POLYIMIDES CONTAINING PENDENT PHOSPHINE OXIDE GROUPS FOR SPACE APPLICATIONS

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ABSTRACT

As part of an ongoing materials development activity to produce high performance polymers that are durable to the space environment, phosphine oxide containing polyimides have been under investigation. A novel dianhydride was prepared from 2,5-dihydroxyphenyldiphenylphosphine oxide in good yield. The dianhydride was reacted with commercially available diamines, and a previously reported diamine was reacted with commercially available dianhydrides to prepare isomeric polyimides. The physical and mechanical properties, particularly thermal and optical properties, of the polymers were determined. One material exhibited a high glass transition temperature, high tensile properties, and low solar absorptivity. The chemistry, physical, and mechanical properties of these resins will be discussed.

KEY WORDS: Polyimides, Atomic Oxygen Resistant Polymers, 4,4'-(2-diphenylphosphinyl-1,4-phenylenedioxy)diphthalic anhydride

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1. INTRODUCTION

Future space mission concepts involving large ultra-lightweight (i.e. “Gossamer”) spacecraft are actively being pursued by several Government Agencies in the United States and abroad (1). Gossamer spacecraft are envisioned to be fabricated from flexible, compliant materials that can be folded or packaged into the small volumes commensurate with those available on conventional launch vehicles. Upon achieving orbit, the Gossamer structure would deploy by mechanical, inflation or other means into a large ultra-lightweight functioning spacecraft. Examples of Gossamer spacecraft include solar sails, antennas, sunshields, rovers, radars, solar concentrators, and reflect arrays. Mission concepts for Gossamer spacecraft encompass a variety of orbits from low Earth orbit (LEO) to the second Lagrangian point (L2) and beyond. The materials used to fabricate Gossamer spacecraft must possess and maintain a specific and unique combination of properties over long time periods in a relatively harsh environment. The materials must be resistant to the radiation and thermal conditions present in the desired spacecraft location and depending upon the function of the spacecraft must possess a combination of mechanical, electrical and optical properties as well. Desirable properties that are common among many of the mission concepts include low solar absorptivity (α), high thermal emissivity (ε), high optical transparency, toughness, tear and wrinkle resistance.

Organic polymers are know to degrade when exposed to atomic oxygen (AO), ultraviolet (UV), and vacuum ultraviolet (VUV) radiation which are present in LEO: 160-800 km in altitude. AO is a very reactive species that readily degrades organic materials leading to erosion and eventually complete mass loss. AO, UV, and VUV are present at sufficient concentration and energy levels in LEO to cause organic bond cleavage. The resulting bond cleavage can give rise to reactions that result in chain scission and/or crosslinking that cause physical, and mechanical property changes in the polymer. Some materials exhibit synergistic degradation when exposed simultaneously to AO and VUV.

AO resistant polymer technology development has recently focused on placing phenylphosphine oxide (PPO) groups in the backbone of aromatic polymers (2-8). The polymers typically contain 3-7% by weight of phosphorous and exhibit high glass transition temperatures and high Young’s moduli. Studies have shown that polymers containing chemically bound PPO units (2-7) as well as phosphazene groups (9-10) have high AO and oxygen plasma resistance. Upon exposure of PPO containing materials to AO, an increase in the oxidation state of phosphorous near the surface of the material has been observed using x-ray photoelectron spectroscopy. Work using X-ray Adsorption Near Edge Structure Spectroscopy (XANES) has shown that a polyphosphate surface layer forms upon exposure of PPO containing polymers to AO (11). The polyphosphate surface layer subsequently protects the underlying polymer from degradation due to AO attack. This mechanism of incorporating AO resistance into a polymeric material provides protection throughout the entire thickness of the film. If the polyphosphate surface is damaged, the underlying polymer becomes exposed to AO and the protective layer is reformed.

Previous work involved the preparation and characterization of two novel diamines containing PPO groups (8, 12). Polyimides prepared from the diamines were resistant to AO and UV radiation and formed films with low solar absorptivities. Current work reported herein involves the synthesis of a novel dianhydride from 2,5-dihydroxyphenyldiphenylphosphine oxide. The chemistry and properties of polyimides prepared from the novel monomer are described.

