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# Polyimides from 2,3,3′,4′-biphenyltetracarboxylic dianhydride and aromatic diamines[☆]

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## Abstract

A series of new polyimides were prepared from the reaction of 2,3,3′,4′-biphenyltetracarboxylic dianhydride (a-BPDA) with various aromatic diamines. The properties of the a-BPDA polyimides were compared with those of polyimides prepared from the reaction of 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA) with the same aromatic diamines. Films of the a-BPDA polyimides had higher glass transition temperatures ($T_g$s) and less color than the corresponding s-BPDA polyimide films. Light transmission at 500 nm, solar absorptivity, and thermal emissivity were determined on certain films. Films of similar polyimides based upon a-BPDA and s-BPDA containing *meta* linkages and others containing *para* linkages were each cured at 250, 300, and 350 °C. The films were characterized primarily by $T_g$, color, optical transparency, tensile properties, dynamic mechanical thermal analysis, and coefficient of thermal expansion. The a-BPDA *meta* linked polyimide films had tensile strengths and moduli higher than films of the a-BPDA *para* linked polyimide. The same phenomenon was not observed for the s-BPDA *meta* and *para* linked polyimides. The chemistry, mechanical, and physical properties of the polymers and films are discussed. © 2002 Elsevier Science Ltd All rights reserved.

*Keywords:* Polyimides; Low color thin films; Structure property relationship

## 1. Introduction

Since 1960, essentially the beginning of the search for high temperature polymers, more attention was focused on polyimides than any other high performance/high temperature polymers. This is primarily due to the availability of polyimide monomers (particularly aromatic dianhydrides and diamines), the ease of polymer synthesis, and their unique combination of physical and mechanical properties [1–3]. A significant amount of technology has been developed such that polyimides have found wide spread commercial use as adhesives, coatings, composite matrices, fibers, films, foams, membranes, and moldings. The market for polyimides in 2000 was about $1B. Although there are many different synthetic routes to polyimides, the most popular is the reaction of an aromatic dianhydride with an aromatic diamine to form a soluble precursor polyamide acid (amic acid) that is subsequently chemically or thermally converted to the polyimide. Most polyimides were and still are made by this method.

So far, more work was concentrated on the polyimide from the reaction of pyromellitic dianhydride and 4,4′-oxydianiline than any other polyimide. Several products are based on this polymer [poly(4,4′-oxydiphenylenepyromellitimide)] such as Pyre ML® wire enamel [I.S.T. (MA) Corporation], commercial films (Kapton® produced by Du Pont and Apical® produced by Kaneka) and a Du Pont molded product, Vespel®. Kapton® and Vespel® constitute the largest markets. Another well-known film made via a polyamide acid from the reaction of 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA) and 1,4-phenylenediamine is Upilex® S produced by Ube Industries, Ltd.

Over the years, a tremendous amount of work has been performed on structure/property relationships in polyimides to obtain fundamental information that could be used to develop polyimides with unique combination of properties for demanding applications. More recently, nanoparticles (e.g. clays, carbon nanotubes, inorganic nanoparticles, etc.) have been incorporated within polyimides to enhance certain mechanical and physical properties. Recently, new

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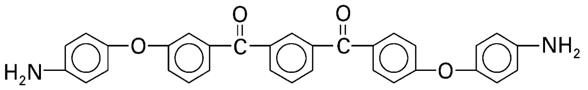
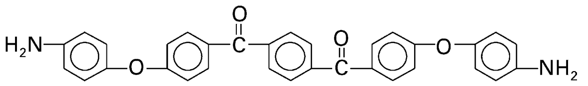
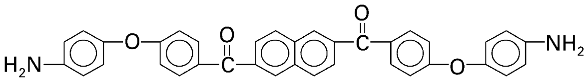
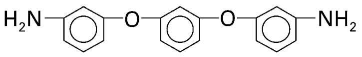
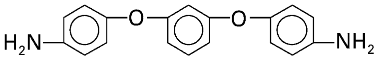
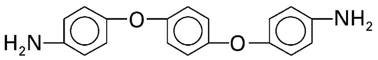
Table 1
Monomer information

| Monomer | Monomer structure | Source | Melting point (°C) | Recrystallization solvent |
|---|---|---|---|---|
| 1 |  | Daychem Laboratories, Inc. | 163–164.5 | Butanol |
| 2 |  | Daychem Laboratories, Inc. | 238.5–239.5 | Used as-received |
| 3 |  | Made in-house | 231–232.5 | Dioxane/water |
| 4 |  | Mitsui Chemicals, Inc. | 107–108.5 | Used as-received |
| 5 |  | Mitsui Chemicals, Inc. | 116–117 | Ethanol/water |
| 6 |  | ChrisKev Co., Inc. | 171–172.5 | Used as-received |

linear polyimides from 2,3,3′,4′-biphenyltetracarboxylic dianhydride (a-BPDA) [4] with unusual and unexpected properties have been reported [5–12]. For example, a-BPDA based polyimides have higher glass transition temperatures ($T_g$s) than the corresponding symmetric BPDA (s-BPDA) based polyimides. Phenylethynyl terminated imide oligomers (PETIs) from a-BPDA had significantly lower melt viscosities and higher $T_g$s for the cured polymers than found for analogous s-BPDA PETIs [13–15]. In addition, a-BPDA based polyimides have a combination of low melt viscosity and high $T_g$ that surpasses other similar polyimides.

NASA has several space applications that currently use or evaluate polyimides. These include thin films as membranes on antennas, concentrators, coatings on second-surface mirrors, solar sails, sunshades, thermal/optical coatings and multi-layer thermal insulation (MLI) blanket materials. Depending on the application, the film will require a unique combination of properties. These may include atomic oxygen resistance, ultraviolet (UV) and vacuum ultraviolet (VUV) resistance, low color/low solar absorption, electron and proton resistance, tear/wrinkle resistance for packaging and deployment, and high mechanical properties (strength, modulus, and toughness). Atomic oxygen resistance coupled with low color and UV stability has been introduced into polyimides by using phenylphosphine oxide containing monomers [16]. Since polyimides derived from a-BPDA were thought to offer an attractive combination of properties such as low color, good solubility, high thermal emissivity, low solar absorptivity and high tensile properties, a series of new linear a-BPDA based polyimides were prepared and these were compared with the corresponding polyimides from s-BPDA. This work was performed to obtain fundamental information on chemical structure/property relationships that could lead to the development of improved films for space use to meet NASA needs. The chemistry and properties of these new polyimides are discussed.

## 2. Experimental

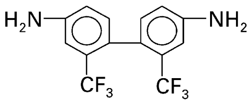
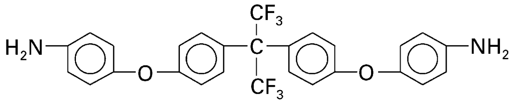
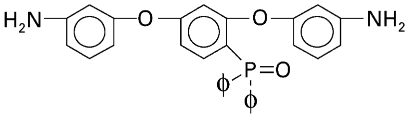
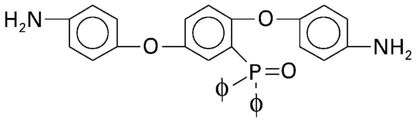
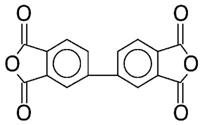
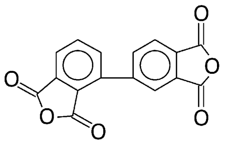
### 2.1. Monomers and other chemicals

The monomers in Tables 1 and 2 were obtained from commercial sources, custom synthesis houses or synthesized in-house. Monomer 3 was synthesized following a literature procedure [17], mp 231–232.5 °C [lit. mp 178–181 °C [17]], compound has different crystalline forms]. The synthesis of monomer 10 is described below. Anhydrous *N*,*N*-dimethylacetamide (99.8%, DMAC) was obtained from Aldrich and used as-received. *meta*-Cresol was obtained from Fluka and redistilled under a nitrogen atmosphere. All other chemicals were obtained from commercial sources and used as-received.

