SPACE ENVIRONMENTALLY STABLE POLYIMIDES AND COPOLYIMIDES

Kent A. Watson and John W. Connell
National Aeronautics and Space Administration (NASA)
Langley Research Center (LaRC)
Hampton, VA 23681-2199

ABSTRACT

Polyimides with a unique combination of properties including low color in thin films, atomic oxygen (AO), ultra-violet (UV) radiation resistance, solubility in organic solvents in the imide form, high glass transition (T_g) temperatures and high thermal stability have been prepared and characterized. The polymers were prepared by reacting a novel aromatic diamine with aromatic dianhydrides in a polar aprotic solvent. The solubility of the polymers in the imide form as well as the color density of thin films were dependent upon the chemical structure of the dianhydride. Several thin films (25-50 μm thick) prepared by solution casting of amide acid or imide solutions exhibited very low color and high optical transparency (~90%) as determined by UV/visible spectroscopy. The polymers exhibited T_gs >200°C depending upon the structure of the dianhydride and temperatures of 5% weight loss ~500°C in air as determined by dynamic thermogravimetric analysis. Thin films coated with silver/inconel were exposed to a high fluence of AO and 1000 equivalent solar hours of UV radiation. The effects of these exposures on optical properties were minor. These space environmentally durable polymers are potentially useful in a variety of applications on spacecraft such as thin film membranes on antennas, second-surface mirrors, thermal/optical coatings and multi-layer thermal insulation (MLI) blanket materials. The chemistry, physical and mechanical properties of the polymers as well as their responses to AO and UV exposure will be discussed.

KEY WORDS: Low Color Polyimides, Atomic Oxygen Resistant Polymers, Phosphine Oxide-Containing Films, Polyimides, UV Resistant Polyimides

1. INTRODUCTION

Atomic oxygen (AO), ultra-violet (UV) and vacuum ultra-violet (VUV) radiation are present in low Earth orbit (LEO): 160-800 km in altitude. At higher elevations AO becomes less prevalent but UV, VUV, electrons, protons and other particulate radiation are of concern. Organic polymers are subject to degradation by these species since they are of sufficient concentration and energy level 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, mechanical and optical property changes in the polymer. Some materials exhibit synergistic degradation when exposed simultaneously to AO and VUV.[1,2]

Thin films from relatively high molecular weight aromatic polyimides generally exhibit good toughness, flexibility, solvent resistance, high glass transition temperatures (T_g) and good thermal stability.[3] In many cases, these materials, due to their aromatic structure exhibit good UV radiation resistance, however they generally exhibit significant color and are susceptible to AO degradation. The preparation of low color polyimides that are UV resistant has been reported.[4]

No commercially available polyimides are resistant to degradation by AO exposure and are typically protected from AO erosion by a coating. Perfluorinated materials such as copoly(fluoroethylene propylene) displayed good resistance to AO, but dramatic increases in the erosion rate (mass loss) were observed when the polymer was exposed simultaneously to AO and UV radiation. Present methods for the elimination or reduction of erosion due to AO involve coating materials with aluminum oxide, silicon dioxide, chromium oxide and fluorinated polymers. This usually requires a specialized facility and a separate processing step. In addition, there are limitations on the shape and size of film that can be coated. Other problems associated with the use of coatings include difficulty in uniformly coating complex shapes and the risk of damage to the coating from manufacturing, handling, storage and from space-based particle impact. Typically, there is a mismatch in the coefficient of thermal expansion of the substrate polymer and the coating, which upon thermal cycling can cause spalling, cracking or dis-bonding. Once damage occurs to the protective surface coating, the underlying polymer becomes exposed to AO and erosion proceeds.

AO resistant polymer technology development has recently focused on placing phenylphosphine oxide groups into the backbone of aromatic polymers.[5-10] The polymers typically contain 3-7% phosphorus and exhibit high T_gs and high Young's moduli. Studies have shown that polymers containing chemically bound phenyl phosphine oxide (PPO) units[5-10] as well as phosphazene groups[11,12] have significantly increased 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.[5-10]

More recent work using X-ray Adsoption Near Edge Structure Spectroscopy has shown that a polyphosphate surface layer forms upon exposure of these materials to AO.[12] This surface layer subsequently protects the underlying polymer from AO erosion.

2. EXPERIMENTAL

2.1 Starting Materials The starting materials for the synthesis of the daimine containing phenylphosphine oxide groups, aromatic diamines and dianhydrides and solvents were either used as-received from commercial sources or purified prior to use using standard methods.

