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## FLUORINE AND PHOSPHINE OXIDE

### **CONTAINING HOMO AND COPOLYIMIDES**

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#### **Graphical Abstract**

Phosphorous containing novel perfluorinated diamine monomer, mDA13FAPO was synthesized and used in the preparation of homo and copolyimides. Due to the fluorous tail of mDA13FAPO polyimides exhibited hydrophobicity with a water contact angle value of 102° and surface energy value of 30 mN/m.





#### Highlights

- > Fluorine and phosphorous containing diamine monomer was synthesized.
- > The new diamine monomer was used to prepare homo- and copolyimides.
- > All homopolyimides displayed moderate Tg values but poor film forming properties.
- > Copolymerization improved the film forming properties.
- Surface energy of the copolyimides were found to be between 30 and 37.5 mN/m.

#### 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, ODPA 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. mDA13FPO containing homopolyimides exhibited moderate Tg 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

Keywords: fluorine; phosphine oxide; polyimides; surface energy

#### 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 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 his group 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 moles 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-d6 and tetramethylsilane was used as an internal reference for proton shifts.

Thermogravimetric analyses (TGA) of polyimide films were performed using a Perkin-Elmer 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 FTT (Fire Testing Technology) type instrument.

Mechanical properties of polyimide films were determined by standard tensile stressstrain tests to measure modules, 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 phosphonium salt was prepared by reacting TPP and fluoroalkyl iodide at 95 °C in

the absence of solvent. The reaction was continued for 24 hours until all of the mixture was solidified. After cooling the resulting solid was washed several times with toluene and ether respectively. Then the white solid was dried at 50 °C under vacuum.

Next, this phosphonium salt was dephenylated to give (3,3,4,4,5,5,6,6,7,7,8,8,8tridecafluorooctyl) diphenyl phosphine oxide (13FADPPO). The procedure of selectively removal of one of the phenyl groups of the phosphonium salt was carried out similar to literature [40]. Briefly, phosphonium salt was placed into a 1 liter round-bottomed flask and treated with 0,271 moles of NaOH (four times excess of phosphonium salt) and with a mixture of isopropyl alcohol/ water (v/v 1:3). The suspension was refluxed for one day at 120 °C. At the end of the reaction, two phases were observed (water (bottom phase) and benzene (top phase) phases). Two phases were separated and water phase was extracted with benzene two times. Then benzene extracts were collected and dried over anhydrous MgSO4. After filtration, benzene was evaporated under vacuum. White crystalline 13FADPPO was dried at 50 °C under vacuum without further purification. 20.4 g of product was obtained (yield: 55%). (m.p. 107°C. **'H-NMR (600MHz, CDCI<sub>3</sub>)** δ 7,78 (4H, m); 7.58 (2H, m); 7.52 (4H, m); 2.54 (2H, m); 2.4 (2H, m). **'PF-NMR (564 MHz, CDCI<sub>3</sub>)** δ -81.00; -114.87; -112.07; -123.05; -123.26; -126.34. **<sup>31</sup>P-NMR (242 MHz, CDCI<sub>3</sub>)** δ 27.63.)

# 2.4. Synthesis of bis(3,3'-nitrophenyl)- (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) phosphine oxide (mDN13FAPO)

In the third step, mDN13FAPO was prepared via nitration of 13FADPPO. A three necked 500 ml round bottom flask, equipped with magnetic stirring, nitrogen inlet and an addition funnel was placed in an ice/salt bath at -5 °C. The flask was first charged with 15 grams of 13FADPPO (0.0273 mol) and dissolved in 150 ml of concentrated sulfuric acid to make a 10 % (w/v) solution. Then a cooled mixture of approximately 3.9 ml (0.06 mol) nitric acid (%69) and 21 ml sulfuric acid was added dropwise for 3 hours while maintaining the temperature below 0 °C. After this period, the yellow colored mixture was further stirred at

room temperature for 24 hours. At the end of the reaction period, the mixture was poured into 1 kg of crushed ice. After the ice was melted, the organic material was extracted with chloroform. Chloroform extracts were washed several times with aqueous sodium bicarbonate (5 wt. %) solutions and distilled water, respectively. Acid free chloroform solution was dried over anhydrous MgSO<sub>4</sub> and yellow organic material was obtained after rotary evaporation. Finally mDN13FAPO was purified by recrystallization from ethanol. 17.4 grams of a lightyellow product was obtained (yield: 95%). The total mole value of the nitric acid used for the reaction was 2.2 excess of the mole value of 13FADPPO. Sulfuric acid which was mixed with nitric acid was used as catalyst and its amount was adjusted to be 10 folds of the weight of nitric acid.

