Macromolecules **2002,** *35,* 4968−4974

Space Environmentally Stable Polyimides and Copolyimides Derived from [2,4-Bis(3-aminophenoxy)phenyl]diphenylphosphine Oxide

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Received February 4, 2002; Revised Manuscript Received April 8, 2002

ABSTRACT: Polyimides with a combination of properties including low solar absorptivity (α) in thin films, atomic oxygen (AO), and ultraviolet (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, [2,4-bis(3-aminophenoxy)phenyl]diphenylphosphine oxide (**2**), with aromatic dianhydrides in a polar aprotic solvent. The diamine was prepared from commercially available starting materials in a two-step reaction in relatively high yield. Copoly(amide acid)s and copolyimides were prepared using **2** in combination with other commercially available aromatic diamines. The chemistry as well as physical and mechanical properties of the polymers and films will be discussed.

Introduction

Organic polymers are subject to degradation when exposed to AO, UV, and vacuum-ultraviolet (VUV) radiation that are present in low Earth orbit (LEO) at altitudes ranging from 160 to 800 km. At higher altitudes AO becomes less prevalent, but UV, VUV, electrons, protons, and other particulate radiation are of concern. These species 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 cross-linking that can cause adverse physical, mechanical, and optical property changes in the polymer. Perfluorinated materials such as copoly(fluoroethylene propylene) exhibit good resistance to AO, but dramatic increases in the erosion rate (mass loss) is observed when the polymer is exposed simultaneously to AO and UV radiation.[1,2]

High molecular weight aromatic polyimide films 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, polyimide films are typically yellow to amber in color and consequently have high solar absorptivities. There are exceptions and the preparation of low color polyimides that are UV resistant has been reported.[4]

The color in polyimide films may originate from chromophoric units, impurities within the starting material, or side reactions (isoimides). However, studies have shown that charge-transfer complex (CTC) formation is the primary cause of color arising in polyimides.[4,5] Bulky side groups and meta-substitution of the aromatic diamine portion have been shown to reduce conjugation and electronic interactions between polyimide chains due to CTC formation. By minimizing or eliminating CTC formation, low color or virtually colorless polyimide films with improved optical transparency can be obtained.[4,5]

Currently there are no commercially available polyimides that are inherently resistant to degradation due to AO exposure. Commercially available polymers used in LEO are typically protected from AO by a protective coating. Present methods for the elimination or reduction of erosion due to AO involve coating the polymer with aluminum oxide, silicon dioxide, chromium oxide, and fluorinated polymers. Usually this coating method requires a specialized facility and a separate processing step. In addition, there are limitations on the shape and size of film that can be protected via coating. 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 space-based particle impact. Another problem that arises is when there is a mismatch between the coefficient of thermal expansion of the substrate polymer and the coating, which upon thermal cycling can cause spalling, cracking, or disbonding. Once damage occurs to the protective surface coating, the underlying polymer becomes exposed to AO, and erosion proceeds that can lead to loss of mechanical and optical properties. In addition, in applications where the film must be folded for stowage prior to launch, the use of a coating may not be viable as it will likely be damaged due to folding and unfolding of the coated film.

AO resistant polymer development has recently focused on incorporating phenylphosphine oxide (PPO) groups into the backbone of aromatic polymers.[6−12] X-ray photoelectron spectroscopy studies have shown that polymers containing chemically bound PPO units[6−11] as well as phosphazene groups[13,14] have significantly increased AO and oxygen plasma resistance. More recent work using X-ray adsorption near edge structure spectroscopy has shown that a polyphosphate surface layer forms upon exposure of these materials to AO,[15] subsequently inhibiting erosion of the underlying polymer. Reports of polyimides containing phosphine oxide

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10.1021/ma0201779

units have appeared previously;[16,17] however, all of these polyimides have been highly colored. This implies that the PPO group when part of the polyimide backbone is not sufficiently bulky to prevent CTC formation.

Recently, we reported the preparation and characterization of a novel diamine containing a PPO group.[12] Polyimides prepared from this diamine were resistant to AO and UV radiation and formed films with low solar absorptivities. However, films formed from these polymers were relatively brittle and exhibited poor thin film mechanical properties. More recently, work has focused on improving thin film properties without detracting from AO or UV resistance.[18] In addition, other properties of interest such as electrical conductivity to mitigate charge buildup are of interest, and preliminary studies involving the incorporation of carbon nanotubes into these polymers have yielded promising results.[19] The current work is focused on developing space environmentally durable polymers with specific combinations of properties for applications on Gossamer spacecraft.[20] The chemistry and properties of PPO containing polyimides are described herein.