2.2 Preparation of 3,5-di(trifluoromethyl)phenyldiphenylphosphine oxide Into a 1L three neck round bottomed flask equipped with a mechanical stirrer, thermometer, nitrogen gas inlet, pressure equalizing addition funnel and reflux condenser with drying tube was placed predried magnesium turnings (4.1 g, 0.17 mol) and dry tetrahydrofuran (THF, 30 mL). The mixture was cooled to ~5 °C using an ice/water bath. A solution of 3,5-bis(trifluoromethyl)bromobenzene (49.5 g, 0.17 mol) in THF (50 mL) was placed in the pressure equalizing addition funnel and added dropwise over a 1.5 hour period. The mixture was allowed to warm to room temperature and additional THF (75 mL) was added. The mixture was stirred at room temperature for 3 hours. A solution of diphenylphosphinic chloride (40.0g, 0.17 mol) in THF (50 mL) was added dropwise over a one hour period. The reaction mixture was allowed to warm to ambient temperature (about 55 °C), and was stirred under nitrogen at room temperature for 15 hours. The resultant brown solution was poured into a mixture of 10% sulfuric acid solution (250 mL) and water (500 mL) to give two layers. The organic layer was extracted successively with water, 5% aqueous sodium bicarbonate and water and subsequently dried over magnesium sulfate. The THF was removed via rotoevaporation to give a dark brown liquid. The liquid solidified upon cooling (61 g, 86% yield). The crude solid was dissolved in 240 mL of a solution of 5% isopropanol in hexanes. A small amount of insoluble brown material was removed via filtration. The resulting filtrate was treated with activated charcoal and filtered. The reddish-brown filtrate was reduced to approximately 200 mL and the hot solution, upon cooling, formed off-white needles. The crystals were collected via filtration, the mother liqueur quickly set aside and the crystals were immediately (before air drying can occur) washed with excess cold 5% isopropanol/hexanes. The crystallization process was repeated using 5% isopropanol/hexanes. Approximately 33 g of off-white crystals were obtained. The solid was collected and air-dried. The solid exhibited a melting point of 102-104 °C [differential scanning calorimetry (DSC) 10 °C/min]. Anal. Calcd. For $C_{20}H_{13}F_6PO$: C, 57.98%; H, 3.16 %; F, 27.52%; P, 7.47%. Found: C, 57.77%; H, 3.33 %; F, 27.05%; P, 7.35%. Mass spectroscopic analysis: M+ 413.2 [$C_{20}H_{13}F_6PO+$].

2.3 Preparation of bis(3-nitrophenyl)-3,5-di(trifluoromethyl)phenylphosphine oxide A 1L round bottom flask equipped with a mechanical stirrer, thermometer and condenser was charged with 230 mL (423 g) of concentrated sulfuric acid and 44 mL (66 g) of fuming (red) nitric acid. The flask was cooled in an ice bath and then 85.0 g (0.205 mol) of the Grignard adduct was added in small portions with stirring. After complete addition, the reaction mixture was allowed to warm to room temperature and then heated to 60 °C for 1 hour. The heat then was removed and the reaction mixture cooled to ~5 °C using an ice water bath. The resulting solution was poured into ~1000 mL of ice water upon which a yellow precipitate formed. The solid was collected via vacuum filtration, stirred in hot water for 30 minutes, filtered, stirred in dilute sodium bicarbonate solution for 1 hour, filtered, and the two washes (water, $NaHCO_3$) repeated. The solid was filtered, stirred with water for 30 minutes and filtered. Washes were repeated until the aqueous layer of a suspension of the dinitro compound in water did not turn litmus paper red. Crude yield: 97.9 g (95%). The crude product was dried in a forced air oven and crystallized from a 50/50 mixture of acetone/isopropanol. After drying at 100°C under vacuum for 24 hours a pale yellow solid was obtained 82.3 g (84%). The solid exhibited a melting point by DSC (10 °C/min) of 173-177 °C. Two successive recrystallizations led to sharper melting points. This material can be recrystallized to the point of being white/off-white or very pale yellow in color. Anal. Calcd. For $C_{20}H_{11}N_2F_6PO_5$: C, 47.63%; H, 2.19 %; N, 5.55%; F, 15.86%; P, 6.14%. Found: C, 47.47%; H, 2.00 %; N, 5.22%; F, 15.31%; P, 5.94%. Mass spectroscopic analysis: M+ 503.2 [$C_{20}H_{11}N_2F_6PO_5$+].