(m.p. 145 °C. <sup>1</sup>**H-NMR** (600 MHz, CDCl3) δ 8.64 (2H, d), 8.48 (2H, d), 8.18 (2H, t), 7.83 (2H, t), 2.7 (2H, m), 2.48 (2H, m). <sup>19</sup>**F-NMR** (564 MHz, CDCl<sub>3</sub>) δ -80.799, -114.55, -121.89, -123.01, -123.03, -126.2. <sup>31</sup>**P-NMR** (243 MHz, CDCl<sub>3</sub>) δ 24.499.)

# 2.5. Synthesis of bis(3,3'-aminophenyl) (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) phosphine oxide (mDA13FAPO)

Bis(3,3'-aminophenyl) (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) phosphine oxide (mDA13FAPO) was obtained by hydrogenation of mDN13FAPO in a high pressure reactor (Parr Instrument Co., USA). mDN13FAPO (15 g), methanol (500 mL), and Pd/C catalyst (0.5 g) were charged into the flame dried pressure reactor. First, the reactor was purged with nitrogen gas for several minutes and then pressured with hydrogen gas to 100 psi. The reaction mixture was heated at 50 °C and allowed to react for 48 h under constant stirring. Next, the reaction mixture was filtered over Celite. The methanol was removed by rotary evaporation and a brownish-white crystals were obtained with a yield of approximately 65%.

(m.p. 126°C. <sup>1</sup>**H-NMR (600MHz, CDCl**<sub>3</sub>) δ 7.28 (2H, m); 7.1 (2H, d); 7.00 (2H, m); 6.84(2H, d); 4.96 ppm (4H, s). <sup>19</sup>**F-NMR (564 MHz, CDCl**<sub>3</sub>) δ -80,8; -114,7; -121,91; -122,9; -123,12; -126,17.<sup>31</sup>**P-NMR (242 MHz, CDCl**<sub>3</sub>) δ 31,48.)

#### 2.6. Synthesis of polyimides by thermal imidization

Thermally imidized polyimides were prepared similar to our previous publications [41, 42]. To synthesize poly(amic acid) (PAA) solutions, calculated amount of mDA13FAPO was first put into a flame dried three-neck flask. The monomer was then dissolved in DMF under a nitrogen purge. The flask was then immersed in an ice/salt bath (-5-0°C). After the diamine was completely dissolved in DMF, an equimolar amount of dianhydride (PMDA, ODPA, BTDA or 6FDA) was added to the flask batch by batch. The mixture was stirred at this temperature for 3 hours than stirred overnight at room temperature to obtain a PAA solution. The solid concentration was afforded as 20 (wt/wt) %. Polyimide membranes were prepared by casting PAA solutions on clean dust-free glass plates. Then thermal imidization was performed stepwise at 100, 150, 200, and 300°C for 1h at each temperature. The procedures for preparing poly(amic acid) and polyimide films are shown in Scheme 2. The yields of these thermally polyimides were found to be between 75-80%.

#### 2.7. Synthesis of polyimides by solution imidization

mDA13FAPO containing aromatic polyimides were also synthesized by a thermal solution imidization method. Polyamic acid solutions were prepared as described above in a three necked flask equipped with a nitrogen inlet, drying tube and a condenser. The poly(amic acid) solution was then heated at 160 °C for 24 h in order to synthesize the desired polyimides The water formed during condensation was removed by nitrogen gas. The polyimide solution was cooled to room temperature and was precipitated into acetone. The polyimide was filtered off and dried under vacuum at 120 °C. Dried polyimide powders were dissolved in solvents like DMF or CHCl<sub>3</sub> and their 5 wt. % solutions were prepared. Then these polyimide solutions were cast on glass slides and polyimide membranes were obtained after removal of

the solvent by heating to 200 °C or below depending on the solvent used. The yields were over 90% for the each of these solution imidized polyimides.

