polymer Laboratories thermal analyser with a heating rate of $4°C\,min^{-1}$. Infra-red (i.r.) spectra were obtained with a Beckman FT-2100 Fourier transform spectrophotometer. ^1H and ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy was performed on a Varian Gemini-2000 operating at 200 MHz. Solvent protons were used as internal standards. Elemental analyses were performed by Galbraith Laboratories. Melting points were determined on a Melt-Temp melting point apparatus and are uncorrected.

Starting materials

p-PDA was obtained from Aldrich and was distilled before being used. 6FDA was obtained from Hoechst-Celanese and dried overnight under reduced pressure at 160°C. Phthalic anhydride was obtained from Aldrich and was dried overnight under reduced pressure. *N*-Methyl-2-pyrrolidinone (NMP) was purchased from Aldrich and distilled under reduced pressure. Dimethylaniline, 4-bromobenzonitrile, 4-bromobenzotrifluoride, 4-pentafluoroiodobenzene, 4-bromobenzophenone, trimethylsilylacetylene, 3-bromoaniline, triphenyl phosphate, 2-methyl-3-butyn-2-ol, triethylamine, *N*,*N*-dimethyl formamide (DMF), copper(I) iodide (CuI), and bis(triphenylphosphine)palladium(II) dichloride $\{PdCl_2[(C_6H_5)_3P]_2\}$ were purchased from Aldrich and used as received. Phenylacetylene was purchased from Fluka and distilled under nitrogen before use. Pentafluorophenylacetylene was prepared by literature procedures[10].

End-cap syntheses

1,2-Dimethyl-4-iodobenzene. Concentrated HCl (315 ml), 3,4-dimethylaniline (150.0 g, 123.5 mmol), and water (315 ml) were heated and stirred in a 3 l Erlenmeyer flask until the dimethylaniline dissolved. After cooling to 0°C, a solution of cold sodium nitrite (91.59 g, 210 ml of H_2O) was slowly added, while the temperature was maintained below 5°C. The mixture was stirred for 30 min and then a solution of KI (217.86 g, 225 ml of H_2O) was added slowly, so that the temperature remained below 5°C. After standing for 1 h, the solution was heated to 100°C over 1 h. The mixture was neutralized with NaOH, cooled and extracted with three portions of ether. The ether extract was washed with a saturated NaCl solution, dried, filtered and evaporated under reduced pressure. 1,2-Dimethyl-4-iodobenzene was distilled under reduced pressure at 120–121°C to yield a clear liquid (236.5 g, 82.35%). The ^1H n.m.r. ($CDCl_3$) spectrum showed peaks at $\delta=7.49$ (s, 1H), 7.42 (d, 1H), 6.87 (d, 1H) and 2.22 (s, 6H) ppm. The ^{13}C n.m.r. ($CDCl_3$) spectrum showed peaks at 139.79, 138.89, 136.89, 135.46, 132.18, 128.97, 91.25 and 19.78 ppm.

4-Iodophthalic anhydride. 1,2-Dimethyl-4-iodobenzene (73.000 g, 314.57 mmol), H_2O (1825 ml), and potassium permanganate (49.714 g, 314.57 mmol) were placed in a 3 l flask equipped with a mechanical stirrer and a reflux condenser. The mixture was heated at reflux until the purple colour faded. Potassium permanganate (3 x 49.714 g) was added in three separate portions when the purple colour resulting from the previous addition faded. The solution was filtered and evaporated to 500 ml under reduced pressure. The solution was acidified with HCl. The precipitate was collected by filtration under reduced pressure and allowed to air dry. The product was sublimated at 100°C under reduced pressure and then recrystallized from chloroform to yield white crystals (24.436 g, 89.160 mmol, m.p. = 119–121°C, literature[11] m.p. of 123°C). The i.r. (KBr) spectrum showed peaks at 1844 and 1773 (C=O) cm^{-1}. The ^1H n.m.r. ($CDCl_3$) spectrum showed peaks at $\delta=8.3$ (s, 1H), 8.2 (d, 1H) and 7.7 (d, 1H) ppm. The ^{13}C n.m.r. ($CDCl_3$) spectrum showed peaks at 162.4, 161.5, 145.3, 134.9, 132.6, 130.4, 126.7 and 103.7 ppm.

4-(Phenylethynyl)phthalic anhydride (PEPA). Phenylacetylene (9.8782 g, 96.712 mmol), 4-iodophthalic anhydride (25.000 g, 91.238 mmol) and triethylamine (100 ml) were placed in a 1 l, round-bottom flask. Nitrogen was bubbled through the solution for 15 min. $PdCl_2[(C_6H_5)_3P]_2$ (0.2136 g, 0.3043 mmol) and CuI (0.1158 g, 0.6082 mmol) were added and the flask was lowered into an oil bath preheated to 100°C. After 2 h, the flask was cooled to room temperature and an aqueous solution of NaOH (1 N, 230 ml) was added. After 2 h, the mixture was extracted three times with 100 ml of toluene. The mixture was acidified with HCl. The diacid intermediate that precipitated was collected by filtration and dried at room temperature under reduced pressure. The diacid was stirred with refluxing acetic anhydride. The solid was collected by filtration, dried under reduced pressure overnight, and recrystallized from $CHCl_3$ to yield white crystals (20.451 g, 82.382 mmol, m.p. = 150–152°C, 90.29%).

The i.r. (KBr) spectrum showed peaks at 2208 (C≡C), and 1843, 1818 and 1772 (C=O) cm^{-1}. The ^{1}H n.m.r. ($CDCl_3$) spectrum showed peaks at $\delta = 8.06$ (1H, m), 7.95 (2H, m), 7.53 (2H, m), 7.36 (3H, m) ppm. The ^{13}C n.m.r. ($CDCl_3$) spectrum showed peaks at 162.4, 138.8, 132.1, 131.8, 129.8, 129.7, 129.6, 128.7, 128.3, 125.7, 121.6, 96.0 and 87.0 ppm. Elemental analysis found: C, 77.23; H, 3.53%. $C_{16}H_8O_3$ requires: C, 77.42; H, 3.53%.

