



# Fluorine and phosphine oxide containing homo and copolyimides



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## ABSTRACT

In recent years the synthesis of fluorinated polyimides has become an active area of research. In this study perfluoroalkyl and phosphine oxide containing diamine monomer, bis(3,3'-aminophenyl)-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) phosphine oxide (mDA13FAPO), was successfully prepared. mDA13FAPO was reacted with four different commercial dianhydrides (BTDA, PMDA, ODPDA and 6FDA) and corresponding homopolyimides were prepared by thermal and solution imidization techniques. However, homopolyimides of mDA13FAPO exhibited poor film forming properties. In order to overcome this problem different amounts of mDA13FAPO containing copolyimides with BTDA and ODA were prepared. The flame retardancy of the copolyimides was examined by limiting oxygen index measurements. The surface energies of the copolyimides were determined by contact angle measurements. mDA13FAPO containing homopolyimides exhibited moderate T<sub>g</sub> values (194–233 °C), good thermal stability and excellent solubility. The presence of ODA greatly improved the film forming properties and crack-free, creasable copolyimide films were obtained. As the amount of mDA13FAPO was increased, the flame retardancy and the water contact angles of the copolyimides increased while the surface energies and the glass transition temperatures decreased.

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## 1. Introduction

Aromatic polyimides which are known as high performance engineering polymers, have a wide range of uses, from gas separation membranes to fuel cell applications, from electric-electronic industry to optic materials, from aerospace industry to military applications due to their outstanding thermal, mechanical, electrical and chemical properties [1–3].

Although polyimides have a wide range of uses they suffer from the lack of processability and solubility which arise from their rigid polymer backbones. In order to increase the processability of polyimides, several efforts such as the use of bulky side groups, flexible side groups, asymmetric monomers, flexible linkages, fluorine containing monomer etc., have been made [4–6]. Among these strategies to improve the solubility/processability of polyimides, the introduction of fluorine containing species as main chain components or as pendant groups has several advantages such as low dielectric constants, low refractive index, low water absorption, optical clarity, high permeability and high selectivity for gas separation, hydrophobicity and oleophobicity, besides the

increased solubility [7–9]. On the other hand one of the main drawbacks of fluorine containing polyimides is their low adhesion properties [9].

Generally fluorine is incorporated into polyimides as trifluoromethyl groups. Bulky trifluoromethyl groups reduce the chain packing which results in high free volume and thus trifluoromethyl group containing polyimides exhibit high solubility and processability [10]. Hexafluoroisopropylidene bisphthalic dianhydride, known as 6FDA, is one of the most widely used fluorinated monomer which contains two trifluoromethyl groups (a hexafluoroisopropylidene group) [11]. Up to now, several different monomers were designed with trifluoromethyl or hexafluoroisopropylidene units which are generally attached to the aromatic backbone of polyimides [12–16]. In addition to these fluorinated polyimides, pendant fluoroalkyl containing polyimides were also prepared [17–19]. Introduction of a fluoroalkyl side chain allows to prepare polyimides with high fluorine content and interesting properties [19]. For instance Bes et al. prepared fluorinated alkoxy side group containing polyimides by using Mitsunobu reaction. The resulting polyimides exhibited good thermal properties and enhanced solubility [19]. In another study, gas separation properties of polyimides prepared from 2-(perfluorohexyl)ethyl-3,5-diamino benzoate, were investigated and it was found that the fluorinated side groups improve the permeability of these

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polyimides [20]. Recently a nice review has been published on the synthesis of fluorinated monomers used in the preparation of polyimides [21].

Phosphorus containing polymers are considered as highly efficient halogen-free flame retardant alternatives [22,23]. Besides, polymers with phosphorus moieties have several advantages such as good adhesion to various substrates, excellent solubility in organic solvents, high thermal oxidative stability and radiation resistance [24–26]. Moreover it was shown that polymers with phosphine oxide groups are resistant to atomic oxygen exposure [27,28]. To date, several phosphorus containing polyimides have been synthesized by using either phosphorus containing diamines/dianhydrides or by using different phosphorylating methods [29,30].

Today, studies concerning fluorinated polyimides mainly focus on the synthesis of polyimides by using new type of monomers. In the last decade to overcome the low adhesion problems associated with fluorinated polyimides, Yoon and co-workers prepared several polyimides from both fluorine and phosphine oxide containing diamine monomers [31–35]. These polyimides displayed excellent adhesion, good thermal properties and low dielectric constants. Similarly different researchers have also designed novel monomers having both fluorine and phosphorus and utilized them in the synthesis of polyimides [36,37].

Previously synthesized both fluorine and phosphine oxide groups containing diamine monomers are presented in Table SI.

Although, in literature several synthetic methods have been proposed for the preparation of fluoroalkyl phosphines and phosphine oxides, to authors' best knowledge there is no published work on the preparation of the dinitro and diamine derivatives of these long fluoroalkyl phosphine oxides and to our best knowledge no attempt was done to prepare polyimides from both long-chain perfluoroalkyl and phosphine oxide containing monomers.