### 2.2. Preparation of [2,5-bis(4-aminophenoxy)phenyl]diphenylphosphine oxide (monomer 10)

Into a flame dried 2 l three neck round bottomed flask equipped with a mechanical stirrer, nitrogen gas inlet, pressure equalizing addition funnel, and drying tube were charged *p*-benzoquinone (30.16 g, 0.2790 mol) and toluene (750 ml). Diphenylphosphine oxide (56.42 g, 0.2790 mol) in toluene (250 ml) was added dropwise over 0.5 h to the stirred solution at room temperature under nitrogen. The solution color changed from a dark brown to yellow with the

Table 2
Monomer information

| Monomer | Monomer structure | Source | Melting point (°C) | Recrystallization solvent |
|---|---|---|---|---|
| 7 |  | ChrisKev Co., Inc. | 179.5–182 | As-received |
| 8 |  | Central Glass Co., Ltd | 159–161 | Isopropanol |
| 9 |  | Sarchem Laboratories, Inc. | 195–196 | Methanol/ethyl acetate |
| 10 |  | Made in-house | 205–208 | Ethanol/water |
| 11 |  | ChrisKev Co., Inc. | 297–298 | Used as-received |
| 12 |  | Ube Industries, Ltd | 195.5–197 | Toluene/acetic anhydride |

formation of a gum. Upon further stirring, a grey solid formed. The solid was isolated, washed with toluene and then diethyl ether, and dried at 110 °C in flowing air to afford 74.0 g (85% crude yield) of an off-white solid. Recrystallization from ethanol afforded 2,5-dihydroxyphenyldiphenylphosphine oxide as a white solid (62.86 g, 73% recovery), mp 216–218 °C [lit. mp 214–215 °C [18]].

2,5-Dihydroxyphenyldiphenylphosphine oxide (27.62 g, 0.0890 mol), 1-chloro-4-nitrobenzene (28.05 g, 0.1780 mol), potassium carbonate (28.00 g, 0.2026 mol), DMAC (150 ml) and toluene (130 ml) were charged into a 1 l three neck round bottom flask equipped with a mechanical stirrer, nitrogen inlet, and a Dean–Stark trap. The mixture was heated to a gentle reflux while removing water via azeotropic distillation. After ~4 h, the toluene was removed from the reaction and the resultant solution heated at ~165 °C for ~16 h. The reaction mixture was cooled to room temperature and then poured into water with vigorous stirring to afford a light brown solid. The crude solid was collected via filtration, washed twice with hot water, and air dried at 110 °C to afford 47.6 g (97% crude yield). Recrystallization from 2-ethoxyethanol afforded [2,5-bis(4-nitrophenoxy)phenyl]diphenylphosphine oxide as a yellow solid (39.21 g, 80% recovery), mp 239–242 °C. $^1$H NMR (DMSO-$d_6$) $\delta$: 6.8 (1H, d), 7.3 (1.5H, m), 7.5 (4H, m), 7.7 (2H, m), 8.05 (1H, d), 8.3 (1H, d). $^{13}$C (DMSO-$d_6$) ppm: 117.705, 118.186, 125.652, 126.325, 126.516, 126.820, 128.646, 128.808, 130.993, 131.296, 131.432, 132.107, 132.144, 132.410, 142.638, 142.903, 151.402, 151.577, 152.194, 152.226, 161.091, 162.177. Anal. calcd for $C_{30}H_{21}N_2O_7P$: C, 65.22%; H, 3.83%; N, 5.07%; P, 5.61%. Found: C, 65.27%; H, 3.93%; N, 5.08%; P, 5.07%.

Into a 250 ml Parr hydrogenation flask were charged [2,5-bis(4-nitrophenoxy) phenyl]diphenylphosphine oxide (5.4 g, 0.0098 mol) and 1,4-dioxane (100 ml). The solution was warmed to effect dissolution with subsequent cooling to room temperature upon which 10% Pd/C (0.59 g) was added. The mixture was degassed prior to the introduction of hydrogen gas. The mixture was agitated under a hydrogen atmosphere for ~24 h at room temperature. After degassing the solution, the Pd/C was removed by filtration and the solution added to stirred water to afford an off-white solid. The crude solid was collected via filtration, washed with water, and dried at room temperature to afford 4.1 g (76% crude yield). Recrystallization from aqueous ethanol afforded [2,5-bis(4-aminophenoxy)phenyl]diphenylphosphine oxide as a tan solid (3.2 g, 80% recovery), mp 205–208 °C. Anal. calcd for $C_{30}H_{25}N_2O_3P$: C, 73.16%; H, 5.12%; N, 5.69%; P, 6.29%. Found: C, 72.87%; H, 5.08%; N, 5.78%; P, 5.64%.

### *2.3. Polyamide acid preparation*

The polyamide acids were prepared by placing the diamine in DMAC in a nitrogen atmosphere and stirring at room temperature to form a solution or slurry and subsequently adding a stoichiometric quantity of the dianhydride as a solid or in some cases as a slurry in DMAC. The solids content was adjusted to 20% (weight to weight, w/w) by the addition of DMAC. The reaction was stirred at ambient temperature for ~24 h to form a viscous solution of the polyamide acid. The inherent viscosities of the polyamide acids are presented in Tables 3–8.

An endcapped polyimide of 30 000 g/mol was also prepared as follows. The polyamide acid was prepared as described above by upsetting the stoichiometry in favor of the diamine. After stirring the polyamide acid solution in a nitrogen atmosphere for ~24 h at ambient temperature, a stoichiometric quantity of phthalic anhydride was added as the endcapping agent and the reaction was stirred for 6 h to yield a polyamide acid with an inherent viscosity of 0.55 dl/g. The polyamide acid was thermally converted to polyimide as described in Section 2.5.

### *2.4. Polyimide preparation in meta-cresol*

Certain polyimides were prepared directly in *m*-cresol because the DMAC solutions of the polyamide acids would not form flexible films after curing at 250 or 300 °C. The polyimides indicated in Tables 5 and 6 were prepared by adding the diamine to *m*-cresol containing a catalytic amount of isoquinoline and stirring under a nitrogen atmosphere for ~0.5 h at room temperature. A stoichiometric quantity of dianhydride was added, the solids content was adjusted to 20% (w/w), the reaction was heated to 200 °C and stirred at 200 °C under a nitrogen atmosphere for 4–6 h to form a viscous solution. The cooled polyimide solution was diluted with *m*-cresol and poured into methanol in a blender to precipitate a fibrous solid that was isolated, subsequently washed in boiling methanol twice and dried in air at 150 °C for 4 h. The polyimides were dissolved in DMAC for inherent viscosity measurements and film casting. Polymer characterization is presented in Tables 5 and 6.

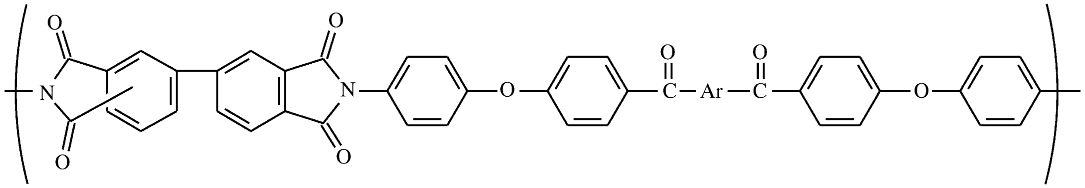
### *2.5. Films*

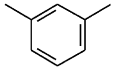
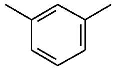
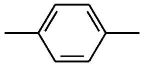
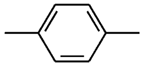
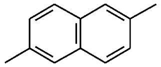
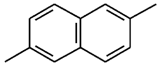
Thin films were cast from polyamide acid and polyimide solutions in DMAC generally at 20% solids (w/w) content. In some cases the solutions of highly viscous polyamide acid solutions were diluted to 10–15% solid contents to allow bubbles to escape from the solution prior to film casting. The solutions were generally centrifuged and the decantate doctored onto clean, dry plate-glass and dried to a tack-free form in a low humidity air chamber overnight at room temperature. At 20% solids content, a wet film (about 0.64 mm) was doctored onto the glass plate. The films were stage-cured (dried) in forced air ovens by heating for 1 h each at 100, 150, 200, and 250 °C and in some cases for an additional hour at 300 °C and another hour at 350 °C. No attempt was made to control the heatup and cooldown rates of the ovens. In most cases, the thin films were removed from the glass by immersion in water. Specimens (15.2 cm long, 0.51 cm wide, 0.038–0.066 mm thick) were cut with a JDC Precision Sample Cutter, Thwing–Albert Instrument Company. The tensile properties were determined following the general procedure in ASTM D882 using four to five specimens per test condition. The test specimen gauge length was 5.1 cm and the crosshead speed for film testing was 0.51 cm/min using a Sintech 2 instrument with an Eaton Model 3397-139 11.4 kg load cell.