2-Methyl-4-[4-(trifluoromethyl)phenyl]-3-butyn-2-ol. Triethylamine (14.4151 g, 142.456 mmol), 4-bromobenzotrifluoride (21.4744 g, 95.4375 mmol), 2-methyl-3-butyn-2-ol (9.6338 g, 114.53 mmol), and DMF (120 ml) were placed in a 500 ml, round-bottom flask equipped with a condenser. Nitrogen was bubbled through the solution for 15 min. $PdCl_2[(C_6H_5)_3P]_2$ (0.6699 g, 0.9544 mmol) and CuI (0.3635 g, 1.909 mmol) were added and the flask was lowered into an oil bath preheated to 80°C. After 3 h, the reaction mixture was allowed to cool and was repeatedly extracted with hexanes. The extract was evaporated to dryness under reduced pressure. The residue was distilled under reduced pressure through a short path distillation head to yield a white solid (19.762 g, 86.596 mmol, 90.74%, m.p. = 52–53°C, b.p. = 125°C). The ^{1}H n.m.r. ($CDCl_3$) spectrum showed peaks at $\delta = 7.49$ (m, 4H), 2.11 (s, 1H) and 1.58 (s, 6H) ppm.

4-(Trifluoromethyl)phenylacetylene[12]. 2-Methyl-4-[4-(trifluoromethyl)phenyl]-3-butyn-2-ol (16.0211 g, 70.2033 mmol), benzene (160 ml), and potassium t-butoxide (1.28425 g, 11.4440 mmol, 0.163 equivalents) were placed in a 250 ml, round-bottom flask equipped with a short-path distillation head. After acetone and benzene were distilled from the flask, the residue was distilled to afford a clear liquid (8.3044 g, 48.812 mmol, 69.7%, b.p. = 134–136°C). The i.r. (neat) spectrum showed a peak at 3315 (C≡C) cm^{-1}. The ^{1}H n.m.r. ($CDCl_3$) spectrum showed peaks at $\delta = 7.61$ (d, 2H), 7.38 (d, 2H) and 3.21 (s, 1H) ppm.

4-[4-(Trifluoromethyl)phenylethynyl]phthalic anhydride (TPEPA). 4-(Trifluoromethyl)phenylacetylene (7.9225 g, 46.567 mmol), 4-iodophthalic anhydride (12.760 g, 46.567 mmol), and triethylamine (50 ml) were placed in a 1 l, round-bottom flask. Nitrogen was bubbled through the solution for 15 min. $PdCl_2[(C_6H_5)_3P]_2$ (0.1090 g, 0.1552 mmol) and CuI (0.0591 g, 0.310 mmol) were added and the flask was lowered into an oil bath preheated to 100°C. After 1 h, the flask was cooled to room temperature and an aqueous solution of NaOH (1 N, 125 ml) was added. After 2 h, the mixture was extracted three times with 100 ml portions of toluene, and acidified with HCl. The diacid intermediate that precipitated was collected by filtration and dried under reduced pressure at room temperature. The diacid was stirred in refluxing acetic anhydride (150 ml) for 30 min. After cooling to 0°C, the product was collected by filtration, dried under reduced pressure, and was recrystallized from $CHCl_3$ to afford white crystals (11.350 g, 35.890 mmol, m.p. = 163–166°C, 77.07%). The i.r. (KBr) spectrum showed peaks at 2216 (C≡C) 1846, 1825 and 1776 (C=O) cm^{-1}. The ^{1}H n.m.r. ($CDCl_3$) spectrum showed peaks at $\delta = 8.11$ (1H, m), 7.99 (2H, m) and 7.65 (4H, s) ppm. The ^{13}C n.m.r. ($CDCl_3$) spectrum showed peaks at 162.2, 162.2, 139.0, 132.4, 131.9, 131.3, 131.0, 130.2, 128.5, 125.8, 125.7, 125.6, 123.7 (q), 94.0 and 88.8 ppm. Elemental analysis found: C, 64.21; H, 2.24; F, 17.78%. $C_{17}H_7F_3O_3$ requires: C, 64.57; H, 2.23; F, 18.02%.

4-(4-Cyanophenyl)-2-methyl-3-butyn-2-ol. Triethylamine (14.176 g, 140.09 mmol), 4-bromobenzonitrile (17.000 g, 93.391 mmol), 2-methyl-3-butyn-2-ol (9.4273 g, 112.07 mmol) and DMF (125 ml) were placed in a 500 ml, round-bottom flask equipped with a condenser. Nitrogen was bubbled through the solution for 15 min. $PdCl_2[(C_6H_5)_3P]_2$ (0.6555 g, 0.9339 mmol) and CuI (0.3557 g, 1.868 mmol) were added and the flask was lowered into an oil bath preheated to 80°C. After 3 h, the reaction mixture was allowed to cool to room temperature and repeatedly extracted with hot hexanes until no DMF remained in the flask. The extract was evaporated to dryness under reduced pressure. The solid residue was dissolved in a minimum amount of $CHCl_3$ and hexanes (25:75) and eluted down a silica gel chromatography column. The eluent was evaporated to dryness under reduced pressure. The residue was recrystallized from $CHCl_3$ to afford a light brown solid (10.8535 g, 58.9947 mmol, 63.16%, m.p. = 67–69°C). The i.r. (KBr) spectrum showed peaks at 3404 (O–H), 2336 (C≡N) and 2236 (C≡C) cm^{-1}. The ^{1}H n.m.r. ($CDCl_3$) spectrum showed peaks at $\delta = 7.5$ (m, 4H), 2.2 (s, 1H) and 1.56 (s, 6H) ppm.

4-Cyanophenylacetylene. 4-(4-Cyanophenyl)-2-methyl-3-butyn-2-ol (20.5000 g, 110.673 mmol), toluene (900 ml) and potassium t-butoxide (2.0833 g, 0.165 equivalents) were placed in a 1 l, round-bottom flask equipped with a short-path distillation head. The flask was heated in a 110°C oil bath for 30 min. When the temperature in the distillation head reached 110°C, the heating was stopped. The solution was filtered, and the toluene removed under reduced pressure. The solid residue was recrystallized from $CHCl_3$ to form tan crystals [11.8754 g, 93.3968 mmol, 84.36%, m.p. = 156–158°C, literature m.p. of 152–153°C (ref. 13) and 156–157°C (ref. 14)]. The i.r. (KBr) spectrum showed peaks at 3231 (C≡C), 2224 (C≡N, C≡C) cm^{-1}. The ^{1}H n.m.r. ($CDCl_3$) spectrum showed peaks at $\delta = 7.56$ (m, 4H) and 3.27 (s, 1H) ppm. The ^{13}C n.m.r. ($CDCl_3$) spectrum showed peaks at 132.7, 132.1, 127.0, 118.3, 112.3, 81.6 and 81.5 ppm.