Experimental Section

Starting Materials. The following materials were used as received: 1,3-bis(3-aminophenoxy)benzene (APB, melting point (mp) 107−108.5 °C, Mitsui Chemicals America, Inc.), 2,2-bis(4-aminophenyl)hexafluoropropane (BIS-A-AF, mp 195−197 °C, Central Glass Co., Ltd.), 2,2′-bis(trifluoromethyl)benzidine (ABL-21, mp 179.5−182 °C, Kriskev Company, Inc.), 9,9-bis(4-aminophenyl)fluorene (9,9-FDA, mp 253−255 °C, TCI America), 4,4′-bis(4-aminophenoxy)biphenyl (BAPB, mp 196−197.5 °C, Kriskev Co., Inc.), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA, mp 297−298 °C, Ube Industries, Ltd.), and 3,4′-oxydianiline (3,4′-ODA, 82−84 °C, Hyvoco, Inc.). Oxydiphthalic dianhydride (ODPA, mp 224−225.5 °C, Imitec, Inc.), pyromellitic dianhydride (PMDA, mp 284−286 °C, Allco Chemical Corp.), 4,4′-perfluoroisopropylidiene dianhydride (6FDA, mp 241−243 °C, Hoechst Celanese Inc.), and 4-aminophenol (mp 186−187 °C, Aldrich Chemical Co.) were purified by vacuum sublimation prior to use. 4,4′-Biphenoxy dianhydride (BPODA, mp 284−286 °C, Oxychem, Inc.) was recrystallized from 1,2,4-trichlorobenzene prior to use. 2,2-Bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (4-BDAF, 159−161 °C, Central Glass Co., Ltd.) was recrystallized from 2-propanol prior to use. Diphenylphosphinic chloride (Zeneca) was vacuum-distilled (163 °C at ∼20 mm), and 1-bromo-2,4-difluorobenzene (Lancaster Synthesis, Inc.) was distilled (165 °C) prior to use. All other materials were used as received.

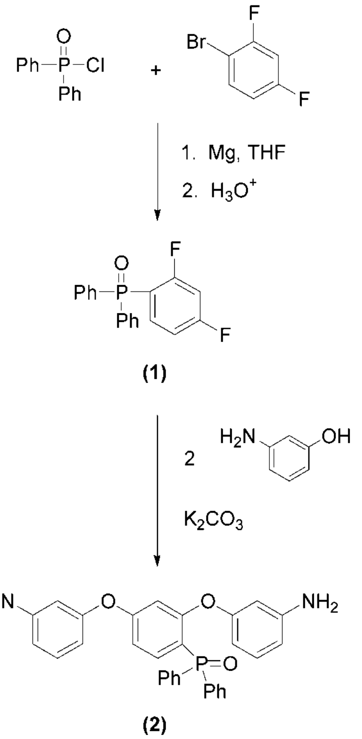
Characterization. Inherent viscosities (η_{inh}) were obtained on 0.5% (w/v) polyimide solutions in *N*-methylpyrrolidinone (NMP) at 25 °C. Differential scanning calorimetry (DSC) was conducted on a Shimadzu DSC-50 thermal analyzer. Melting points ranges were determined by either DSC (10 °C/min recorded at the onset to melt and the endothermic peak) or visually determined on a Thomas-Hoover capillary melting point apparatus (uncorrected). T_g's were determined at 20 °C/min and were taken as the inflection point of the ΔT vs temperature curve. Dynamic thermogravimetric analyses (TGA) were performed on a Seiko model 200/220 instrument on film or 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. UV/vis spectra were obtained on thin films using a Perkin-Elmer Lambda 900 UV/vis/NIR spectrometer. Infrared spectra were obtained on a Perkin-Elmer 1600 series FTIR. A Bruker 300 was used to obtain ^1H and ^{31}P NMR spectra. Thin-film tensile properties were determined according to ASTM D882 using either four or five specimens (0.51 cm wide) per test conditions using a 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/min. Solar absorptivities were measured on an AZ Technology 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 for air mass 0 per ASTM E903. An AZ Technology Temp 2000A infrared reflectometer was used to measure thermal emissivities (ϵ). Atomic oxygen exposure studies were done at NASA Marshall Space Flight Center, Atomic Oxygen Beam Facility.