2.4 Preparation of bis(3-aminophenyl)-3,5-di(trifluoromethyl)phenylphosphine oxide (TFMDA) A 2L round bottom flask equipped with a nitrogen inlet, thermometer, mechanical stirrer and condenser topped with a drying tube was charged with 67.1 g of the dinitro compound, 85.2 g of ammonium formate, 750 mL of anhydrous ethanol and 3.0 g of 10% Pd/C (dry). The reagents were stirred under nitrogen at room temperature. After about 0.5 hour, the temperature of the reaction rose to 45 °C. The reaction was not cooled. The reaction was stirred for 2.5 hrs and then the reaction mixture was filtered through Celite and precipitated in 1.2 L of water. A white solid was obtained and dried in a vacuum oven at 110 °C for 16 hr to yield 63.41 (94 %). The solid exhibited a melting point by DSC (10 °C/min) of 225– 227 °C. The crude diamine was recrystallized twice from isopropanol/toluene (75/25) to give an off-white solid that exhibited a melting point by DSC (10 °C/min) of 228 – 230 °C. Anal. Calcd. For $C_{20}H_{15}N_2F_6PO$: C, 54.06%; H, 3.40 %; N, 6.31%; F, 25.66%; P, 6.97%. Found: C, 53.97%; H, 3.31 %; N, 6.02%; F, 25.17%; P, 6.77%. Mass spectroscopic analysis: M+ 443.1 [$C_{20}H_{15}N_2F_6PO$+].

2.5 Polymer preparation Phenylphosphine oxide-containing polyimides were prepared by reacting stoichiometric quantities of TFMDA with various dianhydrides. Copolymers were prepared by the addition of other aromatic diamines. The following procedure is representative for the preparation of all polymers and copolymers. Into a 100 mL three neck round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet and drying tube filled with calcium sulfate was placed TFMDA (4.4431 g, 0.01 mole) and N,N-dimethylacetamide (DMAc, 15.8 mL). The diamine dissolved within a few minutes and 4,4'-perfluoroisopropylidiene dianhydride powder (6FDA, 4.4424 g, 0.01 mole) was added along with additional DMAc (10.0 mL) to give a solution with a concentration of 25% solids weight/volume. The light yellow solution was stirred overnight at room temperature under a nitrogen atmosphere. A 0.5% solution in DMAc exhibited an inherent viscosity of 0.73 dL/g at 25 °C. A thin film was cast at 15 mils thick onto plate glass using a doctor blade and allowed to dry to a tack-free state in a dust free chamber. The film on plate glass was stage dried in a forced air oven for 1 hour each at 100, 200 and 300 °C. The pale yellow film was subsequently removed from the glass. It exhibited good flexibility and a T_g of 245 °C as determined by DSC at a heating rate of 20 °C/min.

2.6 Films Thin films were cast from polyamide acid and/or imide solutions in DMAc (20% solids). The polymers and copolymers were centrifuged, the decantate doctored onto clean, dry plate-glass and dried to a tack-free form in a low humidity chamber. The films then were treated in a forced air oven staged to 300 °C for one hour. Thin-film tensile properties were determined according to ASTM D882.

2.7 Atomic oxygen and Ultra-violet radiation exposure Prior to the testing of Polymer 1 (6FDA/TFMDA) film to AO and UV, it was sputter coated with silver/inconel. AO testing was conducted at the NASA Marshall Space Flight Center in the Atomic Oxygen Beam Facility (AOBF). The AOBF system produces AO by exciting an oxygen plasma using microwaves at 2.45 GHz and is confined to the center of the plasma chamber using a strong magnetic field. Ions are accelerated from the plasma and neutralized. The neutralization technique provides a direct measurement of the AO flux that in many other systems is not directly known. Under standard operating conditions, the system is capable of producing an AO flux of 10^{16} atoms/cm^2/sec for accelerated testing. The AOBF system produces atomic oxygen atoms with 5eV energy. UV testing was conducted at the NASA Goddard Space Flight Center Thermal Engineering Branch with the Multisedes Vacuum System. The system consists of two sorption pumps, a sputter-ion pump, and a sample chamber with 16 testing positions. An AZ Technology LPRS-200 was used to perform the pre-vacuum and post-vacuum reflectance measurements and solar absorptance calculations. The solar absorptance is calculated in accordance with ASTM E903-82. The LPSR measures the reflectance from 250 to 2500 nm of the sample surface at a 15° angle of incidence. The Geir-Dunkle DB-100 Infrared Reflectometer was used to measure the normal emittance of the surface from 5 to 40 μm.