4-(4-Cyanophenylethynyl)phthalic anhydride (CPEPA). 4-Cyanophenylacetylene (12.7150 g, 100.000 mmol), 4-iodophthalic anhydride (27.4010 g, 100.000 mmol) and triethylamine (160 ml) were placed in a 1 l, round-bottom flask. Nitrogen was bubbled through the solution for 15 min. $PdCl_2[(C_6H_5)_3P]_2$ (0.2340 g, 0.3333 mmol) and CuI (0.1270 g, 0.6667 mmol) were added and the flask was lowered into an oil bath preheated to 100°C. After 3 h, the flask was cooled to room temperature and an aqueous solution of NaOH (1 N, 250 ml) was added. After stirring overnight, the mixture was extracted three times with 100 ml portions of toluene. The mixture was acidified with HCl and then collected by filtration and dried at room temperature under reduced pressure. The diacid was stirred in refluxing acetic anhydride (200 ml) for 30 min. The product was collected by filtration. A second crop of crystals was recovered from the filtrate by concentrating to 25 ml under reduced pressure. The combined solids were dried under reduced pressure at 35°C overnight and then recrystallized from

$CHCl_3$ to afford tan crystals (24.8728 g, 91.0258 mmol, m.p. = 221–223°C, 91.1%). The i.r. (KBr) spectrum showed peaks at 2226 (C≡C), and 1844 and 1773 (C=O) cm^{-1}. The ^{1}H n.m.r. (DMSO) spectrum showed peaks at $\delta = 8.26$ (1H, m), 8.10 (2H, s) and 7.77 (4H, m) ppm. The ^{13}C n.m.r. (DMSO) spectrum showed peaks at 162.9, 162.9, 139.0, 133.0, 132.8, 132.4, 131.3, 129.2, 128.2, 126.2, 126.0, 118.5, 112.1, 92.6 and 91.0 ppm. Elemental analysis found: C, 74.89; H, 2.76; N, 5.08%. $C_{17}H_7N_1O_3$ requires: C, 74.73; H, 2.58; N, 5.13%.

4-(4-Benzoylphenyl)-2-methyl-3-butyn-2-ol. Triethylamine (16.995 g, 167.92 mmol), 4-bromobenzophenone (29.3760 g, 112.500 mmol), 2-methyl-3-butyn-2-ol (11.3565 g, 135.004 mmol) and DMF (15 ml) were placed in a 500 ml, round-bottom flask equipped with a condenser. Nitrogen was bubbled through the solution for 15 min. $PdCl_2[(C_6H_5)_3P]_2$ (0.2633 g, 0.3750 mmol) and CuI (0.1428 g, 0.7500 mmol) were added and the flask was lowered into an oil bath preheated to 80°C. After 3 h, the reaction mixture was allowed to cool to room temperature and repeatedly extracted with hot hexanes until no DMF remained in the flask. The extract was evaporated to dryness under reduced pressure and the product (25.8205 g, 97.6865 mmol, 86.83%, m.p. = 113–115°C) was recrystallized from a minimum amount of $CHCl_3$ and hexane. The i.r. (KBr) spectrum showed peaks at 3458 (O–H) and 1646 (C=O) cm^{-1}. The ^{1}H n.m.r. ($CDCl_3$) spectrum showed peaks at $\delta = 7.7$ (m, 4H), 7.5 (m, 5H), 2.2 (s, 1H) and 1.61 (s, 6H) ppm. The ^{13}C n.m.r. ($CDCl_3$) 196.2, 137.9, 137.3, 133.1, 130.5, 128.9, 127.6, 97.4, 81.8, 78.0, 65.9 and 31.6 ppm.

4-Benzoylphenylacetylene. 4-(4-Benzoylphenyl)-2-methyl-3-butyn-2-ol (25.8205 g, 97.6865 mmol), toluene (500 ml) and potassium t-butoxide (2.1925 g, 19.537 mmol, 0.165 equivalents) were placed in a 1 l, round-bottom flask equipped with a short-path distillation head. The flask was heated for 30 min in an oil bath at 110°C. When the temperature of the distillation head reached 110°C the heating was stopped. The solution was filtered and the reaction mixture was evaporated to dryness under reduced pressure. The product (5.4858 g, 26.599 mmol, 27.23%, m.p. = 46–48°C) was sublimated from the reaction mixture at 50°C. The i.r. (KBr) spectrum showed peaks at 3279 (C≡C) and 1645 (C=O) cm^{-1}. The ^{1}H n.m.r. ($CDCl_3$) spectrum showed peaks at $\delta = 7.75$ (m, 4H), 7.55 (m, 5H) and 3.23 (s, 1H) ppm. The ^{13}C n.m.r. ($CDCl_3$) spectrum showed peaks at 196.2, 137.6, 137.4, 132.8, 132.2, 130.1, 130.0, 128.5, 126.4, 82.8 and 80.1 ppm.

4-(4-Benzoylphenylethynyl)phthalic anhydride (BPEPA). 4-Benzoylphenylacetylene (5.4858 g, 26.599 mmol), 4-iodophthalic anhydride (5.6504 g, 27.397 mmol) and triethylamine (22 ml) were placed in a 250 ml, round-bottom flask. Nitrogen was bubbled through the solution for 15 min. $PdCl_2[(C_6H_5)_3P]_2$ (0.0622 g, 0.0887 mmol) and CuI (0.0338 g, 0.177 mmol) were added and the flask was lowered into an oil bath pretreated to 100°C. After 3 h, the flask was cooled to room temperature and an aqueous solution of NaOH (1 N, 60 ml) was added. After stirring overnight, the mixture was extracted three times with 100 ml portions of toluene and acidified with HCl. The diacid intermediate that precipitated was collected by filtration and dried under reduced pressure at room temperature. The diacid intermediate was stirred in refluxing acetic anhydride (200 ml) for 30 min. The product was collected by filtration. The solid was dried overnight under reduced pressure. The product was recrystallized from $CHCl_3$ to afford white crystals (4.0338 g, 11.448 mmol, m.p. = 212–213°C, 43.03%). The ^{1}H n.m.r. ($CDCl_3$) spectrum showed peaks at $\delta = 8.14$ (m, 1H), 8.00 (d, 2H), 7.81 (m, 4H) and 7.62 (m, 5H) ppm. The ^{13}C n.m.r. ($CDCl_3$) spectrum showed peaks at 228.6, 162.7, 139.3, 138.6, 137.6, 133.3, 132.3, 131.9, 130.9, 130.7, 130.5, 130.3, 128.9, 126.2, 126.0, 95.1 and 89.7 ppm. Elemental analysis found: C, 78.36; H, 3.72%. $C_{23}H_{12}O_4$ requires: C, 78.40; H, 3.43%.