2. EXPERIMENTAL

2.1 Starting Materials 4,4′-Oxydianilne [4,4′-ODA, Wakayama Seika Kogyo Co., melting point (m.p.) 190-192 °C], 4-nitrophthalonitrile (Acros, m.p. 142-144 °C), and *N,N*-dimethylacetamide (DMAc, Aldrich Chemical Co.) were used as-received. Oxydiphthalic dianhydride (ODPA, Imitec Inc., m.p. 224-225.5 °C), pyromellitic dianhydride (PMDA, Allco Chemical Corporation, m.p. 284-286 °C), and *p*-phenylenediamine (*p*-PDA, Aldrich Chemical Co., 143-145 °C) were sublimed prior to use. 2,5-Dihydroxyphenyldiphenylphosphine oxide (13), [2,4-bis(3-aminophenoxy)phenyl]diphenylphosphine oxide (3-APPO) (12) and [2,5-bis(4-aminophenoxy)phenyl]diphenylphosphine oxide (4-APPO) (14) were prepared using previously published procedures. All other chemicals were used as-received without further purification.

2.2 Characterization Inherent viscosities (η_{inh}) were obtained on 0.5% (w/v) poly(amide acid) solutions in DMAc at 25 °C. Differential scanning calorimetry (DSC) was conducted on a Shimadzu DSC-50 thermal analyzer. Melting point (T_m) ranges were determined by either DSC (heating rate of 10 °C/min recorded at the onset to melt and the endothermic peak) or visually on a Thomas-Hoover capillary melting point apparatus (uncorrected). Glass transition temperatures (T_gs) were determined at a heating rate of 20 °C/min and were taken as the inflection point of the ΔT vs temperature curve. UV/VIS spectra were obtained on thin films using a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrometer. Solar absorptivities were measured on an AZ Technology Model LPSR-300 spectroreflectometer with measurements taken between 250 to 2800 nm with a vapor deposited aluminum on Kapton® film (1st surface mirror) as a reflective reference for air mass 0 per ASTM E903. An AZ Technology Temp 2000A infrared reflectometer was used to measure thermal emissivities.

2.3 Preparation of 4,4'-(2-diphenylphosphinyl-1,4-phenylenedioxy)diphthalonitrile 1 Into a 250 mL three neck round bottomed flask equipped with a mechanical stirrer, nitrogen gas inlet, and drying tube were placed 4-nitrophthalonitrile (9.90 g, 0.0572 mol), 2,5-dihydroxyphenyldiphenylphosphine oxide (8.87 g, 0.0286 mol), and DMAc (100 mL). The mixture was stirred for 15 minutes at room temperature and then pulverized anhydrous potassium carbonate (9.89 g, 0.0715 mol, 2.5 equivalents) was added. The reaction mixture was stirred at room temperature for 24 hours. The reddish-brown reaction mixture was poured into ~ 700 mL of stirred water and the resulting off-white precipitate was collected and washed with water. The solid was stirred in 100 mL of methanol for 10 minutes, collected, and dried for 2 hours in a vacuum oven at 100 °C. The solid was recrystallized from acetonitrile to give off-white crystals which were dried for 4 h at 150 °C in a vacuum oven (11.7 g, 73% yield). The crystals exhibited a sharp T_m at 222 °C by DSC.

2.4 Preparation of 4,4′-(2-diphenylphosphinyl-1,4-phenylenedioxy)diphthalic acid 2 Into a 250 mL round bottom flask equipped with a magnetic stirrer were placed 4,4'-(2-diphenylphosphinyl-1,4-phenylenedioxy)diphthalonitrile (11.24 g, 0.0213 mol), ethanol (30 mL), potassium hydroxide (KOH, 11.32 g, 0.1715 mol), and water (30 mL). The mixture was heated at reflux for 24 hours. The reaction was cooled and the ethanol was removed under reduced pressure. The aqueous solution was poured into stirred aqueous hydrochloric acid (HCl) and the resulting precipitate was collected and stirred in 1 L of refluxing water. The off-white solid was collected and dried for 2 hours in a vacuum oven at 150 °C (12.19 g, 90% yield). The solid exhibited a broad melting point of 212-218 °C as determined by DSC.