2.8 Other characterization Inherent viscosities (η_{inh}) were obtained on 0.5% polymer solutions in DMAc or N-methyl-2-pyrrolidinone (NMP) at 25°C. DSC was conducted on a Shimadzu DSC-50 thermal analyzer at a heating rate of 10 °C/min with the melting point taken at the endothermic peak, and a heating rate of 20 °C/min with the T_g taken at the inflection point of the ΔT vs temperature curve. Dynamic thermogravimetric analyses (TGA) were performed on a Seiko Model 200/220 instrument on powder samples at a heating rate of 2.5 °C/min in air and nitrogen at a flow rate of 15 cm^3/min. Elemental Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Gel permeation chromatographic (GPC) analyses were conducted on amide acid solutions in DMAc. The analyses were performed using distilled DMAc containing 0.02M LiBr. Chromatography was performed on a Waters 150-C GPC that was equipped with a differential refractive index detector in parallel configuration with a Viscotek model 150R differential viscometer. A Waters Styragel HT 6E linear column covering a molecular weight range from 10^3 to 10^7 g/mole was used in series with a Styragel HT 3 column, which covers the range from 10^3 to 10^4 g/mole. A universal calibration curve was generated with narrow molecular weight distribution polystyrene standards with molecular weights ranging from 5 X 10^2 to 2.75 X 10^6 g/mole.

3. RESULTS AND DISCUSSION

3.1 Diamine synthesis The phenylphosphine oxide (PPO) containing diamine was synthesized in three steps as shown in Figure 1. The first step involves a Grignard reaction between 3,5-bis(trifluoromethyl)bromobenzene and diphenylphosphinic chloride. The Grignard adduct was nitrated by treating the Grignard adduct with a solution of nitric and sulfuric acid. Reduction of the nitro groups to the corresponding amine groups was accomplished by treating the dinitro compound with palladium on carbon catalyst in the presence of ammonium formate.

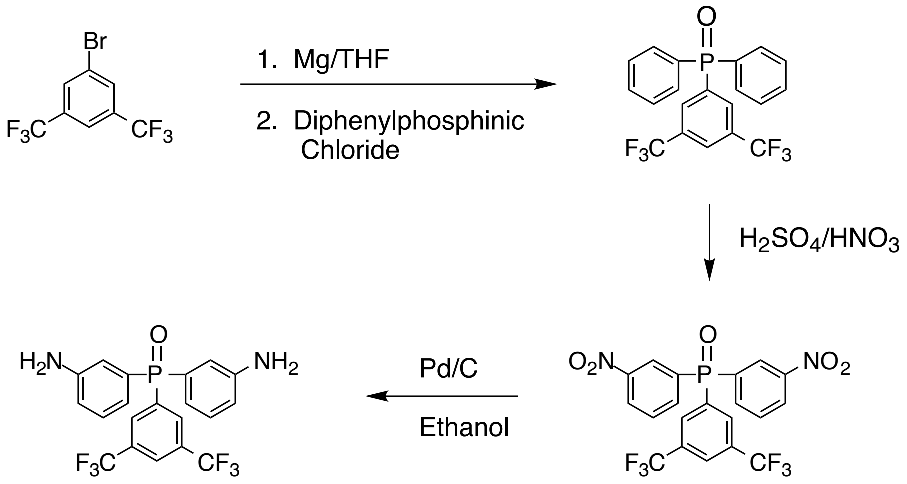


Figure 1. Synthesis of Phenylphosphine Oxide Containing Diamine (TMFDA)

3.2 Polymer synthesis Polyimides containing PPO units were prepared from TMFDA and various aromatic dianhydrides in DMAc under a nitrogen atmosphere as shown in Figure 2. Typically the polyamide acid was prepared by stirring the reactants at room temperature for 24 hours, followed by either chemical or thermal imidization/dehydration. The resulting polymers were isolated in > 95% yield. The chemical structures of the aromatic dianhydrides used are shown in Figure 3.

3.3.1 Polymer characterization Characterization for polymers prepared from TMFDA and various dianhydrides is presented in Table 1. The η_{inh}s ranged from 0.23 to 0.93 dL/g indicating low to high molecular weight polymer formation. The T_gs ranged from 213 to 269°C. All of the polymers except Polymer 4 (PMDA) exhibited solubility in DMAc and NMP in the imide form. The polymers exhibited temperatures of 5% weight loss ranging from 487-503°C in air and 491-527°C in nitrogen as determined by TGA. These values are typical for all aromatic polyimides.