In this study perfluoroalkyl and phosphine oxide containing diamine monomer, bis(3,3'-aminophenyl)-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) phosphine oxide (mDA13FAPO) which contains 13 mol of fluorine per mole of the compound was synthesized. Then four different homopolyimides were prepared from commercial dianhydrides (BTDA, PMDA, ODPA and 6FDA) and mDA13FAPO. The monomers were characterized by FT-IR, <sup>1</sup>H NMR, <sup>19</sup>F NMR and <sup>31</sup>P NMR measurements. However, homopolyimides of mDA13FAPO were highly brittle and these materials exhibited poor film forming properties. Therefore in this study a series of mDA13FAPO containing BTDA/ODA based copolyimides were prepared in order to overcome this problem. Thermal properties of novel polyimides were investigated by TGA and DSC measurements. The mechanical properties of the copolyimides were investigated by tensile measurements. The flame retardancy of these materials was examined by limiting oxygen index (LOI) measurements. Moreover hydrophobicity and the surface energy of the coatings were determined by contact angle measurements. The surface topology of the films was observed by a scanning electron microscope (SEM).

## 2. Experimental

### 2.1. Materials

3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 2,2'-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), pyromellitic anhydride (PMDA), 4,4'-oxydiphthalic anhydride (ODPA), triphenyl phosphine (TPP), dimethyl formamide (DMF), dimethyl acetamide (DMAc), dimethyl sulfoxide (DMSO), *N*-methyl pyrrolidone (NMP), *meta*-cresol, (*m*-Cresol), tetrahydrofuran (THF) and toluene were all purchased from Sigma Aldrich. All dianhydrides were dried under vacuum prior to use.

2-Perfluorohexyl ethyl iodide was obtained from Alfaeaser. Sulfuric acid, nitric acid, sodium hydroxide, ethanol, chloroform, benzene, isopropyl alcohol and 10% palladium on an activated carbon (Pd/C) were purchased from Merck and used as received. Sodium bicarbonate and anhydrous magnesium carbonate were obtained from AcrosOrganics. Celite was purchased from Fluka.

### 2.2. Characterization methods

FT-IR spectra were recorded on Perkin Elmer Spectrum100 ATR-FTIR spectrophotometer.

<sup>1</sup>H NMR, <sup>31</sup>P NMR, <sup>19</sup>F NMR and 2-D NMR spectra were recorded using a Varian Model T-60 NMR spectrometer at room temperature. All samples were dissolved in solvents like CDCl<sub>3</sub>, acetone-d<sub>6</sub> and tetramethylsilane was used as an internal reference for proton shifts.

Thermogravimetric analyses (TGA) of polyimide films were performed using a PerkinElmer Thermogravimetric analyzer Pyris 1 TGA model. Samples were run from 30 to 750 °C with heating rate of 10 °C/min under air atmosphere and nitrogen atmosphere.

DSC measurements were performed using Pyris Diamond DSC. Samples were run from 30 to 300 °C with a heating rate of 10 °C/min. Glass transition temperatures were obtained from the second heating scan.

The flammability characteristics of copolyimides were determined by LOI test. The LOI values of the polyimide materials were measured by using a FTI (Fire Testing Technology) type instrument.

Mechanical properties of polyimide films were determined by standard tensile stress-strain tests to measure modulus, ultimate tensile strength and elongation at break. Standard tensile stress-strain experiments were performed at room temperature on a Materials Testing Machine Z010/TN2S, using a crosshead speed of 2 mm/min.

The wettability characteristics of polyimide surfaces were performed on a Kruss (Easy Drop DSA-2) tensiometer. The contact angles ( $\theta$ ) were measured by means of sessile drop test method in which drops were created by using a syringe. Measurements were made using 3–5  $\mu$ l drops of distilled water. For each sample, at least five measurements were made, and the average was taken. The surface energy of the coatings was calculated using Owens-Wendt-Rabel & Kaelble approach. For the calculation of the surface energy three test solutions were considered, water and ethylene glycol as polar solvents and diiodomethane as an apolar solvent.

The transmission spectra of the novel polyimides were recorded in the wavelength range of 300–800 nm using a Shimadzu 3100 UV-vis-NIR spectrometer.

SEM imaging of the films and mapping technique were performed on Philips XL30 ESEM-FEG/EDAX. The specimens were prepared for SEM by freeze-fracturing in liquid nitrogen and applying a gold coating.

Solubility of the polyimides was determined by dissolving 10 mg of polymer samples in 1 ml of solvent.

### 2.3. Synthesis of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) diphenyl phosphine oxide (13FADPPO)

The synthesis of the diamine monomer, bis(3,3'-aminophenyl)-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) phosphine oxide (mDA13FAPO), involves four synthetic steps: (1) synthesis of the phosphonium salt, (2) hydrolysis (dephenylation) of the phosphonium salt in step1, (3) nitration and (4) reduction. The synthetic route to mDA13FAPO is depicted in Scheme 1.

In the first step, a fluorinated phosphonium salt was synthesized by reacting TPP and 2-perfluorohexyl ethyl iodide according to literature procedures [38,39]. Briefly, the fluorinated

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