### *2.6. Other characterization*

Melting points were determined on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Differential scanning calorimetry (DSC) was conducted on a Shimadzu DSC-50 thermal analyzer with the sample sealed in an aluminum pan. Glass transition temperatures ($T_g$s) were determined with DSC at a heating rate of 20 °C/min with the $T_g$ taken at the inflection point of the $\Delta T$ versus temperature curve. The crystalline melting points ($T_m$s) were taken at the endothermic peak. Inherent viscosities ($\eta_{inh}$) were obtained on 0.5% (w/v) polyamide acid and polyimide solutions in DMAC at 25 °C. Coefficients of thermal expansion were measured with a Perkin Elmer Thermal Mechanical Analyzer-7 at a heating rate of 2 °C/min on thin film specimens, 5.11 mm × 9.1 mm × ~ 0.055 mm, under a force of 25 mN in the extension mode. Dynamic thermogravimetric analyses (TGA) were determined on films using a Seiko Instrument SSC 5200 at a heating rate of 2.5 °C/min in a nitrogen atmosphere. Dynamic mechanical thermal analysis (DMTA) was performed on thin film specimens on a Mac Science TMA-4010 instrument at a heating rate of 5 °C/min and a load frequency (sinusoidal) of 0.1 Hz in a nitrogen atmosphere. Wide angle X-ray diffraction (WAXD) was obtained on thin films with a D5000 Siemens Diffractometer with a nickel filter, a wavelength of 1.54 Å using copper radiation, a graphite monochromator, and step time of 2.0 s at 0.010°/step between the angles of 0 and 40 $2\theta$. Elemental Analyses were performed by Desert Analytics, Tucson, AZ. The percentage light transmission through thin films was measured using a Perkin–Elmer Lambda 900 ultraviolet/-visible/near infrared spectrometer. Solar absorptivities ($\alpha$) of thin films were measured on an AZTek Model LPSR-300 spectroreflectometer with measurements taken between 250 and 2800 nm with a vapor deposited aluminum on Kapton® film (first surface mirror) as a reflective reference per ASTM E903-82. An AZTek Temp 2000A infrared reflectometer was used to measure the thermal emissivity ($\varepsilon$) of thin films.

Table 3
Polyimide structure/property relationship



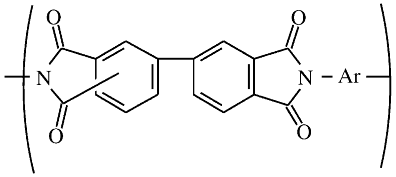
| Polymer no./ dianhydride | Ar | $\eta_{inh}$ (dl/g) PAA | $T_g$ ($T_m$) (°C) film[a] | $T_g$ ($T_m$) (°C) [Lit. Ref.] | Film color | 23°C tensile properties | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Strength, MPa | Modulus, GPa | Elong, % |
| 3-1/A |  | 1.21 | 237 | New | Yellow | 95.1 | 2.61 | 11.2 |
| 3-1/S |  | 1.25 | 223 | 222 [17] | Yellow | 93.1 | 2.40 | 6.5 |
| 3-2/A |  | 1.08 | 256 | New | Yellow | 91.7 | 2.52 | 10.3 |
| 3-2/S |  | 2.13 | 239 (407)<br>262 (378, 403)[b] | 245 (414) [17] | Yellow, opaque<br>Orange, opaque | 114.4<br>124.8 | 3.33<br>3.45 | 15.5<br>10.0 |
| 3-3/A |  | 0.95 | 263 | New | Light orange | 99.3 | 2.43 | 9.0 |
| 3-3/S |  | 1.19 | 252 (417) | 246 (424) [17] | Orange, opaque | 111.7 | 2.35 | 3.4 |

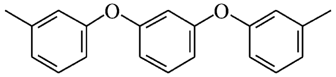
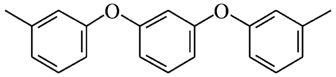
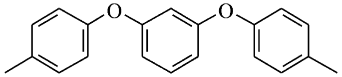
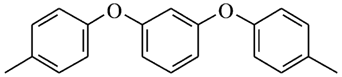
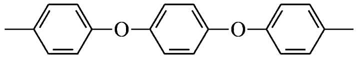
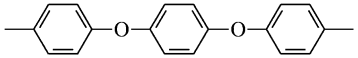
Made via the polyamide acids.

[a] Film cured for 1 h at 250 °C.

[b] Film cured for 1 h at 350 °C.

Table 4
Polyimide structure/property relationship



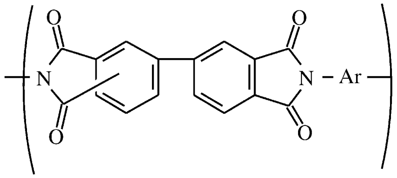
| Polymer no./dianhydride | Ar | $\eta_{inh}$ (dl/g) PAA | $T_g$ ($T_m$) (°C) film[a] | $T_g$($T_m$) (°C) [Lit. Ref.] | Film color | 23 °C tensile properties | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Strength (MPa) | Modulus (GPa) | Elongation (%) |
| 4-1/A |  | 0.73 | 207 | New | Near colorless | 109.6 | 3.02 | 5.9 |
| 4-1/S |  | 0.87 | 200 | 202 [17] | Pale yellow | 118.6 | 3.48 | 25.5 |
| 4-2/A |  | 1.51 | 248 | New | Light yellow | 80.0 | 2.47 | 5.4 |
| 4-2/S |  | 1.22 | 211 (391) | 210 (395) [20] | Yellow, opaque | 122.7 | 3.57 | 90 |
| 4-3/A |  | 1.44 | 276[b] | New | Pale yellow | 98.6 | 2.38 | 8.9 |
| 4-3/S |  | 2.20 | 265[b] (455) | 259 (471) [21] | Yellow | 143.4 | 4.10 | 34 |

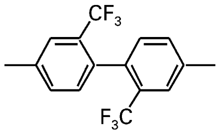
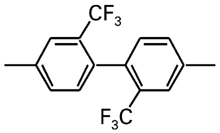
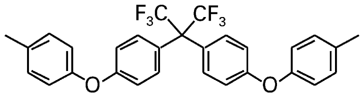
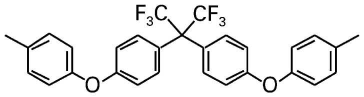
Made via the polyamide acids.

[a] Film cured for 1 h at 250 °C.

[b] Film cured for 1 h at 300 °C.

Table 5
Polyimide structure/property relationship



| Polymer no./dianhydride | Ar | $\eta_{inh}$ (dl/g) PAA | $T_g$ (°C) film[a] | $T_g$ (°C) [Lit. Ref.] | Film color | 23 °C tensile properties | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Strength (MPa) | Modulus (GPa) | Elongation (%) |
| 5-1/A |  | 0.72 | 312 | New | Near colorless | Brittle | | |
| | | 0.83[b] imide | ND[a] | | Near colorless | 65.5 | 2.99 | 2.4 |
| | | | 329[c] | | Orange | 111.0 | 3.05 | 4.6 |
| 5-1/S |  | 1.46 | 280 | 287 [22] | Very pale yellow | 144.1 | 5.18 | 4.2 |
| 5-2/A |  | 1.14 | 261 | New | Pale yellow | 124.1 | 3.04 | 7.4 |
| 5-2/S |  | 1.93 | 254 | 260 [23] | Yellow | 111.0 | 3.03 | 31.2 |

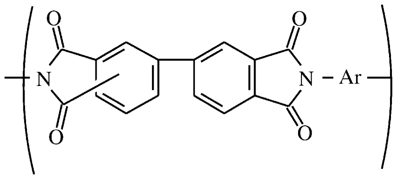
Made via the polyamide acid.

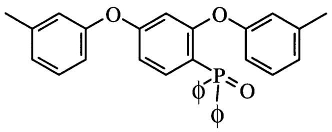
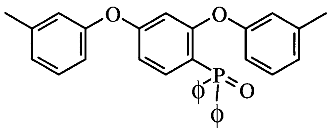
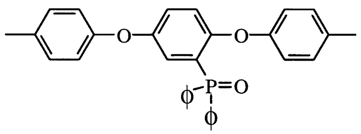
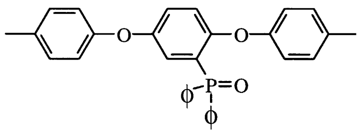
[a] Film cured for 1 h at 250 °C (ND, not detected).

[b] Made in *m*-cresol.

[c] Film cured for 1 h at 350 °C.

Table 6
Polyimide structure/property relationship



| Polymer no./dianhydride | Ar | $\eta_{inh}$ (dl/g) | $T_g$ (°C) film[a] | $T_g$ (°C) [Lit. Ref.] | Film color | 23 °C tensile properties | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Strength (MPa) | Modulus (GPa) | Elongation (%) |
| 6-1/A[b] |  | 0.55 imide | 233 | New | Near colorless | 73.1 | 3.46 | 2.9 |
| 6-1/S[b] |  | 0.69 imide | 230 | 234 [16] | Pale yellow | 99.3 | 3.14 | 4.7 |
| 6-2/A[c] |  | 0.50 | 250 | New | Orange | 112.4 | 3.42 | 5.2 |
| | | 0.59 | 259[d] | | Orange | 108.9 | 3.38 | 12.6 |
| 6-2/S[c] |  | 0.75 | 245 | New | Orange | 128.9 | 3.72 | 9.6 |
| | | 1.00 | 258[d] | | Orange | 151.0 | 4.34 | 31.4 |

[a] Films cured for 1 h at 250 °C.