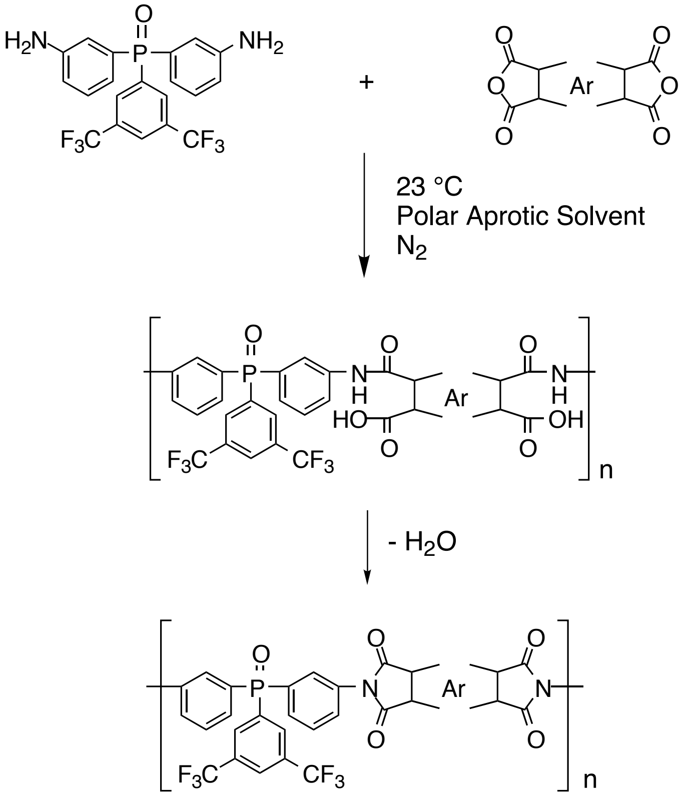
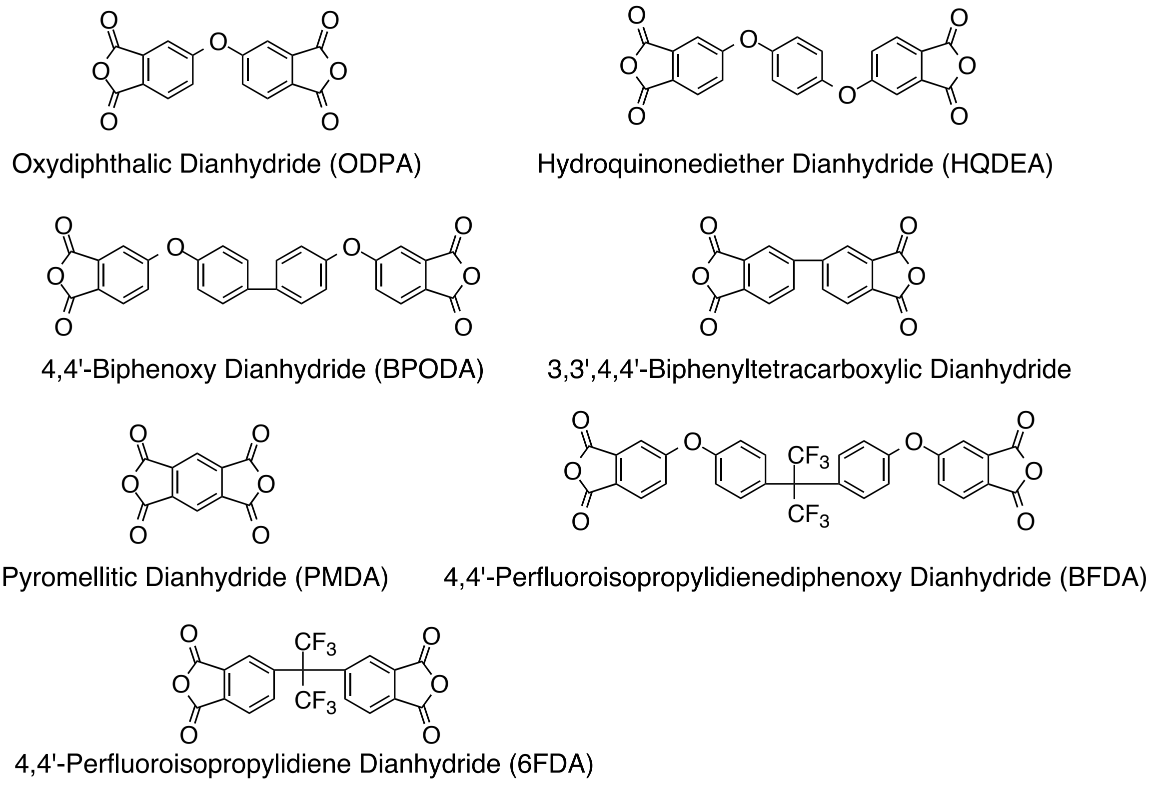