2.5 Preparation of 4,4'-(2-diphenylphosphinyl-1,4-phenylenedioxy)diphthalic anhydride (PPODA-1) Into a 100 mL round bottom flask equipped with a magnetic stirrer and reflux condenser fitted with a nitrogen gas inlet were placed 4,4′-(2-diphenylphosphinyl-1,4-phenylenedioxy)diphthalic acid (12.19 g, 0.0191 mol), glacial acetic acid (25 mL), and acetic anhydride (25 mL). The mixture was heated at reflux for 14 hours. The reaction was cooled and a fine off-white solid formed after several hours. The solid was collected, dissolved in hot glacial acetic acid, treated with charcoal, and filtered. A white solid formed after several hours at room temperature. The solid was collected and dried for 6 hours in a vacuum oven at 220 °C (7.19 g, 62% yield). No T_m was observed by DSC. ^{1}H NMR ($CDCl_3$): δ 7.01 (d, 1H), 7.11 (m, 2H), 7.45 (m, 9H), 7.70 (m, 6H), 8.00 (d, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz. ppm): δ 112.8, 113.2, 122.8, 122.9, 124.8, 125.0, 125.2, 125.4, 126.2, 126.6, 126.7, 127.3, 127.9, 128.4, 128.5, 128.7, 129.6, 130.3, 131.6, 131.7, 132.2, 132.3, 133.3, 134.0, 151.8, 151.9, 152.26, 152.3, 161.7, 161.8, 161.9, 162.1, 162.7, 163.8. ^{31}P NMR ($CDCl_3$, 121 MHz, ppm): d 26.2(singlet).

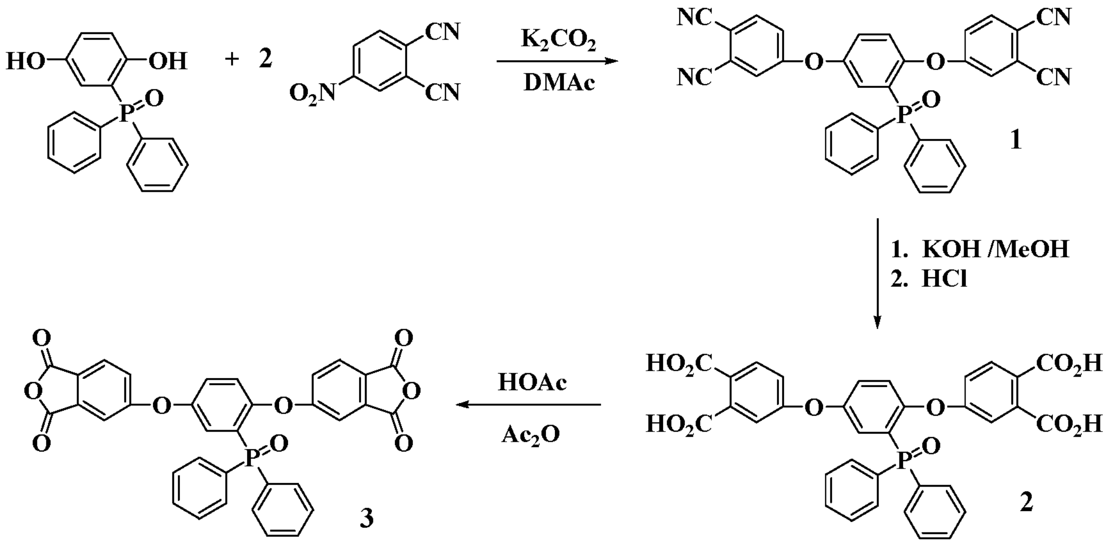
2.6 Polymer synthesis Phenylphosphine oxide-containing polyimides were prepared by reacting stoichiometric quantities of a dianhydride with a diamine to form a poly(amide acid) that was subsequently converted to the polyimide. The following procedure is representative for the preparation of all polymers. Into a 100 mL 3-neck round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet, and drying tube filled with calcium sulfate were placed 4,4′-ODA (1.0000 g, 0.0050 mol) and PPODA-1 (3.0086 g, 0.0050 mol). The solids were washed into the reaction flask with 17 mL of DMAc to prepare a 20 % (w/v) solids solution. The solution was stirred overnight at room temperature under nitrogen. A 0.5% solution in

DMAc exhibited an inherent viscosity of 0.54 dL/g at 25 °C. The remaining polymer solution was chemically imidized by the addition of 1.2 mL of acetic anhydride and 1.0 mL of pyridine. The solution was stirred at room temperature overnight. The polymer was precipitated into a blender containing water, filtered, washed with excess water and dried in a vacuum oven for 6 h at 150 °C to afford a pale yellow fibrous material. The solid was dissolved in DMAc (20 % solids, w/v) and the solution was cast onto plate glass and was allowed to dry to tack-free state in a low humidity air chamber. The film was stage-dried in a forced air oven for 1 h each at 50, 100, 150, 175, 200, and 235 °C. The film exhibited good flexibility and a T_g of 226 °C as determined by DSC.