[b] Made in *m*-cresol.

[c] Made via the polyamide acid.

[d] Films cured for 1 h at 300 °C.

Table 7
Properties of a-BPDA polymers and films cured at different temperatures

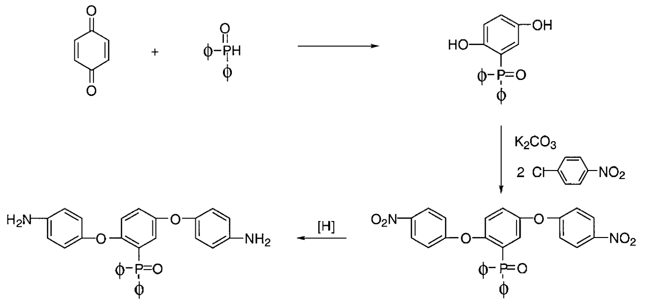
| Diamine | $\eta_{inh}$ (dl/g) PAA | Cure temperature for 1 h (°C)[a] | $T_g$ (°C) (Film) | Film color | Transmission at 500 nm (%) (Film thickness, mm) | 23 °C tensile properties | | | CTE × $10^{-6}$/°C (over temperature range, °C) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Strength (MPa) | Modulus (GPa) | Elongation (%) | |
| 1,3,3-APB[b] | 0.65 | 250 | 204 | Near colorless | 87 (0.066) | 107.5 | 3.31 | 4.1 | 48.8–52.7 (50–128) |
| | | 300 | 207 | Pale yellow | 85 (0.048) | 113.8 | 3.05 | 5.2 | 48.8–51.6 (55–150) |
| | | 350 | 209 | Yellow | 69 (0.058) | 124.0 | 3.28 | 5.7 | 50.9–51.8 (64–154) |
| | 0.66 | 250 | 202 | Near colorless | 86 (0.058) | 105.5 | 2.95 | 4.5 | |
| | | 300 | 207 | Pale yellow | 82 (0.064) | 118.6 | 3.11 | 5.3 | |
| | | 350 | 208 | Yellow | 70 (0.062) | 120.0 | 3.21 | 5.7 | |
| 1,4,4-APB[c] | 1.47 | 250 | 276 | Pale yellow | 85 (0.046) | 102.7 | 2.66 | 6.8 | 56.5–60.0 (60–240) |
| | | 300 | 278 | Yellow | 84 (0.046) | 97.2 | 2.56 | 21.8 | 50.2–65.6 (55–240) |
| | | 350 | 287 | Light orange | 66 (0.043) | 93.8 | 2.33 | 43.7 | 52.7–64.6 (50–240) |
| | 1.49 | 250 | 278 | Pale yellow | 85 (0.046) | 107.5 | 2.69 | 7.9 | |
| | | 300 | 279 | Yellow | 82 (0.041) | 106.2 | 2.65 | 12.9 | |
| | | 350 | 285 | Yellow | 70 (0.043) | 103.4 | 2.65 | 16.5 | |

[a] Cure temperatures are accumulative (i.e. 350 °C cure is 1 h each at 250, 300, and 350 °C).
[b] 1,3-Bis(3-aminophenoxy)benzene (Monomer 4).
[c] 1,4-Bis(4-aminophenoxy)benzene (Monomer 6).

Table 8
Properties of s-BPDA polymers and films cured at different temperatures

| Diamine | $\eta_{inh}$ (dl/g) PAA | Cure temperature for 1 h (°C)[a] | $T_g(T_m)$, (°C) (Film) | Film color | Transmission at 500 nm (%) (film thickness, mm) | 23 °C tensile properties | | | CTE × $10^{-6}$/°C (over temperature range, °C) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Strength (MPa) | Modulus (GPa) | Elongation (%) | |
| 1,3,3-APB[b] | 0.97 | 250 | 202 | Pale yellow | 82 (0.064) | 124.1 | 3.36 | 59 | 45.7 (60–160) |
| | | 300 | 202 | Yellow | 78 (0.061) | 124.1 | 3.34 | 53 | 45.7 (60–160) |
| | | 350 | 204 | Intense yellow | 61 (0.053) | 120.6 | 3.32 | 18 | 45.6 (60–180) |
| 1,4,4-APB[c] | 1.93 | 250 | 263 (461) | Yellow | 77 (0.046) | 135.8 | 3.51 | 26 | 41.2 (80–220) |
| | | 300 | ND(460) | Yellow | 75 (0.043) | 141.3 | 3.38 | 45 | 43.5 (80–220) |
| | | 350 | 278 (385, 455) | Intense yellow | 60 (0.043) | 155.1 | 3.59 | 57 | 47.7 (80–220) |

[a] Cure temperatures are accumulative (i.e. 350 °C cure is 1 h each at 250, 300, and 350 °C).
[b] 1,3-Bis(3-aminophenoxy)benzene (Monomer 4).
[c] 1,4-Bis(4-aminophenoxy)benzene (Monomer 6).



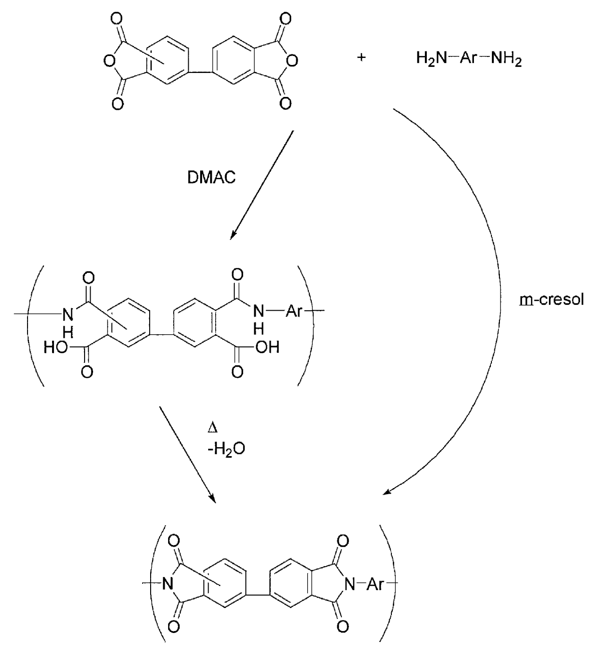
Scheme 1. Synthetic route to monomer 10.

## 3. Results and discussion

### 3.1. Synthesis

Most of the monomers in Tables 1 and 2 were obtained from commercial sources or custom synthesis houses. Only monomers 3 and 10 were synthesized in-house. The melting point of 231–232.5 °C for monomer 3 differs from the literature value of 178–181 °C [17] presumably because of a different crystalline form. Polymorphism has been observed for ketone ether diamines [17]. The elemental analysis of monomer 3 agreed with the theoretical values and the $^1$H NMR spectrum was consistent with the proposed structure. The three step synthesis of monomer 10, a new compound, is depicted in Scheme 1. In many cases, monomers from commercial sources were recrystallized prior to use.

Polyimides in Tables 3–8 were made via the polyamide acids from the reaction of an aromatic diamine with an aromatic dianhydride in DMAC at 20% solids content (w/w) or in *m*-cresol as depicted in Scheme 2. In preparing the various polymers, the reaction solution viscosities of the polyamide acids from a-BPDA were less than those from s-BPDA. Using the same diamine, the DMAC solution viscosity of the polyamide acid from s-BPDA increased substantially within 1 h of reaction time whereas the viscosity of the polyamide acid from a-BPDA increased slowly and only in a few cases attained a solution viscosity comparable to that of the corresponding s-BPDA polyamide acid. For example, the polyamide acids from the reaction of a-BPDA and s-BPDA with 1,3-(3-aminophenoxy)benzene (1,3,3-APB) had inherent viscosities of 0.61 and 0.90 dl/g after 2.5 h and 0.64 and 0.96 dl/g after an additional 67 h, respectively. The a-BPDA polyamide acid had a higher inherent viscosity than the analogous s-BPDA polyamide acid in only one set of polymers (polymers 4-2/A and 4-2/S in Table 4). The difference in the reaction solution viscosity and the inherent viscosity of the a-BPDA and s-BPDA polymers implies that the s-BPDA polymers were of higher molecular weights but this is conjecture since no absolute molecular weights were measured. *meta* Catenated diamines 4 and 9 were less reactive than the *para* catenated diamines due to lower nucleophilicity resulting from the *meta* connection relative to the ether oxygen.



Where the dianhydride is 2,3,3′,4′- and 3,3′,4,4′- and Ar is represented in Tables 3-8.

Scheme 2. Synthetic routes to polyimides.