Preparation of 2,4-Difluorophenyldiphenylphosphine Oxide (1). Into a 1 L three-neck round-bottomed flask equipped with a mechanical stirrer, thermometer, nitrogen gas inlet, pressure equalizing addition funnel, and reflux condenser with drying tube were placed magnesium turnings (13.5 g, 0.55 mol) and anhydrous tetrahydrofuran (THF, 50 mL). The mixture was cooled to ∼5 °C using an ice−water bath. A solution of 1-bromo-2,4-difluorobenzene (107.2 g, 0.55 mol, 20% molar excess) in THF (200 mL) was placed in the pressure equalizing addition funnel and added dropwise over a 1.5 h period. After addition was complete, the mixture was allowed to slowly warm to room temperature and stirred for 3 h, and the flask was subsequently placed in an ice−water bath to cool the mixture to ∼5 °C. A solution of freshly distilled diphenylphosphinic chloride (107.9 g, 0.46 mol) in THF (100 mL) was added dropwise over a 1 h period. The reaction mixture was allowed to slowly warm to room temperature and then stirred under nitrogen for 15 h. The resulting brown solution was poured into an aqueous solution (700 mL) of concentrated ammonium chloride to give two layers. The organic layer was isolated and washed successively with water, 5% aqueous sodium bicarbonate, and water and then dried over magnesium sulfate. The THF was removed via rotoevaporation to give a dark red viscous liquid (142.8 g, 98% crude yield). The crude product was vacuum-distilled (at ∼20 mm Hg) from 178 to 181 °C, and a light-yellow semisolid was collected (118.6 g, 81% yield). The material was subsequently dissolved in 120 mL of hot toluene, treated which charcoal, and filtered while hot through Celite. To the partially cooled toluene solution was carefully added 120 mL of hexanes. The solution was allowed to cool with stirring overnight, yielding **1** as a white crystalline solid: yield 100.9 g, 69%; mp 111.1−112.3 °C as determined by DSC. IR (KBr pellet, cm^{-1}): 1196.5 ($\nu_{P=O}$). Anal. Calcd for $C_{18}H_{13}F_2OP$: C, 68.79%; H, 4.17%; F, 12.09%; P, 9.86%. Found: C, 68.38%; H, 4.26%; F, 11.17%; P, 10.28%.

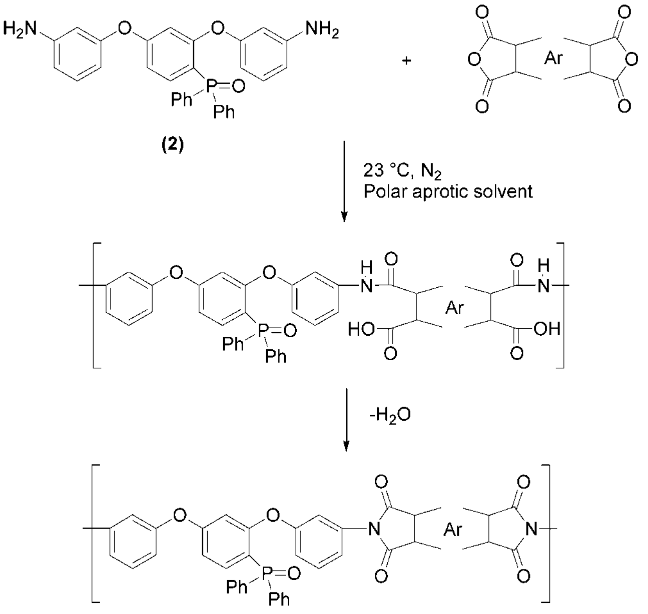
Preparation of [2,4-Bis(3-aminophenoxy)phenyl]diphenylphosphine Oxide (2). Into a 500 mL three-neck round-bottom flask equipped with a mechanical stirrer, thermometer, and a Dean−Stark trap equipped with a drying tube were placed **1** (39.50 g, 0.1257 mol), 3-aminophenol (28.80 g, 0.2639 mol), potassium carbonate (45.58 g, 0.3298 mol), NMP (200 mL), and toluene (115 mL). The mixture was heated with stirring to 135 °C while removing water via azeotropic distillation. After 16 h, the toluene was removed from the reaction, and the resulting solution was heated at 160 °C for 4 h. The reaction mixture was cooled to room temperature and then poured into 1 L of 5% aqueous acetic acid with vigorous stirring. A tan gum formed that eventually solidified with stirring. The crude solid was collected via filtration, washed with excess water, and dried at 110 °C to afford 59.1 g of **2** (95% crude yield). The solid melted from 179.7 to 187.6 °C as determined by DSC. The solid was recrystallized twice from ethanol with charcoal treatment to afford **2**: yield 60%; mp 195.2−196.5 °C (DSC). ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.93 (dd, $J_{ab} = 8.5$ Hz, $J_{bc} = 8.5$ Hz, 1H); 7.40−7.48 (m, 4H); 7.08 (t, $J = 8.1$ Hz, 1H); 6.94 (t, $J = 8.0$, 1H); 6.68−6.72 (m, 1H); 6.32−6.50 (m, 5H); 6.01−6.04 (m, 1H); 5.93 (t, $J = 2.2$ Hz, 1H); 3.62 (br, 4H). ^{31}P NMR (acetone-d_6), 121 MHz, ppm): δ 27.46 (singlet). IR (KBr pellet, cm^{-1}): 1180.2 ($\nu_{P=O}$). Anal. Calcd for $C_{30}H_{25}N_2O_3P$: C, 73.16%; H, 5.12%; N, 5.69%; P, 6.29%. Found: C, 72.85%; H, 5.00%; N, 5.69%; P, 6.22%. Mass spectroscopic analysis: M^+ 492 [$C_{30}H_{25}N_2O_3P^+$].