2.7 Films Thin films were cast from either polyimide or poly(amide acid) solutions in DMAc. The solutions were centrifuged, the decantate doctored onto clean, dry, plate-glass and dried to a tack-free form in a low humidity chamber. Films cast from polyimide solutions were generally stage dried in a forced air oven to a temperature 10 °C over T_g for 1 h. Films cast from poly(amide acid) solutions were dried at 100, 200, and 300 °C for 1 h each. Thin-film tensile properties were determined according to ASTM D882 using either four or five specimens (0.51 cm wide) per test conditions using an Eaton Model 3397-139 11.4 kg load cell on a Sintech 2 test frame. The test specimen gauge length was 5.1 cm and the crosshead speed for film testing was 0.51 cm/minute.

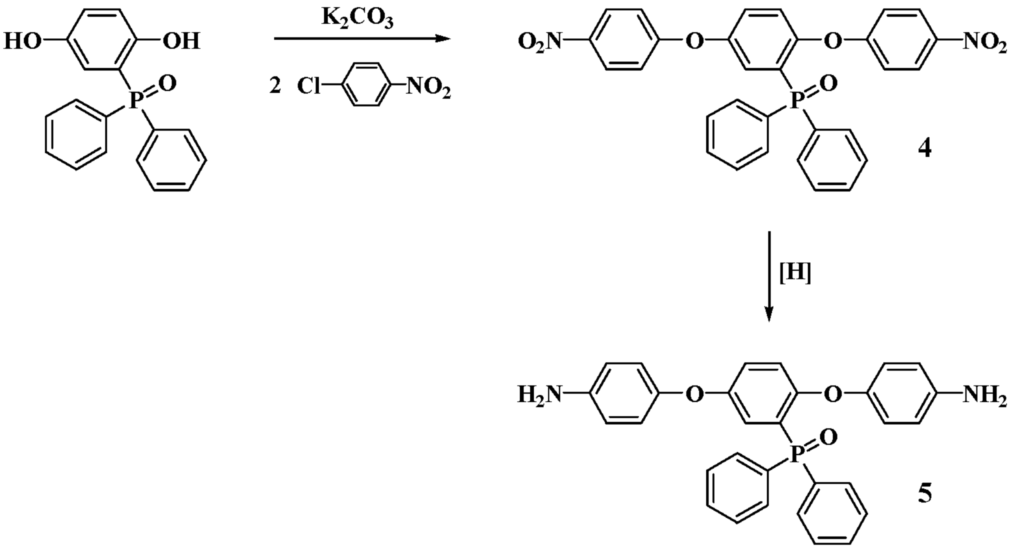
3. RESULTS AND DISCUSSION

3.1 Dianhydride synthesis PPODA-1 was synthesized in three steps as shown in Scheme 1. The first step involved the reaction of 2,5-dihydroxyphenyldiphenylphosphine oxide with 2 equivalents of 4-nitrophthalonitrile to prepare 4,4'-(2-diphenylphosphinyl-1,4-phenylenedioxy)diphthalonitrile **1**. The phthalonitrile was then converted to the corresponding tetracarboxylic acid **2** by heating in aqueous KOH followed by treatment with HCl. Tetra-acid **2** was cyclodehydrated to dianhydride **3** by refluxing in acetic acid/acetic anhydride. The phenylphosphine oxide (PPO) containing dianhydride tenaciously holds onto acetic acid thus it was necessary to dry the material for 6 h at 220 °C in a vacuum oven. At this point the compound was glassy and did not display a crystalline melting point. Purity and structure were assessed by ^{1}H and ^{13}C NMR, and the ability to form high molecular weight polymer from the reaction with pure diamines.