#### 2.8. Preparation of copolyimides by thermal imidization

In this study different amounts of (0 %, 25 %, 50%, 75% and 100%) mDA13FAPO containing copolyimides were prepared with the aid of ODA and BTDA. Polyimides were prepared by the classical thermal imidization method. First calculated amount of mDA13FAPO and ODA diamines were charged into a flame dried three-neck flask. The diamine monomers were then dissolved in DMF under a nitrogen purge. The flask was then immersed in an ice/salt bath (-5-0°C). After complete dissolution of diamines in DMF, an equimolar amount of BTDA was added to the flask batch by batch. The mixture was stirred at this temperature for 3 hours than stirred overnight at room temperature to obtain a PAA solution. The solid concentration was afforded as 20 (wt/wt) %. Polyimide membranes were prepared by casting PAA solutions on clean dust-free glass plates. Then thermal imidization was performed stepwise at 100, 150, 200, and 300°C for 1h at each temperature. The procedures for preparing poly(amic acid) and polyimide films are shown in Scheme 3. The yields were in the range of 80-90%.

#### 3. Results and discussion

In this study it was aimed to prepare polyimides from a new diamine monomer, mDA13FAPO which possesses both fluorine and phosphine oxide groups. Different than the previous studies, in this study fluorine is incorporated into this original monomer as a perfluoroalkyl group and it is separated from the phosphine oxide group via an ethyl spacer group.

# 3.1. Synthesis and characterization of monomers: 13FADPPO, mDN13FAPO and mDA13FAPO

13FADPPO was synthesized by dephenylation of the phosphonium salt obtained from the reaction of TPP and perfluorohexyl ethyl iodide. The melting temperature of the phosphonium salt was found as 170 °C which is in good agreement with literature [38] and the yield was about 90%. After dephenylation, 13FADPPO was obtained with a yield of 55%. From the nitration and subsequent reduction of this compound, mDN13FAPO and mDA13FAPO were synthesized with yields of 95% and 65% respectively. Thus the total reaction yield is 34 % which is comparable to the yield of mDAPPO (bis(3-aminophenyl)phenyl phosphine oxide) [43].

Structural characterization of 13FADPPO, mDN13FAPO and mDA13FAPO were performed by FTIR, <sup>1</sup>H-NMR, <sup>31</sup>P-NMR and <sup>19</sup>F-NMR analysis. In the FTIR spectrum (Figure 1) of 13FADPPO, the P=O stretching absorption was appeared at 1179 cm<sup>-1</sup> while it slightly shifted to 1184 cm<sup>-1</sup> due to the electron withdrawing effect of nitro groups [32]. The absorption band of the same group for mDA13FAPO was found at 1184 cm<sup>-1</sup>. In all FTIR spectra, C-F bond vibrations were detected at 1300-1100 cm<sup>-1</sup>. Characteristic infra-red absorption frequencies of the nitro groups were observed at 1345 cm<sup>-1</sup> (symmetric) and 1532 cm<sup>-1</sup> (asymmetric) for mDN13FAPO. After reduction of the nitro groups to amino groups, these peaks were disappeared and in the spectrum of mDA13FAPO, new peaks were appeared at 3454, 3329 and 1594 cm<sup>-1</sup> which are related to amino groups. Moreover in all FTIR spectra, aliphatic –CH groups' stretching vibrations appeared at around 2980-2840 cm<sup>-1</sup>.