4-(2,3,4,5-Pentafluorophenylethynyl)phthalic anhydride (FPEPA). Pentafluorophenylacetylene (6.1683 g, 32.112 mmol), 4-iodophthalic anhydride (8.7989 g, 32.112 mmol) and triethylamine (120 ml) were placed in a round-bottom flask. Nitrogen was bubbled through the solution for 15 min. $PdCl_2[(C_6H_5)_3P]_2$ (0.2255 g, 0.3212 mmol) and CuI (0.1233 g, 0.6421 mmol) were added and the flask was lowered into an oil bath preheated to 100°C. After 3 h, the flask was cooled to room temperature and an aqueous solution of NaOH (1 N, 128 ml) was added. After stirring overnight, the mixture was extracted three times with 50 ml portions of toluene and acidified with HCl. The diacid intermediate which precipitated was collected by filtration and dried at room temperature under reduced pressure. The product was sublimated and recrystallized from $CHCl_3$ to form tan crystals (5.294 g, 0.01565 mmol, m.p. = 173–174°C, 48.73%). The i.r. (KBr) spectrum showed peaks at 1854 and 1782 (C=O) cm^{-1}. The ^{1}H n.m.r. ($CDCl_3$) spectrum showed peaks at $\delta = 8.16$ (1H, m) and 8.04 (2H, s) ppm. The ^{13}C n.m.r. ($CDCl_3$) spectrum showed peaks at 162.1, 162.0, 150.2 (b, m), 145.3 (b, m), 140.2 (b, m), 139.2, 135.4 (b, m), 131.9, 131.0, 129.9, 128.7, 126.0, 98.0 and 78.8 ppm.

Polymerization

Typical procedure for the preparation of end-capped, amic acid oligomers. *p*-PDA (2.1628 g, 20.000 mmol) and NMP (20 ml) were added to a 250 ml, round-bottom flask equipped with a Teflon coated stirring bar and a gas adapter under a nitrogen atmosphere at room temperature. A solution of 6FDA (8.2109 g, 18.483 mmol) in NMP (50 ml) was added in three portions over 3 h. After the mixture was stirred for 1 h at room temperature, PEPA (0.7531 g, 3.034 mmol) was added as a solid. The amic acid solution (21.6%, w/v) was divided into six equal parts and poured onto six Pyrex discs.

General procedure for the imidization of the amic acid oligomers. The Pyrex discs were placed in a vacuum oven and heated under reduced pressure at 60°C. After the discs were heated at 60°C for 2 h, the temperature was increased to 100°C (1°C min^{-1}) and held there for 15 h. The vacuum in the oven was released, and nitrogen (60 cm^3 min^{-1}) was purged through. The films that formed on the discs were heated at 1°C min^{-1} to 170°C and held at that temperature for 1 h. They were then heated (1°C min^{-1}) to 200°C, held at that temperature for 1 h, heated to 260°C, and held at that temperature for 2 h. The heating was discontinued, and the films were allowed to cool slowly to room temperature. The films were light brown and were quite brittle.

Curing of oligomers. The films were cured at 370, 400 and 420°C for 1 h in a preheated General Signal Lindberg furnace. The oven was continuously purged with 60 cm^3 min^{-1} of nitrogen. All of the films cured at the same temperature were cured simultaneously. After cooling, the tough, black films were removed from the glass. The film thickness was measured with a caliper. The average film thickness varied between 0.164 and 0.348 mm.

Thermo-oxidative stability test. The thermo-oxidative stability test was performed in a General Signal Lindberg furnace. Air was continuously purged through the oven at a rate of 60 cm^3 min^{-1}. Borosilicate glass vials were weighed, heated overnight at 371°C, and reweighed. After sections of film (0.80–0.63 g) were placed in the vials, they were heated in the furnace for 2 h at 371°C and then reweighed. The films were removed from the oven periodically and weighed.

Compression moulding of oligomers. Polyimide oligomers were prepared with a calculated number average molecular weights ($\bar{M}_n$) of 3200, 4200 and 7000 g mol^{-1}. The uncured oligomers were placed inside of a Fluoroglide-coated mould (16.5 cm^2). The mould was placed in a Carver press, and the press was heated at 3°C min^{-1} to the final cure temperature. Pressure was applied at 340°C. The press was allowed to slowly cool to room temperature before the pressure was released.

Preparation of oligomers for adhesive tests. *p*-PDA (2.1628 g, 20.000 mmol) and 15 ml of NMP were added to a round-bottom flask under a nitrogen atmosphere and heated to 60°C. After the diamine dissolved, a solution of 6FDA (8.2109 g, 18.483 mmol) in NMP (30 ml) was added over 3 h in three portions. After 1 h, PEPA (0.7531 g, 3.034 mmol) was added as a solid. Triphenyl phosphate (0.1127 g) was added, and the solution was stirred at 60°C for 24 h. Pyridine (3.1640 g, 40.000 mmol), acetic anhydride (4.0836 g, 40.000 mmol) and NMP (10 ml) were added to effect imidization. After the solution was stirred for 12 h at 60°C, the polyimide oligomer was added to ethanol (500 ml). The solid that precipitated was collected by filtration, and dried under reduced pressure at room temperature overnight.

General procedure for the preparation of Ti–Ti lap shear specimens. The Ti–Ti single lap specimens were prepared and tested according to ASTM D1002. A solution of the oligomer [11.1% (w/v)] in NMP was coated onto glass cloth (J. P. Stevens 112 S) and dried at 300°C for 1 h under reduced pressure. This procedure was repeated until the scrim contained 65 wt% oligomer. The scrim was cut into rectangles slightly larger than 1.27 cm x 2.54 cm.

