

POLYIMIDES CONTAINING FLUORINE AND PHOSPHORUS FOR POTENTIAL SPACE APPLICATIONS

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Introduction

As part of an effort to develop low color, ultraviolet (UV) radiation and atomic oxygen resistant polyimides for potential space applications, a novel diamine containing fluorine and phosphorus was synthesized and used to prepare polyimides. The approach was to combine attributes from colorless, UV resistant polyimides¹ and atomic oxygen (AO) resistant polymers^{2,3} into a single material. Preparation of colorless polyimides has focused on minimization of charge transfer complex formation by incorporation of bulky substituents and disrupting conjugation by using meta-catenated monomers. AO resistant polymer technology development has focused on placing phenylphosphine oxide groups into the backbone of aromatic polymers. However, polyimides prepared utilizing this approach thus far have all exhibited significant color. Thus in an attempt to combine these features in a polyimide a new diamine, bis(3-aminophenyl)-3,5-di(trifluoromethyl)phenylphosphine oxide (TMFDA) was synthesized and used to prepare polyimides. The polyimides were cast into films and characterized for physical and mechanical properties, optical transmission and AO and UV resistance.

Experimental

Materials The starting materials for the synthesis of the diamine 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. The synthesis of the diamine has been previously described.⁴

Characterization Inherent viscosities (η_{inh}) were obtained on 0.5% polymer solutions in and N,N-dimethylacetamide (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 glass transition temperature (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 cm³/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 10³ to 10⁷ g/mole was used in series with a Styragel HT 3 column, which covers the range from 10³ to 10⁴ g/mole. A universal calibration curve was generated with narrow molecular weight distribution polystyrene standards with molecular weights ranging from 5 X 10³ to 2.75 X 10⁶ g/mole.

Polymer preparation Phenylphosphine oxide-containing polyimides were prepared by reacting stoichiometric quantities of TMFDA 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 TMFDA (4.4431 g, 0.01 mole) and DMAc, (15.8 mL). The diamine dissolved within a few minutes and 4,4'-perfluoroisopropylidene 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.

Films Thin films were cast from polyamide acid and/or imide solutions in DMAc (20% solids). The polymers and copolymers were centrifuged, the decantate doctoried 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.

Atomic oxygen and ultraviolet radiation exposure Prior to the testing of Polymer 1 (6FDA/TMFDA) 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 10¹⁶ atoms/cm²/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.

Results and Discussion

Diamine synthesis The phenylphosphine oxide 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 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.

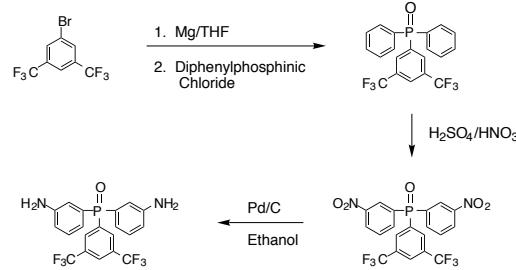


Figure 1. Synthesis of Diamine (TMFDA)

Polymer synthesis Polyimides containing PPO units were prepared from TMFDA and various aromatic dianhydrides in DMAc under a nitrogen atmosphere. 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 below in Figure 2.

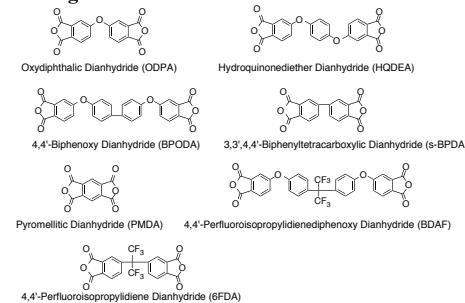


Figure 2. Chemical structures of aromatic dianhydrides

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_g s 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.

Table 1. Polymer Characterization

Polymer	Dianhydride	η_{inh} (dL/g)*	5% Weight Loss, °C		
			T_g (°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	BDAF	0.23	213	487	491
7	s-BPDA	0.93	260	500	514

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

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 μ m 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	T_g , °C	Tensile		Elong. @ Break, %
			Strength, MPa	Modulus, GPa	
3	BPODA	226	118.2	2.84	9.8
5	HQDEA	222	79.2	2.90	3.1
6	BDAF	213	93.0	2.92	3.8

Optical transparency Thin films were measured for optical transparency using UV/visible spectroscopy. The results are presented in Table 3. Two of the films exhibited optical transparencies in excess of 85%. All of the films in Table 3 were clear to pale yellow in color depending on the thickness of the film.

Table 3. Optical Transparency of Polyimide Films

Polymer	Dianhydride	Thickness, μ m	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

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 μ m thick, was coated with silver/inconel on one side to form a second surface mirror. The sample was exposed to fluences of 1.6×10^{21} AO/cm² and the effect of the exposure on solar absorbance (α), solar emittance (ϵ) and surface erosion was determined. The results are presented in Table 4. The film exhibited an initial change in α and ϵ , but they subsequently remained unchanged out to a fluence of 1.6×10^{21} AO/cm². The 6FDA/TFMDA film exhibited a non-linear erosion rate and superior erosion resistance relative to Kapton® HN film, which exhibited an

erosion of 2.0×10^{-3} cm after exposure to a fluence of only 7.5×10^{20} AO/cm². It can also be seen from the data in Table 4 that this material does not exhibit a linear erosion rate.

Table 4. Effect of Fast AO Exposure of Polyimide/Silver Film (Polymer 1)

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

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 μ m 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 5. The film exhibited minor changes in α and ϵ with exposure to 1000 equivalent solar hours indicating excellent resistance to UV radiation.

Table 5. UV Exposure of Polyimide/Silver Film (Polymer 1)

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

Copolymer synthesis A series of copolymers were prepared using 25 mol % of an aromatic diamine and 75 mol % of TMFDA and 100 mol % of an aromatic dianhydride. Two dianhydrides were used: ODPA and 6FDA. The diamines used for copolymer consisted of 1,3-bis(3-aminophenoxy)benzene, 1,3-diaminobenzene, 9,9-bis(4-aminophenyl)fluorene, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane, and 3,4'-oxydianiline. The 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_g s ranged from 213-268 °C. In general, GPC data indicates moderate to high M_n values. The GPC chromatograms exhibited low molecular weight tails which affected the polydispersity and M_n values. Films cast from the copolymers were nearly colorless depending on film thickness.

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.

References

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