Figure 2. Synthesis of Phenylphosphine Oxide Containing Polyimides

Table 1. Polymer Characterization

Polymer	Dianhydride	η_{inh} (dL/g)*	T_g (°C)	5% Weight Loss, °C	
				Air	Nitrogen
1	6FDA	0.73	245	500	510
2	ODPA	0.39	217	498	501
3	BPODA	0.57	226	503	527
4	PMDA	-----	269	500	510
5	HQDEA	0.47	222	496	511
6	BFDA	0.23	213	487	491
7	BFDA	0.93	260	500	514

*Inherent viscosities determined on 0.5% polyamide acid solutions in DMAc at 25°C.


Oxydiphthalic Dianhydride (ODPA)

Hydroquinonediether Dianhydride (HQDEA)

4,4'-Biphenoxy Dianhydride (BPODA)

3,3',4,4'-Biphenyltetracarboxylic Dianhydride

Pyromellitic Dianhydride (PMDA)

4,4'-Perfluoroisopropylidienediphenoxy Dianhydride (BFDA)

4,4'-Perfluoroisopropylidiene Dianhydride (6FDA)

Figure 3. Dianhydrides used for Polymer Synthesis

3.3.2 Thin film tensile properties Thin films were cast from amide acid and/or imide solutions and thermally treated in a forced air oven to facilitate imidization and to remove residual solvent. Most of the films prepared were tough, creasable and exhibited low color. The color of the thin films (~37 μm thick) ranged from light yellow to clear and were dependent upon the dianhydride used. Polymers prepared from PMDA and BPDA gave relatively dark orange films. Thin film mechanical properties are presented in Table 2. The films exhibited room temperature tensile strengths and moduli from 79-122 MPa and 2.8-3.7 GPa, respectively. The elongations to break ranged from 3-10%.

Table 2. Thin Film Tensile Properties at Room Temperature

Polymer	Dianhydride	Tg, °C	Tensile Strength, MPa	Tensile Modulus, GPa	Elong.@ Break, %
4	BPODA	226	118.2	2.84	9.8
6	HQDEA	222	79.2	2.90	3.1
7	BDAF	213	93.0	2.92	3.8
9	6FDA	237	122.0	3.77	3.7

3.3.3 Gel permeation chromatography Polyamide acids in DMAc solutions were analyzed by GPC to determine number average $\overline{M}_n$), weight average $\overline{M}_w$) and z average $\overline{M}_z$) molecular weights and molecular weight distributions. The results of the GPC analyses are presented in Table 3. In general, the polymers exhibited low to moderate $\overline{M}_n$ values and polydispersities ranging from 1.88 to 2.43. The GPC chromatograms typically exhibited a low molecular tail that caused a significant reduction in the $\overline{M}_n$ values. The low molecular weight species could be due to cyclic oligomers or impurities in the diamine such as monoamine. The presence of a small amount of monoamine would upset the stoichiometry and thus the molecular weight distribution but would be difficult to detect by mass spectroscopy or elemental analysis.

Table 3. GPC Analyses of Polyamide acids

Polymer	$\overline{M}_n$, g/mole	$\overline{M}_w$, g/mole	$\overline{M}_z$, g/mole	Intrinsic Viscosity, dL/g
3	21630	71750	135300	0.559
4	10190	43450	96860	0.540
6	9096	28690	59960	0.125
7	25470	213100	519600	0.884

3.3.4 Optical transparency Thin films were measured for optical transparency using UV/visible spectroscopy. The results are presented in Table 4. Two of the films exhibited optical transparencies in excess of 85%. All of the films in Table 4 were clear to pale yellow in color depending on the thickness of the film.