General Procedure for the Preparation of Polyimides. Phenylphosphine oxide-containing polyimides were prepared by reacting stoichiometric quantities of **2** with various dianhydrides. The following procedure is for the preparation of **P1**

Scheme 1. Synthesis of [2,4-Bis(3-aminophenoxy)phenyl]diphenylphosphine Oxide (2)



Scheme 2. Synthesis of Phenylphosphine Oxide Containing Polyimides



and is representative for the preparation of all polymers. Into a 100 mL three-neck round-bottom flask equipped with a mechanical stirrer, nitrogen gas inlet, and drying tube filled with calcium sulfate were placed **2** (2.3768 g, 4.8258×10^{-3} mol) and NMP (7.0 mL). Once dissolved, oxydiphthalic dianhydride (1.4970 g, 4.8258×10^{-3} mol) was added with additional NMP (8.0 mL) to give a solution with a concentration of 20% (w/w) solids. The resulting light yellow solution was stirred overnight at room temperature under a nitrogen atmosphere. A 0.5% (w/v) solution in NMP at 25 °C exhibited an η_{inh} of 1.01 dL/g. The remaining polymer solution was chemically imidized by the addition of 1.49 g of acetic anhydride and 1.15 g of pyridine (3 molar excess). The solution was stirred at room temperature overnight. The polymer was precipitated in a blender containing a 50/50 mixture of water/methanol, filtered, washed with excess water, and dried in a vacuum oven at 110 °C overnight to afford a white, fibrous material. Films were cast as described below. Copolymers were prepared in a similar manner using 75 mol % of **2**, 25 mol % of another diamine, and a stoichiometric amount of dianhydride.

Film Preparation. Thin films were cast from polyimide solutions in *N*,*N*-dimethylacetamide (DMAc), NMP, or chloroform (typically 10–20% w/w solids). The polymer solutions were centrifuged, and the decantate was doctored onto clean, dry plate glass and dried to a tack-free form in a low-humidity chamber. The films then were stage-dried in a forced air oven to 250 °C and held for 1 h.

Results and Discussion

Preparation of [2,4-Bis(3-aminophenoxy)phenyl]-diphenylphosphine Oxide (2). This novel diamine was synthesized in two steps as shown in Scheme 1. The first step involved a Grignard reaction between 1-bromo-2,4-difluorobenzene (20% molar excess) with diphenylphosphinic chloride. Since diphenylphosphinic chloride readily hydrolyzes to diphenylphosphinic acid, it was vacuum-distilled prior to use and stored under a nitrogen atmosphere. The crude product was obtained in 81% yield. Initial purification of this material was difficult since phosphine oxide compounds, in general, are soluble in many organic solvents, and purification via crystallization is often difficult. Purification of the crude Grignard product (**1**), typically obtained as viscous red oil, was accomplished by vacuum distillation to yield a light yellow semisolid. The semisolid was subsequently crystallized from a 50/50 mixture of toluene/hexanes to achieve a white crystalline solid in 69% overall yield. The Grignard adduct was subsequently reacted with 2 molar equivalents of 3-aminophenol in the presence of potassium carbonate in NMP to yield **2**. Two recrystallizations of diamine **2** from ethanol afforded polymer grade monomer in 60% overall yield. Characterization by mass spectrometry, ^{1}H and ^{31}P nuclear magnetic spectroscopy (NMR), and elemental analysis indicated high purity with the data being consistent with the expected chemical structure. The structure of the diamine was designed to impart several desirable properties into polyimides. The polymers formed were anticipated to have AO resistance due to the presence of the PPO functional group, UV resistance due to the aromatic imide ring, and low color due to the presence of meta linkages and bulky pendant groups (PPO group). In addition, enhanced processability of the fully imidized polyimides is expected due to the improved solubility of the polymers resulting from the presence of a bulky pendant PPO group.