Titanium coupons were sandblasted with silicon carbide, brushed clean, degreased with acetone, washed with water and dried at 100°C under reduced pressure. The coupons were coated with the polyimide oligomer solution and dried at 300°C for 1 h. This procedure was repeated four times. The titanium coupons were placed in a metal frame that allowed them to overlap in the horizontal direction. A piece of scrim was placed between the two coupons with an overlap of 1.27 cm. The frame was placed in a press. The press was heated at 3°C min^{-1} to the cure temperature and held for the specified time. Pressure was applied at 340°C.

Adhesive testing. The Ti–Ti lap shear specimens were mounted between two grips of an Instron model TTD. The load was increased at a rate of 8.964 MPa min^{-1} under failure. For testing at elevated temperatures the specimens were enclosed in a preheated Conrad-Missimer model FTU 3.2 oven. The samples were allowed to equilibrate for 15 min at temperature prior to testing.

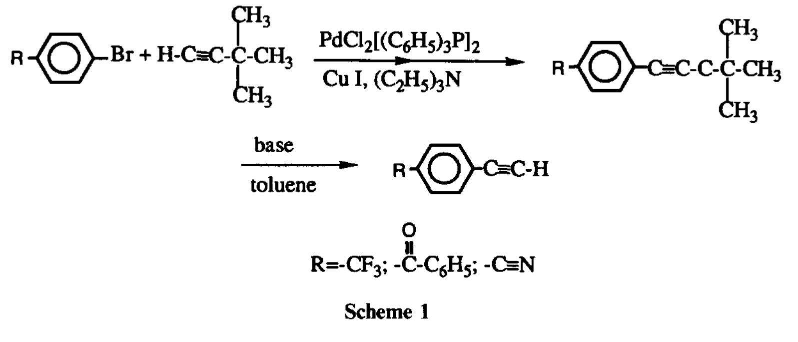
RESULTS AND DISCUSSION

Synthesis of end-capping agents

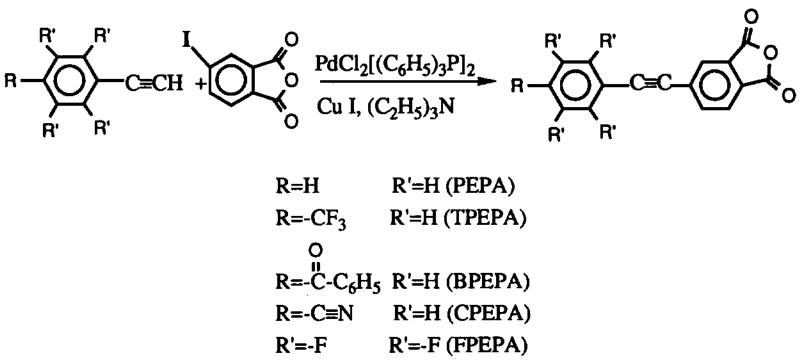
The initial objective of this research was to attach electron-withdrawing groups to the phenyl ring of PEPA. Thus, TPEPA, CPEPA, BPEPA and FPEPA were synthesized by the synthetic route outlined in *Schemes 1* and *2*. Substituted phenylacetylenes were prepared by coupling the appropriate *para*-substituted bromobenzene with 2-methyl-3-butyn-2-ol using the Stevens–Castro reaction[15]. In the case of FPEPA, the coupling was carried out with trimethylsilylacetylene[10]. The intermediates were deprotected with base to afford the phenylacetylenes (*Scheme 1*). The intermediates were coupled with 4-iodophthalic anhydride using the Stevens–Castro conditions (*Scheme 2*). PEPA was prepared for comparison purposes in a similar manner. All of the end-capping agents were sublimated under reduced pressure prior to use.

Synthesis of end-capped oligomers

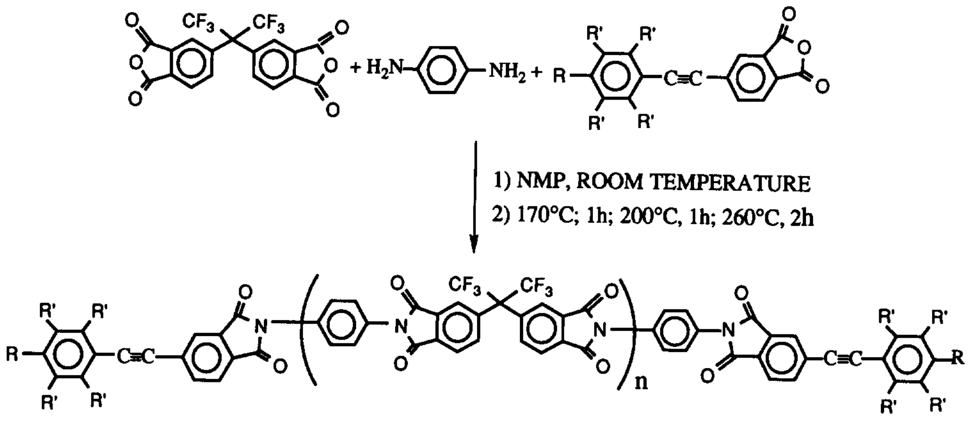
A series of amic acid oligomers was prepared by allowing appropriate amounts of *p*-PDA and 6FDA to react in NMP at room temperature (*Scheme 3*). In order to avoid an interfacial reaction between the two reactants that would generate a broad molecular weight distribution[16], both monomers were dissolved in NMP prior to mixing. The monomer stoichiometry was offset in favour of the diamine so as to generate oligomers with



Scheme 1



Scheme 2



Scheme 3

$\bar{M}_n = 3200$, 4200 and 7000 g mol^{-1}. The various end-capping agents were added as solids after the reaction mixtures had been stirred for 20 h. Control samples were prepared by end-capping the oligomers with phthalic anhydride (PA). The inherent viscosity of the 7000 molecular weight oligomers in NMP was 0.1 ± 0.01 dl g^{-1} (0.5 dl g^{-1} at 30°C).

Imidization of amic acid oligomers

Thin films of the amic acid oligomers were cast from the NMP solutions dried at 100°C under reduced pressure for 15 h. The films were then heated at 1°C min^{-1} to 170°C and held at that temperature for 1 h. The imidization process was completed by heating the films at 200°C for 1 h and at 260°C for 2 h. The films were allowed to slowly cool to room temperature.