Table 4. Optical Transparency of Polyimide Films

Polymer	Dianhydride	Thickness, μm	Wavelength, nm	Transparency, %
1	6FDA	37	500-600	88
3	BPODA	45	540-600	80
5	HQDEA	62	540-600	80
6	BDAF	57	500-600	86

3.3.5 AO exposure tests A thin film sample of Polymer 1 (6FDA/TFMDA) was exposed to AO at the Marshall Space Flight Center fast AO facility. The film, approximately 25 μm thick, was coated with silver/inconel on one side to form a second surface mirror. The sample was exposed to fluences of 1.6 x 10^{21} AO/cm^2 and the effect of the exposure on solar absorbance (α), solar emmitance (ε) and surface erosion was determined. The results are presented in Table 5. The film exhibited an initial change in α and ε, but they subsequently remained unchanged out to a fluence of 1.6 x 10^{21} AO/cm^2. The 6FDA/TFMDA film exhibited a non-linear erosion rate and superior erosion resistance relative to Kapton® HN film, which exhibited an erosion of 2.0 x 10^{-3} cm after exposure to a fluence of only 7.5 x 10^{20} AO/cm^2. It can also be seen from the data in Table 5 that this material does not exhibit a linear erosion rate.

Table 5. Effect of Fast AO Exposure of Polyimide/Silver Film (Polymer 1, 6FDA/TFMDA)

Exposure	α	ε	Erosion, cm
None	0.15	0.74	0
7.5 x 10^{20} AO/cm^2	0.24	0.79	5.3 x 10^{-4}
1.0 x 10^{21} AO/cm^2	0.23	0.79	6.8 x 10^{-4}
1.6 x 10^{21} AO/cm^2	0.23	0.79	9.0 x 10^{-4}

3.3.6 UV radiation exposure A thin film sample of Polymer 1 (6FDA/TFMDA) was exposed to UV for a total of 1000 equivalent solar hours (ESH) at the Goddard Space Flight Center. Prior to exposure, the 25 μm thick film was coated with silver/inconel on one side to form a second surface mirror. The effect of the exposure on α and ε were determined and the results are presented in Table 6. The film exhibited minor changes in α and ε with exposure to 1000 equivalent solar hours indicating excellent resistance to UV radiation.

Table 6. UV Exposure of Polyimide/Silver Film (Polymer 1, 6FDA/TFMDA)

Exposure	α	ε	$\Delta\alpha$
None	0.184	0.820	0
500 ESH	0.205	0.822	0.025
1000 ESH	0.202	0.817	0.018

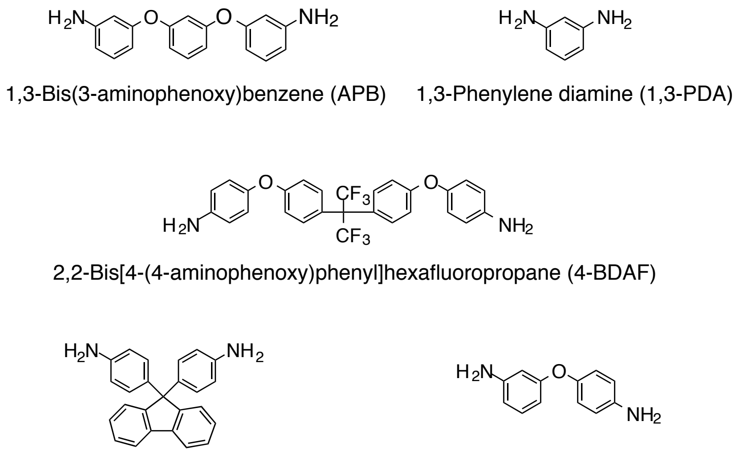
3.4 Copolymer synthesis A series of copolymers were prepared using 25 mol % of an aromatic diamine and 75 mol % of TFMDA and 100 mol % of an aromatic dianhydride. Two dianhydrides were used: ODPA and 6FDA. The structures of the diamines used for copolymer synthesis are shown in Figure 4. The characterization of the copolymers are summarized in Table 7. η_{inh}s, measured on 0.5% polyimide solutions in NMP at 25°C, ranged from 0.60 to 0.91 dL/g and T_gs ranged from 213-268 °C. In general, GPC data indicates moderate to high $\overline{M}_n$ values. As previously mentioned, the GPC chromatograms exhibited low molecular weight tails which affected the polydispersity and $\overline{M}_n$ values. Films cast from the copolymers were nearly colorless depending on film thickness.