Polymer Synthesis. Polyimides containing PPO groups were prepared from **2** and various aromatic dianhydrides in NMP or DMAc under a nitrogen atmosphere as shown in Scheme 2. Typically, the poly(amide acid) was prepared by dissolving the diamine and then adding a molar equivalent of dianhydride as a solid. Solvent was then added to make a 20% (w/w) solution. The reaction mixture was stirred at room temperature for 24 h followed by chemical imidization/cyclodehydration using a mixture of acetic anhydride and pyridine. The resulting polymers were isolated in >95% yield. The chemical structures of the aromatic dianhydrides used in this study are shown in Figure 1.

Polymer Characterization. Characterization of polymers prepared from **2** and various dianhydrides is presented in Table 1. The η_{inh}'s ranged from 0.53 to 1.01

Table 1. Characterization of Polyimides Prepared from 2

polymer	dianhydride	η_{inh} (dL/g)	T_g (°C)	tensile strength (MPa)	tensile modulus (GPa)	elong (%)	5% weight loss (°C)	
							air	nitrogen
P1	ODPA	1.01	212	97	2.8	4.7	461	478
P2	BPODA	0.81	227	82	2.5	4.0	464	494
P3	6FDA	0.66	230	87	2.9	3.3	453	465
P4	s-BPDA	0.97	234	90	2.8	3.1	455	471
P5	PMDA	0.53	251				421	430

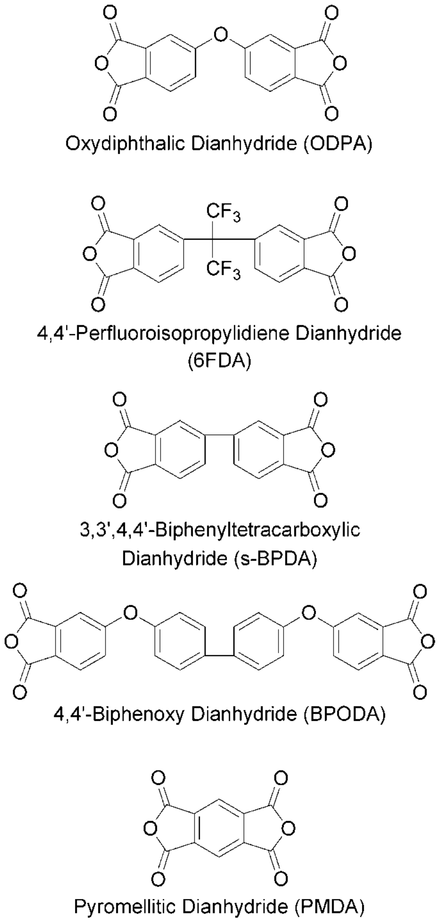


Figure 1. Dianhydrides used for polyimide synthesis.

Table 2. Optical Properties of Films Prepared from 2

polymer	dianhydride	transparency at 500 nm (%)	film thickness (cm)	α	ϵ	α/ϵ
P1	ODPA	85	4.06×10^{-3}	0.06	0.56	0.10
P2	BPODA	80	5.08×10^{-3}	0.09	0.68	0.13
P3	6FDA	87	4.32×10^{-3}	0.05	0.55	0.09
P4	s-BPDA	76	6.10×10^{-3}	0.10	0.62	0.15

dL/g, indicating medium to high molecular weight polymer formation. The T_g's ranged from 212 to 251 °C. All of the polymers exhibited solubility in DMAc and NMP in the imide form; polymers **P1** and **P3** were also soluble in chloroform. The polymers exhibited good solubility presumably due to the bulky pendant PPO group. **P3**'s high solubility can also be attributed to the trifluoromethyl groups. **P5**, despite having an inherent viscosity of 0.53 dL/g, formed only a brittle film, and thus tensile properties and other characterization tests were not performed. The polymers exhibited temperatures of 5% weight loss ranging from 421 to 464 °C in air and 430 to 494 °C in nitrogen. The typical thermal cycle experienced by spacecraft in LEO is ±100 °C; thus, the thermal properties of these polymers are sufficient for use in LEO.