Polymers 6-1/A and 6-1/S in Table 6 were made in *m*-cresol containing a catalytic amount of isoquinoline because polyamide acids with inherent viscosities >0.40 dl/g could not be obtained. Polymer 5-1/A in Table 5 was made via the polyamide acid but also in *m*-cresol in an attempt to obtain a higher molecular weight version. The synthesis in *m*-cresol provided an improvement in the molecular weight (inherent viscosity in DMAC increased from 0.72 dl/g for the polyamide acid to 0.83 dl/g for the polyimide). All of the s-BPDA based polyimides made in this study except for 6-2/S (Table 6) has been previously reported and references are cited in the appropriate tables. Polyimide 5-1/S (Table 5) is known and has exhibited high mechanical properties [24,26], low coefficient of thermal expansion (CTE) [22], and excellent thermooxidative stability [28]. This polymer was previously made in *m*-cresol [22] and has been extensively studied as a film [22,24,25] and a fiber [26–28]. Literature reports intrinsic viscosities in *m*-cresol generally in the range of 4.5–5.5 dl/g [22,26,27] and an extrapolated $T_g$ (based on the change in the CTE) of 287 °C [22]. The polymer reported herein (5-1/S) was made via the polyamide acid and had an inherent viscosity in DMAC of 1.46 dl/g and a $T_g$ of 280 °C.

### 3.2. Glass transition temperatures

All of the polyamide acids in Table 3 from the reaction of diamine monomers 1–3 with a-BPDA and s-BPDA were made in high molecular weights as indicated by inherent viscosities of 0.95–2.13 dl/g. In Table 3, the a-BPDA polyimides had $T_g$s higher than the corresponding s-BPDA derived polyimides. Higher $T_g$s for a-BPDA derived polyimides versus the s-BPDA polyimides have been reported by others [6–9]. The higher $T_g$s for the a-BPDA polyimides has been attributed to the asymmetric structure requiring a larger sweep volume for the crank shaft motion and accordingly more energy (higher temperature) to obtain this motion [8]. Two of the s-BPDA polyimides in Table 3 were semi-crystalline while the a-BPDA counterparts were amorphous. No semi-crystalline polyimides based on a-BPDA were observed in this study and it is unlikely any a-BPDA based polyimides will show crystallinity because the highly irregular structure of the polymer emanating from the asymmetric dianhydride appears to prohibit the formation of crystalline regions. On comparing the $T_g$s of polymers from one study to another, the thermal history should be considered since it has a pronounced effect on the $T_g$. The thermal histories of the referenced polymers in Tables 3–6 differ from those in this study. Hence, it is not surprising to observe some differences in the $T_g$s. The film of polymer 3-2/S cured for 1 h at 250 °C had a $T_g$ of 239 °C and a $T_m$ of 407 °C. When the film was further cured at 350 °C for 1 h, the $T_g$ had increased to 262 °C and two $T_m$s were present at 378 and 403 °C. An increase in the $T_g$ is common when films are cured at higher temperature particularly in air but an increase of 23 °C is higher than normal. Higher $T_g$s for polyimides upon curing at higher temperatures in air are generally associated with several factors such as an increase in molecular weight, completion of ring closure, removal of residual solvent, cross-links, and molecular packing.

All of the polyamide acids in Table 4 were prepared in relatively high molecular weights with inherent viscosities of 0.73–2.20 dl/g. The same $T_g$ trend was observed where all of the a-BPDA polyimides had $T_g$s higher than the s-BPDA polyimides. The diamines were *meta*-catenated [monomer 4, 1,3-bis(3-aminophenoxy)benzene, 1,3,3-APB], *meta–para* connected [monomer 5, 1,3-bis(4-aminophenoxy)benzene, 1,3,4-APB] and *para*-catenated [monomer 6, 1,4-bis(4-aminophenoxy)benzene, 1,4,4-APB]. As expected, polyimides made from the flexible 1,3,3-APB had $T_g$s less than those made from the less flexible 1,3,4-APB which were less than those from the slightly stiff 1,4,4-APB. At the beginning of this study, phthalic anhydride endcapped polyimide 4-1/A in Table 4 was made at a controlled molecular weight of 30 000 g/mol with an inherent viscosity of 0.55 dl/g. Films were cast from the polyamide acid solution and cured through 1 h at 250 and 1 h at 300 °C. The 250 °C cured film had a $T_g$ of 201 °C while the 300 °C cured film had a $T_g$ of 204 °C, slightly lower than polymer 4-1/A.

Table 5 contains information on four polyimides containing trifluoromethyl groups from diamine monomers 7 and 8. Again, the a-BPDA polyimides had $T_g$s higher than the s-BPDA polyimides. The semi-rigid polymers (5-1/A and 5-1/S) from the substituted benzidine had $T_g$s significantly higher than the hexafluoroisopropylidene containing polymers as expected.

Four polyimides containing the phenylphosphine oxide group from monomers 9 and 10 are reported in Table 6. The trend of a-BPDA polyimides having higher $T_g$s than s-BPDA polyimides continued. As expected, the polyimides from 1,3,3-APB containing phenylphosphine oxide had $T_g$s about 30 °C less than polyimides from the slightly stiff 1,4,4-APB containing phenylphosphine oxide. The s-BPDA/1,4,4-APB phenylphosphine oxide polyimide failed to show any crystallinity apparently because the bulky diphenylphosphine oxide group disrupts the symmetry or regularity leading to highly ordered regions. Polymers 6-2/A and 6-2/S were made twice because the first set of films was inadvertently cured at 300 °C instead of 250 °C. Upon making the polyamide acids again, the inherent viscosities were lower and the tensile properties of films of 6-2/S cured at 250 °C were significantly lower than those cured at 300 °C.

### 3.3. Films

In forming films, all of the polyamide acid and polyimide solutions in Tables 3–8 were doctored onto clean plate glass and stage-dried in a forced air oven for 1 h each at 100, 150, 200, and 250 °C. No intentional orientation was performed although some may have occurred while curing on the glass plates. The films were generally removed from the glass plates by immersion in water. In most cases, the film pulled glass from the surface of the plates, resulting in wrinkles. Although the $T_g$ of several of the cured films exceeded 250 °C, all of the initial films were cured at 250 °C because in this study, film color was of particular interest. Generally, polymers are cured beyond the $T_g$ because the molecular motion above the $T_g$ allows tenaciously held molecules (e.g. solvent) to depart more easily and induces molecular packing. However, most films in this study cured at temperatures $>250$ °C in air tend to darken slightly in color. Near colorless films turned pale yellow while yellow films often became more intense yellow to orange. Some films were also cured at temperatures $>250$ °C. Higher cure temperatures generally improved the tensile properties at the sacrifice of color. Curing in a nitrogen atmosphere would have been desired and probably would have helped reduce the color of some films but the ovens were not properly rigged to provide a good nitrogen atmosphere. Since the presence of residual solvent and complete conversion of the polyamide acid to polyimide was a concern, a study was performed primarily to evaluate color, $T_g$, and tensile properties as a function of cure temperature. This is reported later in this paper.

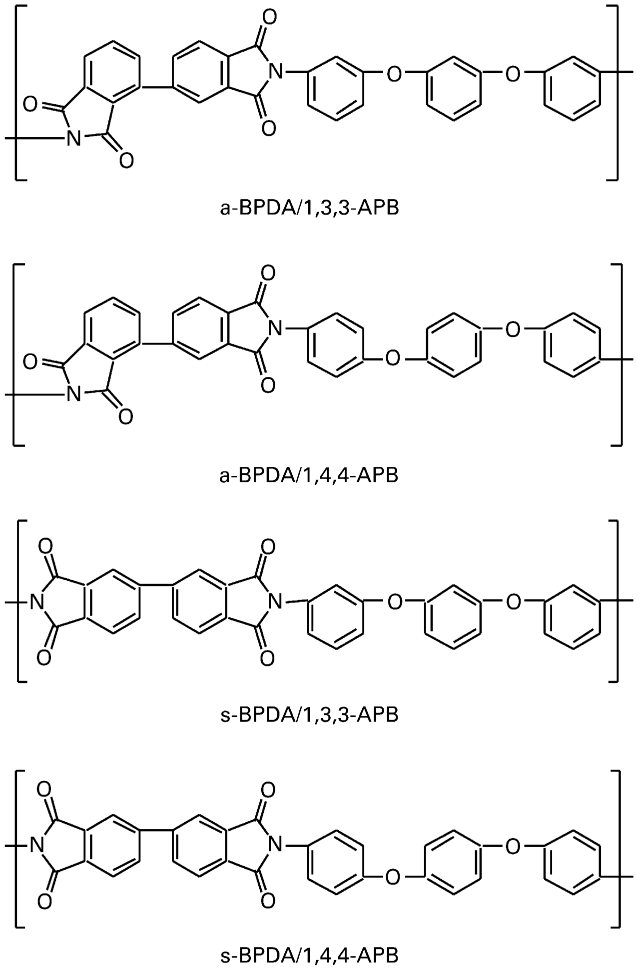
All of the thin film tensile properties are reported as averages of four to five specimens. The coefficient of variation (COV) within four to five specimens for the tensile strengths was 2–10% while the COV for the moduli was about 0.2–8%. The COV for the elongation was high with values ranging from 7 to 50%. Film elongation is more sensitive to flaws within the test specimens caused by foreign particles (e.g. gel particles and dust), wrinkles, etc. and minor specimen misalignment during the test than strength or modulus. The 23 °C tensile properties, particularly strength and modulus, of the s-BPDA based polyimide films were higher, and in some cases significantly higher, than those of the a-BPDA based polyimide films with a few exceptions. The best overall 23 °C tensile properties are those for the film from polymer 6-2/S in Table 6 with the strength of 151.0 MPa, modulus of 4.34 GPa and an elongation of 31%. Polymer 4-2/S had the highest elongation (90%) while polymer 5-1/S gave the highest modulus (5.18 GPa).