Table 1 Thermal properties of imide oligomers[a]

End-cap	Initial T_g[b] (°C)	Final T_g[b,c] (°C)	Cure onset (°C)	Cure maximum (°C)
PA	294	301	–	–
PEPA	309	365	397	436
TPEPA	308	365	355	425
BPEPA	300	358	358	424
CPEPA	306	364	357	434
FPEPA	314	382[d]	362	430

[a] Calculated $\bar{M}_n = 7000$ g mol^{-1}

[b] Mid-point in the change in the slope on the d.s.c. thermogram obtained with a heating rate of 20°C min^{-1}

[c] T_g of sample after being heated to 475°C in the first d.s.c. run

[d] D.s.c. thermogram of sample contained small exotherm indicating incomplete cure

Thermal properties of imide oligomers

The film samples of the imide oligomers with calculated $\bar{M}_n$s of 3200 and 7000 g mol^{-1} were characterized with d.s.c. The T_gs of the lowest molecular weight oligomers were all near 270°C, while the T_gs of the higher molecular weight materials were near 300°C (*Tables 1* and *2*). Surprisingly, the d.s.c. thermograms of the oligomers with calculated $\bar{M}_n$s of 3200 g mol^{-1} also contained melting endotherms with minima between 370 and 410°C. The PA end-capped oligomer displayed the highest melting point. The melting endotherms obscured the onset of the reaction exotherms associated with the polymerization of the phenylethynyl groups. The d.s.c. thermograms of the oligomers with $\bar{M}_n = 7000$ g mol^{-1} did not contain melting endotherms. The terminal phenylethynyl groups in these systems began to polymerize between 358 and 397°C, as witnessed by the onset of definitive reaction exotherms. The groups containing electron-withdrawing substituents began to polymerize at lower temperatures than did the unsubstituted group in PEPA (*Figure 1*). The difference between the oligomers' T_gs and cure onsets, i.e. their processing windows, when heated at 20°C min^{-1} ranged from 50 to 120°C.

Curing study of imide oligomers

Film samples of the imide oligomers with $\bar{M}_n = 7000$ g mol^{-1} were initially heated for 30 min at 370, 400 and 420°C. An attempt was made to follow the cure reaction by the disappearance of the disubstituted ethynyl stretching absorption in the films' i.r. spectra. In the

Table 2 Thermal properties of imide oligomers[a]

End-cap	Heating rate (°C min^{-1})	Initial T_g[b] (°C)	Final T_g[b,c] (°C)	Cure exotherm maximum (°C)
PA	10	263		–[d]
PEPA	10	266		409
TPEPA	10	263		424
BPEPA	10	267		407
CPEPA	10	262		424
FPEPA	10	258		430
PA	20	262	264	–[d]
PEPA	20	278	379	424
TPEPA	20	271	364	437
BPEPA	20	270	388	421
CPEPA	20	264	402	437
FPEPA	20		380[e]	[f]

[a] Calculated $\bar{M}_n = 3200\,\mathrm{mol\,g^{-1}}$
[b] Mid-point in the change in the slope on the d.s.c. thermogram
[c] T_g of sample after being heated to 475°C in the first d.s.c. run
[d] D.s.c. did not contain an exotherm
[e] Exothermic peak present
[f] Exotherm continued to increase to 475°C

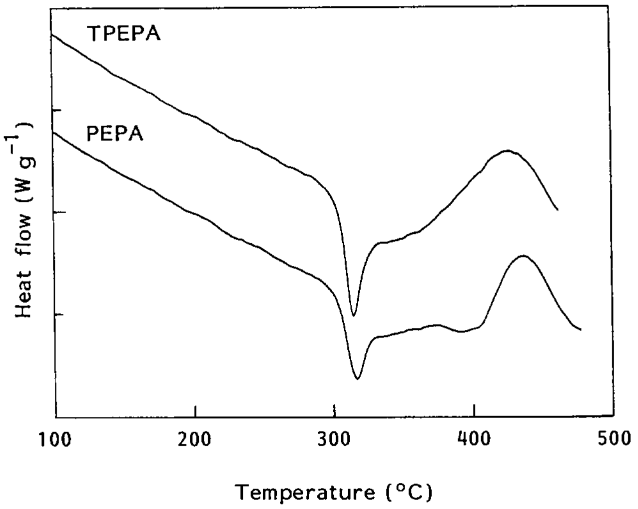


Figure 1 D.s.c. thermograms of TPEPA and PEPA

PEPA end-capped oligomer a dramatic reduction in the strong band at 2217 cm^{-1} occurred as the curing proceeded. However, the band was very weak in the i.r. spectrum of the TPEPA oligomer, making the estimate of cure difficult. The ethynyl band in the spectrum of the CPEPA end-capped oligomer was obscured by the strong cyano absorption at 2230 cm^{-1}. Since a significant absorption band at 2217 cm^{-1} was still present in the i.r. spectra of the PEPA end-capped samples cured at all three temperatures, the curing time was increased. The ethynyl band could not be detected after the films were heated for 1 h at 370°C. The T_gs of the cured samples ranged from 327 to 349°C. However, the curing reaction was evidently not complete as the T_gs of the samples heated for 1 h at 400°C and at 420°C were higher (*Table 3*).

The CPEPA and FPEPA end-capped oligomers appeared to cure at the fastest rates, as witnessed by their faster rise in T_g, while the PEPA and TPEPA end-capped systems cured the slowest. The BEPA systems apparently underwent curing at a rate intermediate between those of the two groups. The T_gs of the oligomers were all near 360°C after being heated for 1 h at 420°C. The T_g of the PA end-capped control also increased slightly during the thermal treatments. This was most likely due to loss of residual solvent.

The curing process for the PEPA end-capped oligomer was also monitored by following the oligomers' rise in T_g with time as the material was held isothermally at 371°C (*Figure 2*). The T_g increased dramatically to 320°C in 1 h. Although it continued to increase after this point, the rate of increase decreased with time. After 14 h, the T_g increased very slowly, reaching 360°C in 45 h.

Thermal and thermo-oxidative stability studies

The thermal and thermo-oxidative stability of the oligomers with calculated $\bar{M}_n$s of 7000 g mol^{-1} that were cured for 1 h at 400°C were initially evaluated with t.g.a. A heating rate of 0.3–0.4°C min^{-1} was used in an attempt to detect small stability differences that might exist due to the different end-capping groups. However, no significant differences were found (*Table 4*). All of the samples underwent 5% weight losses near 470°C in air and near 495°C in nitrogen.