Thin Film Tensile Properties. Thin films were cast from polyimide solutions (NMP, DMAc, or chloroform) and thermally exposed in a forced air oven to remove residual solvent. All of the films prepared except for **P5** were tough and creasable and exhibited low color. Thin film mechanical properties are presented in Table 1. The films exhibited room tensile strengths and moduli from 82 to 97 MPa and 2.5 to 2.9 GPa, respectively. The elongations to break ranged from 3.1 to 4.7%.

Optical Transparency. Diamine **2** contains meta linkages and a bulky pendant group and thus provides a highly irregular structure to the polyimide. This was expected to disrupt the formation of charge transfer complexes and lead to low color polyimide films. Depending on the dianhydride used, virtually colorless polyimide films were prepared. **P1** and **P3** were nearly colorless, **P2** was light yellow, **P4** was medium yellow, and **P5** was orange in color. Thin films were measured for optical transparency using UV/vis spectroscopy with the percent transmission at 500 nm (the solar maximum) reported in Table 2. Film thicknesses ranged from 4.06×10^{-3} to 6.10×10^{-3} cm. Polymers **P1** and **P3** exhibited optical transparency as high as 87%. **P3**, which contains trifluoromethyl groups, exhibited the highest transparency. The film from **P5** was too brittle for transparency measurements, but the orange color of the film indicates lower percent transmission values compared to those of other films.

Solar Absorptivities and Thermal Emissivities. Two of several important properties of materials for space applications are α and ϵ. Solar absorptivity pertains to the fraction of incoming solar energy that is absorbed by the film, and 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. Thin films were measured for α and ϵ, and the results are shown in Table 2. α values ranged from 0.05 to 0.10, and ϵ values ranged from 0.56 to 0.68. Consistent with the optical transparency measurements, **P1** and **P3** films exhibited the lowest α values.

Atomic Oxygen Exposure. Ground-based AO exposure was performed on three thin film samples of **P1** at the Marshall Space Flight Center fast AO facility. The exposed films had an area of 3.6575 cm^2, the thickness was 2.54×10^{-3} cm, and the weights of the films ranged from 1.1817×10^{-2} to 1.844×10^{-2} g. The films were exposed to AO fluences ranging from 1.71×10^{20} to 2.13×10^{20} AO/cm^2, and the effects on α, ϵ, and mass loss were determined. Exposure of 2.0×10^{20} AO/cm^2 is roughly equivalent to 6 months exposure to AO in a LEO environment. The results are presented in Table 3. The ability of a material to undergo minimal changes in α, ϵ, and other properties upon exposure to radiation in space is of significant importance. The films exhibited a slight initial increase in α and negligible changes in ϵ after initial exposure to AO. The sample exposed to 2.13×10^{20} AO/cm^2 exhibited a weight loss

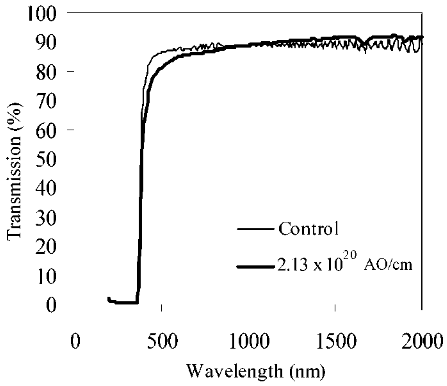


Figure 2. Transmission spectrum of **P1** before and after AO exposure.

Table 3. Effect of Fast AO Exposure on P1

exposure (AO/cm^2)	α	ϵ	mass loss (g)	mass loss (%)
none	0.187	0.74	0	0
1.71×10^{20}	0.221	0.74	4.1×10^{-4}	2.24
2.00×10^{20}	0.218	0.73	3.2×10^{-4}	1.74
2.13×10^{20}	0.227	0.74	5.0×10^{-4}	2.73

of 2.7%. This calculates to a reaction efficiency of 4.8×10^{-25} cm^3/AO. For comparison purposes the reaction efficiency of Kapton HN is 3.0×10^{-24} cm^3/AO. However, since phosphine oxide containing polyimides do not exhibit linear erosion rates, this comparison is not quantitative. Other phosphine oxide-containing polyimides have exhibited nonlinear erosion rates after longer duration AO exposure.[12] The results suggest that AO reacts indiscriminately with the polymer, resulting in off-gassing of volatile organic species and eventual buildup of a polyphosphate layer which subsequently retards additional erosion. This is analogous to what has been reported to occur with silicon-containing polymers.[21] The preliminary results observed with the polyimide tested herein are consistent with previous results.