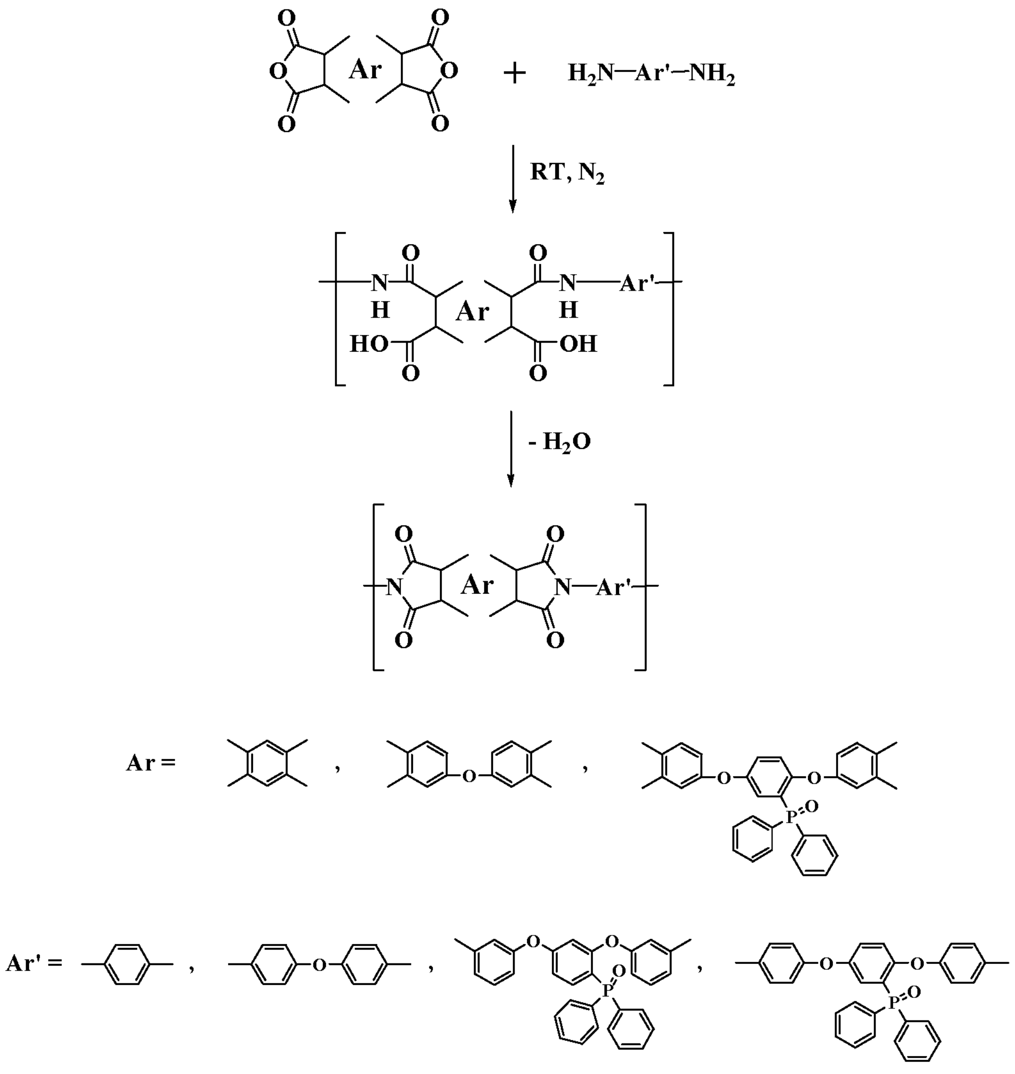
Scheme 1. Synthesis of 4,4'-(2-diphenylphosphinyl-1,4-phenylenedioxy)diphthalic anhydride (PPODA-1)

3.2 Diamine Synthesis Details on the synthesis of [2,5-bis(4-aminophenoxy)phenyl]diphenylphosphine oxide **5** have previously been reported (14). The synthesis is a two-step process as shown in Scheme **2**. The first step is the reaction of 2,5-dihydroxyphenyldiphenylphosphine oxide with two equivalents of 1-chloro-4-nitrobenzene to give [2,5-bis(4-nitrophenoxy)phenyl]diphenylphosphine oxide **4** in high yield. Dinitro compound **4** was reduced to the desired diamine **5** with hydrogen and a palladium catalyst.



Scheme 2. Synthesis of [2,5-Bis(4-aminophenoxy)phenyl]diphenylphosphine oxide

3.3 Polymer Synthesis Polyimides containing PPO units were prepared by reacting stoichiometric amounts of dianhydride and diamine in DMAc at a concentration of 20 % solids (w/v) under a nitrogen atmosphere as shown in Scheme 3. The specific dianhydride/diamine combinations are listed in Table 1. Typically the poly(amide acid) was prepared by stirring the reactants at room temperature for 24 hours, followed by chemical imidization/dehydration using a mixture of acetic acid and pyridine. In the case of polymers **P3**, **P4,** and **P7,** films were cast from the poly(amide acid) solutions and thermally imidized.