The oligomers with calculated $\bar{M}_n$s of 3200 and 7000 g mol^{-1} were then subjected to isothermal ageing studies at 371°C in recirculating air. Three samples of each oligomer were evaluated. The samples were cured for 1 h at 370, 400 or 420°C prior to testing. The weight retention data shown in *Tables 5* and *6* represent the average weight retained by three replicates of each sample. PA end-capped oligomers and a copolyimide of 6FDA, *p*-PDA (95 mol%) and 1,3-diaminobenzene

Table 3 T_gs (°C)[a] of cured imide oligomers[b]

End-cap	Cure temperature 370°C	400°C	420°C
PA	304	305	311
PEPA	327	339	360
TPEPA	323	347	362
BPEPA	336	349	358
CPEPA	348	360	364
FPEPA	349	362	ND[c]

[a] Mid-point in the change in the slope on the d.s.c. thermogram obtained with a heating rate of 20°C min^{-1}
[b] Calculated $\bar{M}_n = 7000\,\mathrm{g\,mol^{-1}}$
[c] Not determined

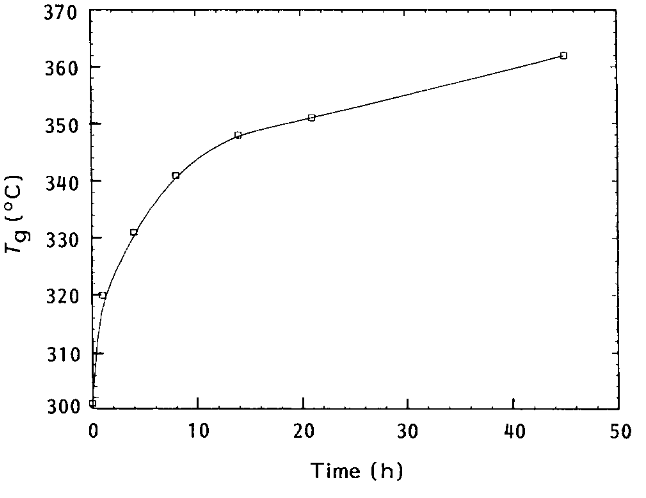


Figure 2 T_g of PEPA end-capped oligomer ($M_n = 7000\,\mathrm{g\,mol^{-1}}$) as a function of time at 370°C

Table 4 Thermogravimetric analysis of cured imide oligomers[a]

	Thermal stability[b,c] (°C)		Thermo-oxidative stability[b,d] (°C)	
End-cap	2%	5%	2%	5%
PA	453	488	434	467
PEPA	469	493	445	473
TPEPA	472	493	448	473
BPEPA	477	496	449	473
CPEPA	475	496	451	476
FPEPA	478	495	433	465

[a] Calculated $\bar{M}_n = 7000\,\mathrm{g\,mol^{-1}}$; cured at 400°C for 1 h

[b] Samples heated at 50°C min^{-1} to 300°C and at 10°C min^{-1} to 350°C, and then slowly to higher temperature

[c] Temperature at which sample lost 2 or 5% of its weight when heated at a rate of 0.4°C min^{-1} in nitrogen

[d] Temperature at which sample lost 2 or 5% of its weight when heated at a rate of 0.3°C min^{-1} in air

Table 5 Thermo-oxidative stability[a] of cured imide oligomers at 371°C[b]

End-cap (cure temp., °C)	Time				
	100 h	300 h	600 h	1000 h	1500 h
PA(370)	97.3	96.8	96.4	94.7	93.8
PA(400)	97.7	96.6	96.0	94.4	93.1
PA(420)	98.3	97.5	96.7	95.3	93.3
PEPA(370)	97.2	96.1	93.7	90.2	85.5
PEPA(400)	97.9	96.8	94.7	92.1	86.8
PEPA(420)	98.6	97.1	95.5	91.3	84.2
CPEPA(370)	97.7	96.2	93.9	90.9	85.9
CPEPA(400)	98.2	97.2	95.1	93.7	88.7
CPEPA(420)	99.0	97.5	94.7	92.0	85.5
TPEPA(370)	97.1	94.9	93.4	89.9	82.8
TPEPA(400)	98.3	95.5	94.6	90.5	83.8
BPEPA(370)	97.7	95.6	93.7	89.2	81.4
BPEPA(400)	97.9	96.2	93.1	87.1	76.9
BPEPA(420)	98.4	97.0	93.9	88.0	78.0
FPEPA(400)	97.2	94.3	90.8	86.7	78.4
Polyimide[c]	97.9	97.7	97.1	96.7	96.6

[a] Average percentage of weight retained by three replicates after indicated time at 371°C

[b] Calculated $\bar{M}_n$ of oligomer before cure was 7000 g mol^{-1}

[c] A copolyimide of 6FDA, *p*-PDA (95 mol%), and 1,3-diaminobenzene (5 mol%) was used as a control

(5 mol%) were used as controls. The thermo-oxidative stabilities of the oligomers with calculated $\bar{M}_n$s of 7000 g mol^{-1} were higher than those of the oligomers with calculated molecular weights of 3200 g mol^{-1}. In both series of oligomers the best thermo-oxidative stabilities were displayed by the PA end-capped controls. In fact, the copolyimide prepared from 6FDA that was not end-capped retained the highest percentage of its weight (96.6%) during the tests. The phenylethynyl end-capped oligomers ($\bar{M}_n = 7000\,\mathrm{g\,mol^{-1}}$) retained between 76.9 and 86.8% of their weight after 1500 h at 371°C.

Compression moulding of oligomers

A compression moulding study was carried out to determine whether the oligomers could be moulded at low pressure. Powder samples of PEPA end-capped oligomers with calculated $\bar{M}_n$s of 3200, 4200 and 7000 g mol^{-1} were heated in a mould at 3°C min^{-1} to 340°C. After 0.34 MPa pressure was applied, the samples were heated to 350°C and held at that temperature for 6 h. The oligomers with a calculated $\bar{M}_n$ of 3200 g mol^{-1} underwent considerable flow to yield a well consolidated plaque. The d.m.t.a. thermogram obtained from this plaque showed a tan δ maximum at 405°C. However, the thermogram also revealed that the curing process was not complete. The higher molecular weight oligomers afforded poorly consolidated plaques due to their lack of flow under these conditions.

A powder sample of the oligomer with a calculated $\bar{M}_n$ of 7000 g mol^{-1} was then subjected to more stringent moulding conditions. In this case 3.45 MPa pressure was applied, and the sample was held at 370°C for 20 min. The oligomer underwent considerable flow to yield a well consolidated plaque.