On comparing the tensile properties of the films in Table 4, it was interesting to note that the tensile strength and modulus of the a-BPDA polymer made with the most flexible diamine (monomer 4, 1,3,3-APB) was significantly higher than films of polymers made with the less flexible diamines (monomer 5, 1,3,4-APB and monomer 6, 1,4,4-APB). This was unexpected. The same trend was not present in the s-BPDA polyimides in Table 4. This phenomenon was reflected in the tensile strength and modulus but not in the $T_g$. The high tensile properties were not anticipated because the polymer with the highest stiffness (highest rigidity) should have provided the highest modulus. The same trend was not as pronounced for the polymers in Table 6 where the a-BPDA/1,3,3-APB phenylphosphine oxide polymer had a higher modulus in spite of a lower inherent viscosity than the corresponding s-BPDA polymer.

At the beginning of this study, films of a 30 000 g/mol phthalic anhydride endcapped polyimide of polymer 4-1/A in Table 4 were cured for 1 h at 250 °C and 1 h at 300 °C in air. The films showed slightly lower $T_g$s as mentioned previously but no visual difference in color when compared with the corresponding films in Tables 4 and 7. The thin film 23 °C tensile properties for the 250 and 300 °C cured films were virtually the same with the strength of 100.0 MPa, modulus of 3.02 GPa and an elongation of 4.0%. These values compare favorably with the tensile properties of the corresponding films in Tables 4 and 7. Since no advantage was observed for the endcapped polyimide, endcapping was not done on any other polymers in this study. The endcapping of high performance polymers obviously offers certain distinct advantages over unendcapped polymers such as better long term thermoxidative stability (durability) and significantly better melt stability than unendcapped polymers. Neither of these properties were of concern in this study.

### 3.4. Films cured at different temperatures

Films of the four polyimides whose chemical structures are shown in Fig. 1 were cured on clean plate glass in a forced air oven with the final cure of 1 h each at temperatures of 250, 300, or 350 °C. Table 7 contains information on the a-BPDA polyimides while Table 8 presents the data on the s-BPDA polyimides. In Table 7, the



a-BPDA/1,3,3-APB

a-BPDA/1,4,4-APB

s-BPDA/1,3,3-APB

s-BPDA/1,4,4-APB

Fig. 1. Polyimide structures.

properties of two batches of the polyamide acids from a-BPDA/1,3,3-APB and a-BPDA/1,4,4-APB and their films cured at different temperatures are presented. Two batches of each of the two polymers were made to assess the reproducibility of the polyamide acid formation and polyimide properties. The inherent viscosity of the polyamide acids and the $T_g$, color and tensile properties of the films overall showed excellent reproducibility. The only large variation was the 43.7% elongation of one 350 °C cured film. As observed for the same polyimides in Table 4 (4-1/A and 4-3/A) and previously discussed, the tensile strengths and especially the moduli of the a-BPDA/1,3,3-APB films were higher than those of the a-BPDA/1,4,4-APB films. The advantageous effects of curing at high temperatures are evident from the increase in $T_g$s for both polymers and the increase in film elongation for the 1,4,4-APB polymer. The disadvantage is the increase in color.

In Table 8, the properties of the s-BPDA/1,3,3-APB and 1,4,4-APB polyamide acids and polyimide films are presented. Unlike that of the a-BPDA polymers, the s-BPDA polyimides showed the expected trend with the polyimide from the slightly stiff diamine (1,4,4-APB) having the higher tensile strength and modulus, albeit only marginally higher. Overall the properties of the 250 °C cured films in Table 8 compared favorably with the properties of the corresponding polymers (4-1/S and 4-3/S) in Table 4. The $T_g$ and the elongation of the 1,4,4-APB polymer film increased with an increase in the cure temperature.

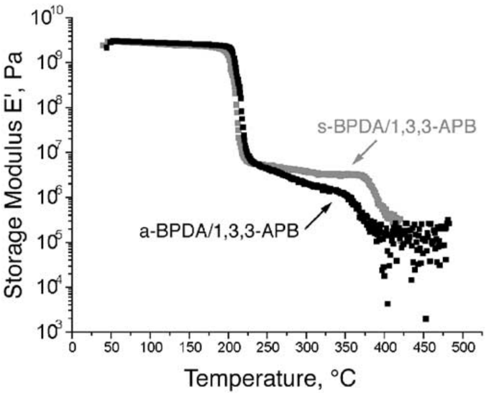


Fig. 2. DMTA curves of 350 °C cured films.

### 3.5. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis was performed at a heating rate of 5 °C/min on specimens from thin films of a-BPDA/1,3,3-APB, a-BPDA/1,4,4-APB, s-BPDA/1,3,3-APB and s-BPDA/1,4,4-APB that were cured at 250, 300, and 350 °C. Representative DMTA curves for the 350 °C cured specimens are shown in Figs. 2 and 3. All of the materials were amorphous based on DSC results except for the s-BPDA/1,4,4-APB specimen which exhibited $T_m$s of 385 and 455 °C. After the drop in storage modulus at the $T_g$, a plateau is observed that decreases slightly with temperature and then drops more than a decade beginning at about 350 °C for a-BPDA/1,3,3-APB, about 375 °C for s-BPDA/1,3,3-APB, about 400 °C for a-BPDA/1,4,4-APB, and slightly >400 °C for s-BPDA/1,4,4-APB. The plateau is similar to that seen for cross-linked, semi-crystalline or oriented materials. The s-BPDA/1,4,4-APB specimen is semi-crystalline and thus the DMTA curve is consistent with what was expected, exhibiting relatively high storage

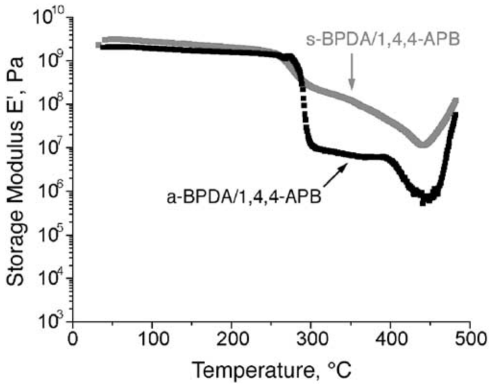


Fig. 3. DMTA curves of 350 °C cured films.

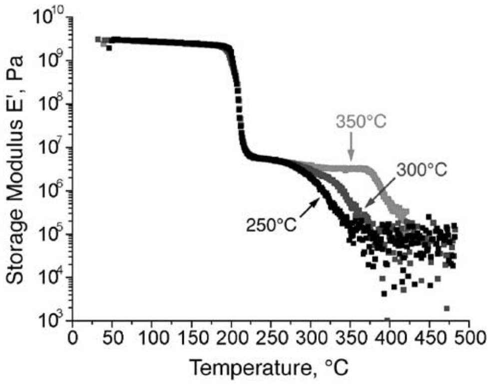


Fig. 4. DMTA curves of s-BPDA/1,3,3-APB films.

modulus beyond the $T_g$. However, the a-BPDA based specimens as well as the s-BPDA/1,3,3-APB specimens are amorphous and the plateaus observed beyond the $T_g$ were unexpected. The plateaus may arise from different effects such as polymer chain entanglement, ordered structure, and cross-linking. Cross-linking is ruled out because some of the films have high elongations (Tables 7 and 8) that are not commensurate with cross-linked polymers. Chain entanglement is obviously present in high performance amorphous thermoplastic polyimides but their DMTA curves do not show the plateaus. Chain entanglement restrained by ordered regions may be partly responsible for the plateaus. The most probable cause is order, not long-range order because no $T_m$s were observed in the DSC curves. In Fig. 4 for the s-BPDA/1,3,3-APB series, the 250 and 300 °C cured specimens were virtually identical to those of the 350 °C specimens up to the $T_g$ region. After the drop in the storage modulus at the $T_g$, the 250 °C specimen had a small plateau, the 300 °C specimen had a broader plateau, and the 350 °C specimen had a very broad plateau extending from 225 to 375 °C. Thus as the cure temperature increased, the plateau grew presumably due to an increase in conformational order. The same trend was observed in the DMTA curves of all the amorphous materials except the plateaus for the a-BPDA films were not as broad as those for the s-BPDA films.