Scheme 3. Synthesis of Phenylphosphine Oxide Containing Polyimides

3.4 Polymer Characterization Characterization data for the PPO containing polymers is presented in Table 1. Inherent viscosities ranged from 0.47 to 1.0 dL/g at 25 °C in DMAc indicating moderate to high molecular polymers. The T_gs ranged from 203 to 251 °C. All samples formed flexible films with color ranging from colorless to dark yellow. Room temperature thin film tensile properties are presented in Table 1 with tensile strengths ranging from 90 to 127 MPa, tensile moduli ranging from 2.8 to 3.8 GPa and elongations at break ranging from 4 to 15 %.

Table 1. Polymer Properties

Polymer	Dianhydride	Diamine	η_{inh}, dL/g, 25 °C	T_g, °C[b]	Tensile Properties at RT		
					Strength, MPa	Modulus, GPa	Elong. @ Break, %
P1	PPODA-1	3-APPO	0.55	203	90	3.5	5
P2	PPODA-1	4-APPO	0.47	215	104	3.5	10
P3[a]	PPODA-1	*p*-PDA	0.99	248	90	3.8	4
P4[a]	PMDA	4-APPO	0.78	251	127	3.8	15
P5	PPODA-1	4,4′-ODA	0.54	226	104	3.2	12
P6	ODPA	3-APPO	1.0	212	97	2.8	5
P7[a]	ODPA	4-APPO	0.80	236	125	3.7	14

a. Film cast from poly(amide acid)
b. DSC, heating rate of 20 °C/min, 2nd heat.
RT = room temperature

3.5 Optical Transparency Thin films were measured for optical transparency using UV/Visible spectroscopy with the percent transmission (%T) at 500 nm (the solar maximum) reported in Table 2. The %T values ranged from 22 to 85% while film thickness ranged from 20 to 43 μm. Optical transparency is a function of film thickness, thus it is difficult to compare polymer **P3** with the other samples because the film was considerably thinner. It is expected that the %T for **P3** would decrease with a thicker film in the range of the other samples. Polymers **P4** and **P7** have much lower %T values because of increased yellowing of the samples resulting from heating to 300 °C during thermal imidization of the film. It is believed these samples would have higher %T values if they would have been chemically imidized prior to casting the film. Polymer **P3** was also thermally imidized but had a higher %T relative to **P4** and **P7** because of the reduced thickness of the film.

3.6 Solar Absorptivity and Thermal Emissivity Two properties important for materials for space applications are α and ε. Solar absorptivity, α, pertains to the fraction of incoming solar energy that is absorbed by the film and solar emissivity, ε, is a measure of the films ability to radiate energy from the film surface. Typically a low colored film exhibits a low α value. The α and ε values for the thin films are shown in Table 2. Alpha values ranged from 0.07 to 0.22 and ε values ranged from 0.51 to 0.65. Alpha and ε are also a function of film thickness thus it is difficult to directly compare polymer **P3** with the other samples. Polymers **P3**, **P4**, and **P7** have higher α/ε values compared to the other samples presumably due to increased yellowing that occurred while thermally imidizing the films.

Table 2. Thermal/Optical Characterization

Polymer	Dianhydride	Diamine	α	ε	α/ε	%T @ 500 nm	Film Thickness, μm
P1	PPODA-1	3-APPO	0.07	0.65	0.11	81	41
P2	PPODA-1	4-APPO	0.11	0.59	0.18	65	38
P3[a]	PPODA-1	*p*-PDA	0.11	0.51	0.22	73	20
P4[a]	PMDA	4-APPO	0.22	0.65	0.34	22	38
P5	PPODA-1	4,4′-ODA	0.08	0.63	0.13	81	43
P6	ODPA	3-APPO	0.06	0.56	0.11	85	41
P7[a]	ODPA	4-APPO	0.17	0.62	0.27	53	38

a. Film cast from poly(amide acid)

4. SUMMARY

A novel dianhydride was prepared from 2,5-dihydroxyphenyldiphenylphosphine oxide. The dianhydride was reacted with commercially available diamines, and a previously reported diamine was reacted with commercially available dianhydrides to prepare isomeric polyimides. These polyimides displayed desirable properties such as good tensile properties, low color, and high optical transparency. Due to the presence of the pendent PPO group, these polyimides are anticipated to have similar AO resistance as other PPO containing polyimides. This combination of properties makes these polymers potentially useful for space applications.

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

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6. Biographies

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John W. Connell is a senior polymer scientist in the AMPB of the SMC at NASA LaRC. He received B.S. and Ph.D. degrees from Virginia Commonwealth University in 1982 and 1986, respectively. Prior to joining NASA LaRC in January 1988, he was a research associate at Virginia Commonwealth University. Since coming to NASA, his work has focused on the development of high performance polymers for aerospace applications.