Table 7. Copolymer Characterization

Polymer	Diamine[1]	Dianhydride	η_{inh}, dL/g[2]	T_g, °C	$\overline{M}_n$ g/mol	$\overline{M}_w$ g/mol
8	9,9'-FDA	6FDA	0.60	268	32600	169300
9	9,9'-FDA	ODPA	0.72	233	31650	148900
10	APB	6FDA	0.62	229	13650	17300
11	APB	ODPA	0.72	213	29050	183350
12	3,4'-ODA	6FDA	0.91	250	32350	266000
13	3,4'-ODA	ODPA	0.78	233	----	----
14	1,3-PDA	6FDA	0.70	253	----	----
15	1,3-PDA	ODPA	0.89	238	----	----
16	4-BDAF	6FDA	0.68	241	----	----
17	4-BDAF	ODPA	0.88	231	----	----

1. Copolymers prepared with 25 mole % diamine and 75 mole % TMFDA.

2. Inherent viscosities determined on 0.5% polyamide acid solutions in NMP at 25°C.



1,3-Bis(3-aminophenoxy)benzene (APB) 1,3-Phenylene diamine (1,3-PDA)

2,2-Bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (4-BDAF)

9,9'-Bis(4-aminophenyl)fluorene (9,9'-FDA) 3,4'-Oxydianiline (3,4-ODA)

Figure 4. Diamines used in Copolymer Synthesis

4. SUMMARY

A novel phosphine oxide containing diamine was prepared and subsequently reacted with various dianhydrides to prepare phenylphosphine oxide containing polyimides. Several of the resulting polyimides exhibited a combination of desirable properties such as low color, high optical transparency and good tensile properties. In several cases, GPC data indicate the presence of low molecular weight species. The low molecular weight components probably contributed to the low film elongations. One polymer was metallized with silver/inconel and exposed to UV radiation and AO. The polymer exhibited very minor changes in α and ε as a result of these exposures. A series of copolymers was prepared using 75 mole % of TMFDA and 25 mole % of an additional aromatic diamine. The copolymers exhibited relatively high inherent viscosities, but GPC analyses indicated the presence of low molecular weight species.

5. REFERENCES

1. Leger, L; Visentine, J.; Santos-Mason, B. *SAMPE Q*. **1987**, *18*(2), 38.
2. Stiegman, A. E.; Brinza, D. E.; Anderson, M. S.; Minton, T. K.; Laue, G. E.; Liang, R. H. Jet Propulsion Laboratory Publ. 91-10, May 1991.
3. Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M. *Polyimides*; Blackie & Son: Glasgow and London, 1990..
4. St. Clair, A. K.; St. Clair, T. L.; Slemp, W. S. *Recent Advances in Polyimide Science and Technology*, Weber, W. and Gupta, M. eds., Soc. of Plastics Engineers, Poughkeepsie, New York, 1987, pp. 16-36.
5. Smith, C. D.; Grubbs, H.; Webster, H. F.; Gungor, A.; Wightman, J. P.; McGrath, J. E. *High Perf. Polym*, **1991**, *3*(4), 211.
6. Smith, J. G. Jr.; Connell, J. W.; Hergenrother, P. M. *Polymer* **1994**, *35*(13), 2834.
7. Connell, J. W.; Smith, J. G. Jr.; Hergenrother, P. M. *Polymer* **1995**, *36*(1), 5.
8. Connell, J. W.; Smith, J. G. Jr.; Hedrick, J. L. *Polymer* **1995**, *36*(1), 13.
9. Connell, J. W.; Smith, J. G. Jr.; Halil, C. G.; Siochi, E. J. *Polymers for Advanced Technologies* **1998**, *9*, 11.
10. Connell, J. W.; Smith. J. G. Jr.; Hergenrother, P. M.; *J. Fire. Sci.* **1993**, *11*, 137.
11. Fewell, L. L.; *J. Appl. Polym. Sci.* **1990**, *41*, 391.
12. Fewell, L. L.; Finney. L. *Polymer* **1991**, *32*, 393.
13. Sanders, J.; Cuttler, J.; Connell, J. W.; Watson, K. A.; Choi, S. Unpublished results, 1998.

6. BIOGRAPHIES

Kent A. Watson is a National Research Council Postdoctorial Fellow working at the Advanced Composites and Polymers Branch of the Structures and Materials Competency at NASA Langley Research Center.

John W. Connell is a senior polymer scientist in the Advanced Materials and Processing Branch of the Structures and Materials Competency at the NASA Langley Research Center.