The transmission spectrum of **P1** before and after AO exposure is shown in Figure 2. The sample exposed to AO exhibited a slight decrease in transmission from around 500−700 nm. At 500 nm, the transmission of the control sample was 85%. For the AO-irradiated sample, the transmission decreased to 81%. The slight lowering in transmission is likely due to the formation of a polyphosphate surface layer on the film. This is consistent with similar tests performed on this same polymer by a private company.[22]

Although exposure of these polyimides to UV radiation was not conducted as part of this study, they are anticipated to exhibit good resistance based on previous studies of polyimides of a similar chemical structure.[23,24] Other radiation effects on these polyimides have been studied as well.[25,26] In general, these polyimides have exhibited good stability with only slight changes in optical properties as a result of UV exposure.

Copolymer Synthesis. A series of copolymers were prepared in order to further investigate effects of polymer structure on the color, α, ϵ, and other film properties. Copolymers were prepared using 75 mol % of **2**, 25 mol % of a second commercially available aromatic diamine, and 100 mol % of an aromatic dianhydride. Three dianhydrides were chosen because they tended to give polyimide films with low solar absorptivities. The dianhydrides selected were ODPA, 6FDA, and s-BPDA (structures shown in Figure 1). The structures of the diamines used for copolymer synthesis are shown in Figure 3. Characterization of the copolymers is summarized in Table 4. Inherent viscosities ranged from 0.26 to 1.07 dL/g and T_g's ranged from 203 to 249 °C. Copolymers prepared from ODPA typically had the lowest T_g's, while films prepared from s-BPDA typically had the highest T_g's.

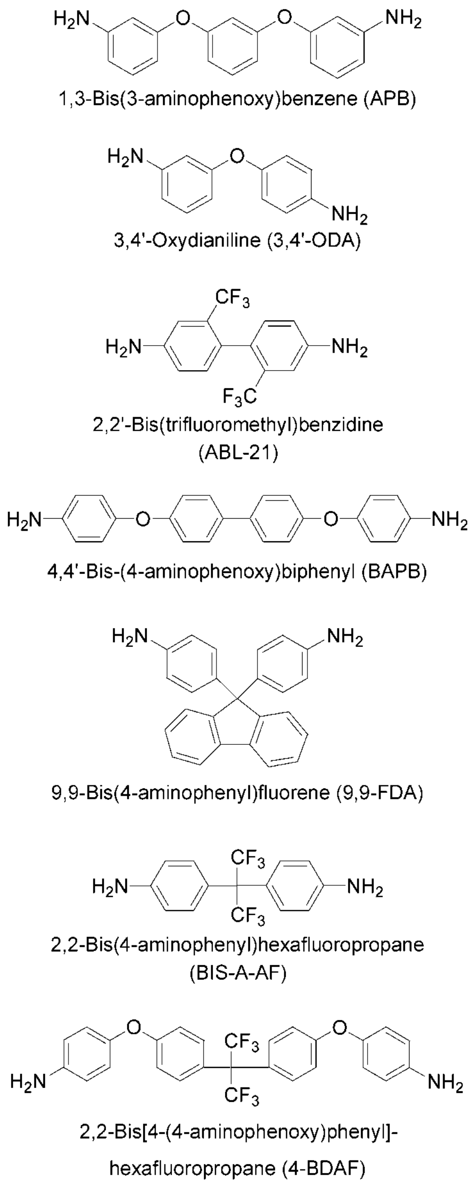


Figure 3. Diamines used in copolymer synthesis.

Thin Film Tensile Properties, Copolymers. Table 4 lists thin film mechanical properties of the copolymers at room temperature. Tensile strengths ranged from 79 to 113 MPa and moduli ranged from 2.7 to 3.5 GPa. Elongations to break ranged from 3.1 to 9.7%. **P14**, with an inherent viscosity of 0.34 dL/g, gave a brittle film; thus, no tensile properties were obtained.

Optical Properties, Copolymers. Optical properties of the copolymers were measured using UV/vis spectroscopy on thin films. The optical properties are listed in Table 5. Transparencies of thin films at 500 nm ranged from 80 to 89%, and most of the films were colorless or nearly colorless. Film color was partially dependent upon which dianhydride and diamine were used to prepare the copolymer as well as thickness of the film. Film thickness ranged from 2.0×10^{-3} to 5.3