In the DMA curves, a-BPDA/1,3,3-APB and 1,4,4-APB specimens exhibited drops in storage moduli of slightly more than three decades at the $T_g$ whereas the storage modulus for s-BPDA/1,3,3-APB decreased about two and a half decades. In all cases, the a-BPDA specimens showed higher temperatures ($T_g$s) than the s-BPDA specimens before the drop in modulus. This agrees with the DSC findings in Tables 7 and 8, namely that the a-BPDA materials had higher $T_g$s than the corresponding s-BPDA polymers.

### 3.6. Wide angle X-ray diffraction

Since the DMTA curves for the 350 °C cured films showed plateaus (retention of storage modulus) beyond the $T_g$s, the films were characterized by WAXD. The a-BPDA/1,3,3-APB and 1,4,4-APB 350 °C cured films were amorphous as evidenced by WAXD curves with essentially Gaussian distribution indicating no distinct structure, particularly long range structure. This was somewhat surprising since the DMTA curve for the a-BPDA/1,3,3-APB film in Fig. 2 showed a significant plateau after the $T_g$, suggesting some type of order. The WAXD of a 350 °C cured film of s-BPDA/1,4,4-APB in Fig. 5 showed sharp peaks characteristic of a crystalline polymer. Crystallinity in this film was already known because the DSC showed two crystalline melts (Table 8) and crystallinity in this polymer was previously reported [21]. No crystalline melt was detected in the DSC of the 350 °C cured s-BPDA/1,3,3-APB film but WAXD in Fig. 5 showed a non-Gaussian distribution pattern suggestive of some degree of order. The 250 °C cured s-BPDA/1,3,3-APB film had a Gaussian distribution typical of an amorphous polymer. As the exposure time at temperature and the temperature increased (1 h each at 250, 300, and 350 °C), some type of order appeared to be forming as evidenced by changes in the WAXD curves.

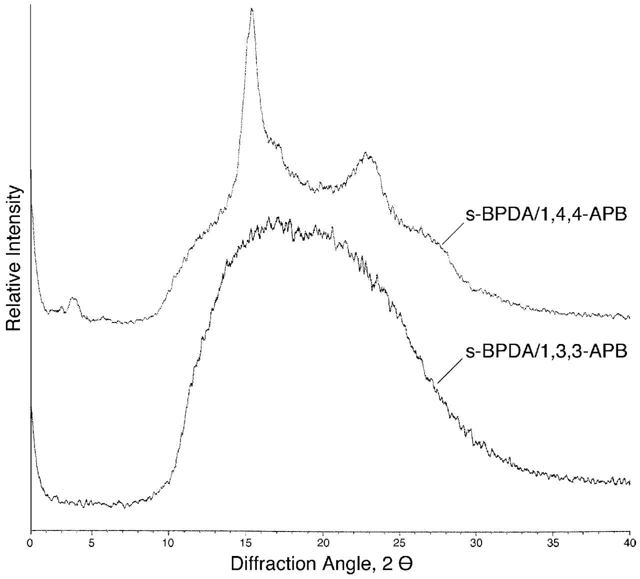


Fig. 5. Wide angle X-ray diffractograms of polyimide films.

### 3.7. Coefficient of thermal expansion

The CTE was measured by Thermal Mechanical Analysis in the extension mode at a heating rate of 2 °C/min on unoriented thin films cured individually for 1 h each at 250, 300 or 350 °C. Kapton® HN 100 was run as a standard and the measured CTE agreed with the published value. The CTE data is presented in Tables 7 and 8. The CTE of a polymer would generally be expected to be a function of the cure temperature, the higher the cure temperature, the lower the CTE. As previously mentioned, higher cure temperatures provide several attributes such as

Table 9
Thermogravimetric analysis of films in nitrogen

| Polymer | Film curing temperature (°C) | Weight loss (%) at temperature (°C) | | | |
|---|---|---|---|---|---|
| | | 300 | 350 | 450 | 500 |
| a-BPDA/1,3,3-APB | 250 | 0.12 | 0.17 | 0.67 | 1.94 |
| | 300 | 0.00 | 0.03 | 0.59 | 2.25 |
| | 350 | 0.00 | 0.00 | 0.54 | 3.30 |
| a-BPDA/1,4,4-APB | 250 | 0.09 | 0.17 | 0.55 | 1.36 |
| | 300 | 0.00 | 0.03 | 0.59 | 2.15 |
| | 350 | 0.00 | 0.00 | 0.35 | 2.30 |

Films were dried at 100 °C for 0.5 h prior to analysis.

more efficient packing of the molecules. Unfortunately, no trend was observed in the CTE as a function of cure temperature with these films. For the a-BPDA/1,3,3-APB films, the CTE ($\sim 50 \times 10^{-6}$/°C) remained about the same for films cured at the three temperatures. Surprising the films from the polymer, a-BPDA/1,4,4-APB, had about the same CTE at the lower temperatures as the more flexible a-BPDA/1,3,3-APB films. The *para* catenation from the diamine in the a-BPDA/1,4,4-APB polymer should have provided a stiffer backbone which was expected to be reflected in a lower CTE. The more rigid backbone provided $T_g$s for this polymer cured at different temperatures that were $\sim$70 °C higher that those of the a-BPDA/1,3,3-APB polymers. No sound scientific reason is offered to explain why the CTE data did not follow the expected trends.

In Table 8, the CTEs of unoriented thin films from the s-BPDA/1,3,3-APB and the s-BPDA/1,4,4-APB polymers cured at 250, 300, and 350 °C are presented. The CTE showed no change for films of the s-BPDA/1,3,3-APB polymer as a function of cure temperature. Whereas the films of the s-BPDA/1,4,4-APB polymer showed a change but in the reverse direction than expected. The film cured at 250 °C had a CTE lower than one cured at 350 °C. The films from the s-BPDA did however, show lower CTEs than comparable films from a-BPDA.

### 3.8. Thermogravimetric analysis of films

Samples of the films in Table 7 were characterized by TGA in nitrogen at a heating rate of 2.5 °C/min. Prior to TGA, the films were dried for 0.5 h at 100 °C in nitrogen to remove absorbed moisture. The weight losses at different temperatures are reported in Table 9. This analysis was performed on films of two polymers cured at 250, 300, and 350 °C to determine the weight loss as a function of curing temperature. As presented in Table 9, very low weight losses (0.09 and 0.12%) were detected at 300 °C for the 250 °C cured films. The $T_g$ of the a-BPDA/1,3,3-APB polyimide was 204 °C while the $T_g$ for the a-BPDA/1,4,4-APB polyimide was 276 °C. Hence curing the later film at 250 °C, significantly less than the $T_g$, had virtually no effect on retention of residual DMAC from film casting. The low weight losses at 300 and even 350 °C are presumably due to residual DMAC and/or water from further cyclodehydration of the amide acid to the imide. Other films were not characterized by TGA because it was assumed that the results would be similar. The excellent thermal stability of the polymers is obvious from the low weight losses at 500 °C at a heating rate of 2.5 °C/min.

### 3.9. Color, solar absorptivity and thermal emissivity

Color in polyimide films may be caused by several sources such as chromophoric groups, impurities in the monomers or solvent, isoimide formation, charge transfer complexes and oxidation during the curing (drying) process. Charge transfer complexes have long been associated with color in polyimide films and factors that disrupt charge transfer complex formation contribute to less color in polyimide films. The asymmetric dianhydride provides a highly irregular structure to the polyimide that was expected to disrupt the formation of charge transfer complexes and lead to low color films. In virtually all cases, the a-BPDA films had less color than the corresponding s-BPDA films. A few of the a-BPDA films cured at 250 °C were virtually colorless. The color designation in Tables 3–8 follows the trend from lightest to most intense or darkest: near colorless < pale yellow < light yellow < yellow < intense yellow < light orange < orange. The optical transparency or percentage light transmission through the film at a wavelength of 500 nm (the solar maximum) was determined for several films with the values reported in Tables 7 and 8. Film thickness varied from 0.041 to 0.066 mm. The thickest film (0.066 mm) from the a-BPDA/1,3,3-APB polyimide had the highest optical transparency (87%). The a-BPDA films in Table 7 have a higher percentage light transmission than the corresponding s-BPDA films in Table 8. The films derived from the polyimides made with the flexible 1,3,3-APB diamine had greater light transmission than those made from the slightly stiff 1,4,4-APB diamine. Light transmission decreased as the cure temperature of the film increased and this is clearly shown in Fig. 5 for the a-BPDA/1,3,3-APB film in Table 7. The percentage light transmission at 500 nm for four other lightly colored films (thickness in mm in parenthesis) was 87 (0.043) for 5-1/A (0.83 dl/g polymer), 85 (0.041) for 5-1/S, 85 (0.043) for 6-1/A and 75 (0.048) for 6-1/S (Fig. 6). Again the a-BPDA films had better optical transparency than the s-BPDA films.