In the <sup>1</sup>H-NMR spectrum of 13FADPPO three peaks were resonated at 7.78 (4H, m), 7.58 (2H, m) and 7.52 (4H, m) ppm in the aromatic region (Figure 2). Also in this spectrum peaks at 2.54 (2H, m) and 2.4 (2H, m) ppm are due to the spacer –CH<sub>2</sub>CH<sub>2</sub>- group between the fluorus tail and the P=O group. These two peaks are both multiplets and it shows that –

CH<sub>2</sub> protons also split into neighbour fluorines. It can be seen from the proton spectrum of mDN13FAPO that the peaks in the aromatic region were downfield shifted due to the electron withdrawing effect (deshielding effect). Four aromatic proton peaks were observed at 8.64 (2H, d), 8.48 (2H, d), 8.18 (2H, t) and 7.83 (2H, t) ppm, respectively. Aliphatic –CH<sub>2</sub> peaks were also observed as multiplets at 2.7 (2H, m) and 2.48 (m) ppm. Similarly mDA13FAPO has four different aromatic protons which resonate at 7.28 (2H, m), 7.1 (2H, d), 7.00 (2H, m) and 6.84(2H, d). As expected these peaks appeared at lower chemical shift values (shifted upfield) due to the electron donating effect of amino groups. Moreover the peak at 4.96 ppm (4H, s) is due to amino groups.

<sup>31</sup>P-NMR spectra are important that they display the purity of the synthesized compounds (Figure 3). In all phosphorous NMR spectra, only one single sharp peak was observed and this indicates high purity of the monomers. Phosphorous NMR peaks were observed at 27.63 ppm, 24.49 ppm and 31.48 ppm for 13FADPPO, mDN13FAPO and mDA13FAPO, respectively. Contrast to proton NMR results, phosphorous NMR peaks were upfield shifted upon nitration and downfield upon reduction [32-34].

<sup>19</sup>F-NMR spectra of the compounds are given in Figure 4. In all <sup>19</sup>F-NMR spectra six different sharp peaks were observed at almost same chemical shifts for 13FADPPO, mDN13FAPO and mDA13FAPO, respectively. Furthermore these peaks are also in good agreement with the <sup>19</sup>F-NMR spectrum of 1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)diphenylphosphine [44].

Melting points of the newly synthesized monomers were determined by DSC measurements. The melting points were found as 107 °C, 145 °C and 126 °C for 13FADPPO, mDN13FAPO and mDA13FAPO, respectively. These compounds exhibited narrow melting points which indicate high degree of purity.

Finally the percent amine content of mDA13FAPO was determined by titration and found as 5.35 wt. % which is very close to the theoretical value, 5.54 wt. %.

#### 3.2. Structural characterization of homo and copolyimides

In this study four different homopolyimides were synthesized via thermal and solution imidization techniques. Moreover three copolyimides were synthesized via thermal imidization technique. Also BTDA/ODA homopolyimide was prepared for comparison. Figure S1 shows the FTIR spectra of the polyamic acids (PAA) of the corresponding homopolyimides. All PAAs exhibited similar spectra. –P=O absorptions were detected at around 1180 cm<sup>-1</sup>. The characteristic carbonyl stretchings due to –NHCO- bonds were observed at 1660 cm<sup>-1</sup>. Also the peaks at 1548 cm<sup>-1</sup> corresponds to –NH bending vibrations. The FTIR spectra of synthesized homopolyimides and the copolyimides can be seen in Figure 5 and Figure S2 respectively. For all homo and copolyimides, characteristic imide peaks were observed at 1780-1785 cm<sup>-1</sup> (asymmetric stretching of imide carbonyls), 1720 cm<sup>-1</sup> (symmetric stretching of imide carbonyls) and at 1360 cm<sup>-1</sup> (C-N stretchings). These results confirm that all polyimides were successfully synthesized. Different than the other polyimides, BTDA- mDA13FAPO homopolyimide exhibited an additional carbonyl peaks at 1675 cm<sup>-1</sup> due to the carbonyl group of BTDA. Finally after imidization –P=O absorptions shifted to wavenumbers at around 1190 cm<sup>-1</sup>.

#### **3.3.** Solubility and film forming properties of polyimides

Generally polyimides obtained from solution imidization are much more soluble and processable than the thermally imidized ones. This situation is related to crosslinking reactions occur at high temperatures and thermal imidization favors chain packaging which provides higher molecular order [44]. In this study homopolyimides prepared via the thermal imidization technique were not soluble. But mDA13FAPO containing solution imidized

polyimides exhibited excellent solubility (Table 1) in several organic solvents owing to the asymmetric phosphine oxide moiety and the flexible fluorous tail which increase the free volume of the homopolyimides. Also phosphine oxide groups' polarity and their ability to form strong interactions with solvents enhanced the solubility properties of these polyimides [32].