Table 4. Copolymer Characterization: 75% (2), 25% Codiamine

polymer	dianhydride	codiamine	η_{inh} (dL/g)	T_g (°C)	tensile strength (MPa)	tensile modulus (GPa)	elong (%)
P6	ODPA	APB	1.07	203	97	3.1	5.0
P7	ODPA	4-BDAF	0.66	216	105	2.8	7.9
P8	ODPA	3,4′-ODA	0.57	218	101	3.2	6.3
P9	ODPA	BIS-A-AF	0.57	220	104	3.0	6.6
P10	ODPA	BAPB	0.73	222	99	3.3	9.5
P11	6FDA	APB	0.53	224	101	3.4	4.1
P12	ODPA	9,9-FDA	0.39	226	113	3.3	8.7
P13	ODPA	ABL-21	0.46	227	108	3.0	6.2
P14	6FDA	ABL-21	0.34	233	*a*	*a*	*a*
P15	6FDA	3,4′-ODA	0.42	234	108	3.2	4.9
P16	6FDA	4-BDAF	0.58	234	92	2.9	4.3
P17	s-BPDA	4-BDAF	0.49	237	90	3.0	9.6
P18	6FDA	BAPB	0.57	238	94	2.8	5.0
P19	6FDA	BIS-A-AF	0.39	238	88	2.7	4.3
P20	s-BPDA	3,4′-ODA	0.26	240	102	3.5	9.7
P21	s-BPDA	9,9-FDA	0.28	246	90	3.5	3.9
P22	6FDA	9,9-FDA	0.48	249	79	3.2	3.1

[a] Brittle film.

Table 5. Copolymer Optical Properties: 75% (2), 25% Codiamine

polymer	dianhydride	codiamine	transparency at 500 nm (%)	film thickness (cm)	α	ϵ	α/ϵ
P6	ODPA	APB	83	3.1×10^{-3}			
P7	ODPA	4-BDAF	80	2.5×10^{-3}	0.07	0.60	0.12
P8	ODPA	3,4′-ODA	88	2.0×10^{-3}	0.06	0.38	0.16
P9	ODPA	BIS-A-AF	85	3.6×10^{-3}			
P10	ODPA	BAPB	82	2.8×10^{-3}			
P11	6FDA	APB	86	4.3×10^{-3}	0.07	0.64	0.11
P12	ODPA	9,9-FDA	87	3.8×10^{-3}			
P13	ODPA	ABL-21	81	3.6×10^{-3}			
P14	6FDA	ABL-21	89	2.0×10^{-3}			
P15	6FDA	3,4′-ODA	88	3.3×10^{-3}	0.06	0.59	0.10
P16	6FDA	4-BDAF	87	5.3×10^{-3}			
P17	s-BPDA	4-BDAF	85	2.8×10^{-3}			
P18	6FDA	BAPB	88	4.1×10^{-3}			
P19	6FDA	BIS-A-AF	89	2.5×10^{-3}			
P20	s-BPDA	3,4′-ODA	80	3.6×10^{-3}			
P21	s-BPDA	9,9-FDA	85	3.3×10^{-3}			
P22	6FDA	9,9-FDA	86	3.8×10^{-3}	0.06	0.53	0.11

$\times 10^{-3}$ cm. Copolyimides prepared from 6FDA formed films with the highest optical transparency with two films (**P14** and **P19**) having optical transparency as high as 89%. It appears that the second diamine used had little effect on optical transparency but that may be expected using only 25 mol %. The α and ϵ values of selected copolymer films that had high optical transparency are shown in Table 5.

Conclusions

A novel diamine, [2,4-bis(3-aminophenoxy)phenyl]diphenylphosphine oxide, was prepared, characterized, and subsequently reacted with various dianhydrides to prepare phenylphosphine oxide-containing polyimides. A series of copolymers were prepared using 75 mol % of **2** and 25 mol % of another aromatic diamine. Several of the resulting polyimides and copolyimides exhibited a combination of desirable properties such as low solar absorptivity, high optical transparency, good tensile properties, AO resistance, and enhanced solubility. The PPO pendant to the polymer backbone not only is responsible for imparting AO resistance to the polymer films but also is also partially responsible for imparting low color to the films by reducing charge transfer complex formation. The bulky PPO group also serves to increase the solubility of the fully imidized polymers. The trifluoromethyl groups and meta linkages present in some of the polymers also aid in forming low or no color films. As part of the Materials International Space Station Experiment (MISSE), several representative samples have been placed on the international space station and are being exposed to LEO for 1 year. The samples will subsequently be returned to Earth and analyzed.

Acknowledgment. The authors gratefully acknowledge Dr. Dave Edwards, Marshall Space Flight Center, for performing the AO exposure test and Mr. Bob Mojazza, Triton Systems, Inc., for his assistance in obtaining additional AO exposure data.

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MA0201779