Two of the several properties of importance for space applications are solar absorptivity ($\alpha$) and thermal emissivity ($\varepsilon$). Solar absorptivity pertains to the fraction of incoming solar energy that is absorbed by the film or more precisely a measure of light reflected by a second surface mirror between 250 and 2500 nm. Generally a low color film exhibits a low $\alpha$. The $\varepsilon$ is a measure of the film to radiate energy from the surface or more specifically a

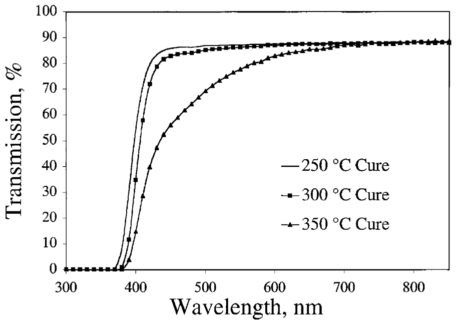


Fig. 6. Light transmission of a-BPDA/1,3,3-APB films.

measure of the infrared transmission of the film. A highly colored film exhibits high $\varepsilon$. Both of these properties were measured for films in Tables 4–6 and are reported in Table 10. Film thickness must be considered in comparing values. Depending on the space application, the ratio of $\alpha$ to $\varepsilon$ is more important than the individual values because it helps to determine the actual temperature a film will reach in a particular orbit. The ability of a material to undergo minimal changes in these properties upon exposure to radiation in space is of significant importance. In general, the a-BPDA polymeric films exhibited lower $\alpha$s than films from s-BPDA polyimides. This is consistent with the color of the films.

## 4. Concluding remarks

Ten new polyimides based on a-BPDA were prepared and their properties were compared with the corresponding s-BPDA derived polyimides. Polyimides from a-BPDA had higher $T_g$s, less color (higher optical transparency), and generally lower thin film tensile properties than polyimides from s-BPDA. Films of the a-BPDA polyimides had elongations as high as 43.7% whereas films of the s-BPDA had elongations as high as 90%. Unexpectedly, films from the a-BPDA/1,3,3-APB polyimide gave significantly higher tensile strengths and moduli than those from the less flexible a-BPDA/1,4,4-APB polyimide. This was unexpected and contrary to that found for films of the s-BPDA/1,3,3-APB and s-BPDA/1,4,4-APB polyimides. Films from the same a-BPDA polyimide cured at 250, 300, and 350 °C failed to show a distinct trend in tensile properties as a function of cure temperature but the $T_g$s increased. However, films from the same s-BPDA polyimide cured at 250, 300, and 350 °C showed higher $T_g$s, film elongations and moduli as a function of cure temperature. Dynamic mechanical thermal analysis showed a plateau in the storage modulus curves that broadened as the cure temperature increased, suggesting the formation of ordered regions. No trend in CTE was observed for films cured at different temperatures.

Table 10
Solar absorptivity and thermal emissivity of polyimide films

| Polymer no. | Solar absorptivity, $\alpha$ | Thermal emissivity, $\varepsilon$ | Film thickness (mm) |
|---|---|---|---|
| 4-1/A | 0.072 | 0.665 | 0.064 |
| 4-1/S | 0.082 | 0.583 | 0.028 |
| 4-2/A | 0.092 | 0.596 | 0.033 |
| 4-2/S | 0.168 | 0.592 | 0.046 |
| 4-3/A | 0.089 | 0.558 | 0.046 |
| 4-3/S | 0.121 | 0.491 | 0.036 |
| 5-1/A | 0.101 | 0.620 | 0.051 |
| 5-1/S | 0.108 | 0.511 | 0.033 |
| 5-2/A | 0.108 | 0.590 | 0.038 |
| 5-2/S | 0.096 | 0.461 | 0.020 |
| 6-1/A | 0.051 | 0.575 | 0.025 |
| 6-1/S | 0.108 | 0.620 | 0.048 |
| 6-2/A | 0.159 | 0.622 | 0.041 |
| 6-2/S | 0.288 | 0.533 | 0.023 |

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## References

[1] Bessonov MI, Koton MM, Kudryavtsev VV, Laius LA, editors. Polyimides: thermally stable polymers. New York: Consultants Bureau-Plenum; 1987.
[2] Wilson D, Stenzenberger HD, Hergenrother PM, editors. Polyimides. Glasgow: Blackie; 1990.
[3] Ghosh MK, Mittal KL, editors. Polyimides fundamentals and applications. New York: Marcel Dekker; 1996.
[4] Itatani H, Yoshimoto H. J Org Chem 1973;38:76.
[5] Inoue H, Okamoto H, Hiraoka Y. Radiat Phys Chem 1987;29:283.
[6] Yamaguchi H. In: Yokota R, Hasegawa M, editors. Recent advances in polyimides. Tokyo, Japan: Raytech Co; 1997. p. 5.
[7] Hasegawa M, Sensui N, Shindo Y, Yokota R. J Photopolym Sci 1996; 9:367.
[8] Hasegawa M, Sensui N, Shindo Y, Yokota R. Macromolecules 1999; 32:387.
[9] Hasegawa M, Sensui N, Shindo Y, Yokota R. J Polym Sci, Part B: Polym Phys 1999;37:2499.
[10] Takahashi T, Takabayashi S, Inoue H. High Perf Polym 1998;10: 33.
[11] Yokota R, Yamamoto S, Yano S, Sawaguchi T, Hasegawa M, Yamaguchi H, Ozawa H, Sato R. In: Mittal KI, editor. Polyimides and other high temperature polymers. The Netherlands: Zeist/VSP; 2001. p. 101.
[12] Hasegawa M, Shi Z, Yokota R, He F, Ozawa H. High Perf Polym 2001;13:355.
[13] Yokota R. In: Takeichi T, Kochi M, editors. Proceedings of the Seventh Japan Polyimide Conference; 1998. p. 21.

[14] Yokota R. In: Yokota R, editor. Proceedings of the Ninth Japan Polyimide Conference; 2000. p. 12.

[15] Yokota R, Yamamoto S, Yano S, Sawaguchi T, Hasegawa M, Yamaguchi H, Ozawa H, Sato R. High Perf Polym 2001;13:S61.

[16] Watson KA, Connell JW, Palmieri FL. Sci Adv Mater Proc Engng Ser 2001;46:1853.

[17] Hergenrother PM, Havens SJ. J Polym Sci, Part A: Polym Chem 1989; 27:1174.

[18] Brown JM, Woodward S. J Org Chem 1991;56:6803.

[19] Li S, Hsu B-L, Li F, Li CY, Harris FW, Cheng SZD. Thermochim Acta 1999;340–341:221.

[20] Srinivas S, Caputo FE, Graham M, Gardner S, Davis RM, McGrath JE, Wilkes GL. Macromolecules 1997;30:1012.

[21] Ratta V, Ayambem A, McGrath JE, Wilkes GL. Polymer 2001;42:6173.

[22] Arnold Jr FE, Cheng SZD, Hsu SL-C, Lee CJ, Harris FW. Polymer 1992;33:5179.

[23] Yang C-P, Hung K-S, Chen R-S. J Polym Sci, Part A: Polym Chem 2000;38:3954.

[24] Cheng SZD, Arnold Jr FE, Zhang A, Hsu SL-C, Harris FW. Macromolecules 1991;24:5856.

[25] Arnold Jr FE, Shen D, Lee CF, Harris FW, Cheng SZD, Starkweather Jr HW. J Mater Chem 1993;3:183.

[26] Cheng SZD, Wu Z, Eashoo M, Hsu SL-C, Harris FW. Polymer 1991; 32:1803.

[27] Eachoo M, Shen D, Wu Z, Lee CJ, Harris FW, Cheng SZD. Polymer 1993;34:3209.

[28] Li F, Huang L, Shi Y, Jin X, Wu Z, Shen Z, Chuang K, Lyon RE, Harris FW, Cheng SZD. J Macromol Sci, Phys 1999;B38:107.