Adhesive testing of polymers

Thd Ti–Ti lap shear strengths of a series of PEPA end-capped oligomers with calculated $\bar{M}_n$s of 3200, 4200 and 7000 g mol^{-1} were determined. In this case, the oligomers were obtained by chemically imidizing their amic acid precursors at room temperature. Solutions of the oligomers in NMP were used to prepare glass scrim that was placed between two titanium coupons. An oligomer–metal bond was established by applying 0.34 MPa pressure at 365°C for 6 h. The lap shear strength of the sample was then evaluated on an Instron instrument.

The oligomer with a calculated $\bar{M}_n$ of 7000 g mol^{-1} was the first to be tested. Unfortunately, the material did not undergo sufficient flow under the standard bonding conditions to establish a strong bond. The Ti–Ti lap shear strength of the sample was only 7.59 MPa at 23°C (*Table 7*). Increasing the bonding temperature to 390°C did not significantly increase the flow and the lap shear strength remained low. Increasing the bonding pressure to 2.76 MPa, however, did afford a good bond with a lap shear strength of 17.0 MPa.

The oligomer with a calculated $\bar{M}_n$ of 3200 g mol^{-1} was the next to be evaluated. Although the oligomer flowed well under the bonding conditions, the cured resin was quite brittle and did bond well to the titanium. The resin's lap shear strength was very low at all the test temperatures. The brittleness was most likely associated with the material's high crosslink density.

Table 6 Thermo-oxidative stability[a] of cured imide oligomers at 371°C[b]

End-cap (cure temp., °C)	Time				
	100 h	268 h	402 h	605 h	778 h
PA(370)	97.9	97.6	96.9	96.8	96.1
PA(400)	97.4	96.8	96.2	94.8	94.3
PA(420)	98.0	97.7	97.2	96.6	96.4
PEPA(370)	97.0	95.0	90.8	85.9	81.2
PEPA(400)	96.6	91.7	85.4	76.1	72.0
PEPA(420)	97.5	94.8	90.0	84.3	80.5
CPEPA(370)	96.1	93.7	91.1	87.6	83.9
CPEPA(400)	96.1	93.2	89.0	83.8	81.0
CPEPA(420)	98.1	96.4	94.0	90.3	87.5
TPEPA(370)	96.1	93.9	91.1	87.5	83.5
TPEPA(400)	95.7	92.4	88.3	82.8	79.9
TPEPA(420)	96.9	93.7	89.3	83.1	78.7
FPEPA(370)	90.7	88.2	84.0	81.0	75.8

[a] Average percentage of weight retained by three replicates after indicated time at 371°C

[b] Molecular weight of oligomer before cure was 3200 g mol^{-1}

Table 7 Lap shear strength of imide oligomers[a]

Calculated $\bar{M}_n$ of oligomer (g mol^{-1})	Test temperature (°C)	Shear strength (MPa)
7000	23[b]	17.0
	23	7.59
4200	23	18.5
	282	14.5
	302	13.8
	343	9.58
	371	6.69
3200	23	3.81
	302	3.14
	342	5.20
	371	2.82

[a] Adhesive bond formed at 365°C for 6 h under 0.34 MPa pressure
[b] Adhesive bond formed at 2.76 MPa

The oligomer with a calculated $\bar{M}_n$ of 4200 g mol^{-1} was then subjected to testing. This resin also flowed well under the standard bonding conditions. In this case, however, the cured resin formed a surprisingly strong bond to the titanium. The resin's lap shear strength at 23°C was 18.5 MPa. The resin also showed good retention of its adhesive strength at elevated temperatures (*Table 7*). The lap shear strength at 302°C was 13.8 MPa.

SUMMARY AND CONCLUSIONS

A series of imide oligomers was prepared from 6FDA and *p*-PDA and end-capped with 4-(phenylethynyl)anhydrides. The monomer stoichiometry was varied so as to produce oligomers with calculated $\bar{M}_n$s of 3200, 4200 and 7000 g mol^{-1}. The T_gs of the materials ranged from near 270°C to near 300°C. The oligomers with the lowest molecular weights were semicrystalline while the others were amorphous. When heated to 360–400°C the oligomers underwent an exothermic reaction to produce insoluble, crosslinked resins. The cure reaction was promoted by electron-withdrawing groups attached to the phenylethynyl moiety. Oligomers end-capped with 4-(phenylethynyl)anhydrides containing these groups cured at lower temperatures and at faster rates than those end-capped with 4-(phenylethynyl)phthalic anhydride. The T_gs of the cured resins ranged between 323 and 402°C, depending on the oligomer's molecular weight and the cure conditions.

The oligomers with calculated $\bar{M}_n$ of 7000 g mol^{-1} retained between 77 and 89% of their weight when subjected to recirculating air at 371°C for 1500 h. A control oligomer end-capped with phthalic anhydride retained 93% of its weight under these conditions. Thus, the chemical structure generated by the reaction of the phenylethynyl groups was evidently not as thermally stable as the imide oligomer. The oligomers end-capped with anhydrides containing cyano and perfluoromethyl groups displayed comparable thermo-oxidative stability to the 4-(phenylethynyl)phthalic anhydride end-capped oligomer. The oligomers end-capped with anhydrides containing benzoyl and perfluorophenyl groups, however, displayed slightly lower thermo-oxidative stability.

The Ti–Ti lap shear strengths of a series of 4-(phenylethynyl)phthalic anhydride end-capped oligomers with calculated $\bar{M}_n$s of 3200, 4200 and 7000 g mol^{-1} were determined. In order to induce flow and establish a strong bond (17.0 MPa at 23°C) with the oligomer with a calculated $\bar{M}_n$ of 7000 g mol^{-1}, the Ti test specimen had to be subjected to 2.76 MPa of pressure at 365°C. Although the lowest molecular weight oligomer flowed well under 0.34 MPa pressure at 365°C, the bond formed was weak. The oligomer with a calculated $\bar{M}_n$ of 4200 g mol^{-1}, however, not only flowed well under these conditions, but also formed a strong bond (18.5 MPa at 23°C). The oligomer also displayed a very good adhesive strength above 300°C.

ACKNOWLEDGEMENT

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Note added in proof

Subsequent to the submission of this paper, two other preliminary studies[17,18] on polyimides end-capped with PEPA were reported.

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