However, both the solution and the thermally imidized homopolyimides exhibited poor film forming properties. It is known that a sufficient level of molecular weight should be reached in order to prepare polymeric films with good filming properties thus monomers with high purity are needed for the polycondensation reactions according to well-known Carother's equation. Although in our case NMR and other techniques indicate that monomers were in high purity but the relatively small amounts of impurities and monofunctional species found in mDA13FAPO monomer could have adversely affected the film forming properties of these polyimides by preventing to reach high molecular weights. The relatively low viscosities for mDA13FAPO containing polyimides support this view that the synthesized polyimides had low molecular weights. The viscosity of both the polyamic acid and the polyimide solutions were generally low (results are not given). On the other hand low viscosities can also be due to the fluorous pendant groups which decrease the interactions between chains and decrease the intrinsic viscosity of the polyimides.

It was previously reported that fluorine containing diamines have low reactivity due to the electron withdrawing effect of fluorine [17, 45]. The reason for the poor filming properties of the mDA13FAPO containing polyimides could also be related to the decreased reactivity of this monomer bearing both electron withdrawing fluorine and phosphine oxide moieties. Different than the previously synthesized mDA3FPPO, mDA6FPPO, and mDA7FPPO monomers, mDA13FAPO monomer has higher amounts of fluorine and these fluorine atoms

are not attached to an aromatic ring. The long flexible fluorinated pendant alkyl group could have caused steric hindrance and thus have decreased the reactivity of mDA13FAPO.

Although in literature there are several studies that report successfully preparation of fluorine containing polyimide films, there are also several examples where polyimide films were produced with poor filming properties. For instance G. Hougham at al., tried to prepare several perfluorinated polyimide films and some of these polyimide films were found to be highly brittle [17]. They then utilized a new method, which they referred as "cyclic process" in order to increase molecular weight of the polyimides by redissolving the cured cracked polyimide materials and redrying. This procedure was repeated until obtaining a crack free polyimide films. Also Auman et al., prepared perfluorinated polyimides and found that most of the films cracked during imidization [19]. In this study films prepared from BTDA and 6FPA had better film forming properties than ODPA and PMDA based polyimides.

Since both the solution and thermally imidized homopolyimides of mDA13FAPO exhibited low mechanical strength and poor film forming properties we prepared its copolymers with ODA in order obtain continuous films. 25 wt.% and 50 wt.% mDA13FAPO containing films were found to be crack free and creasable. %75 mDA13FAPO containing films were fair, but rather brittle.

#### **3.5.** Thermal properties

Generally long perfluoroalkyl groups adjacent to hydrogen bearing carbon atoms (i.e.: -CH groups) cause a reduction in the thermal properties of polymers due to their relatively low thermo-oxidative stability when compared to fluorine containing aromatic analogues [9, 18]. In this study the synthesized monomer mDA13FAPO, also addresses this problem by combining a perfluoralkyl group with highly thermo-oxidative phosphine oxide groups.

Thermal properties of homopolyimides are given in Table 2. Figure S3 and Figure S4 show the thermal degradation behavior of mDA13FAPO containing homopolyimides under

air and nitrogen atmospheres. It can be seen from the results that all homopolyimides exhibited high thermo-oxidative stability and high char yields. Parallel to the studies of Yoon, ODPA-mDA13FAPO polyimides exhibited the highest thermal stability under air atmosphere among other polyimides [32]. The higher thermal stability of these polyimides was attributed to both fluorine and phosphine oxide groups. The obtained char yields were not as much as expected due to the high inorganic content of the polyimides. This situation can be attributed to early decomposition of the fluorous pendant group or rapid HF elimination at elevated temperatures. On the other hand, owing to the presence of phosphine oxide groups, this situation did not result a dramatic decrease in the thermal properties of these polyimides.

Thermal properties of copolyimides are given in Table 3. Thermograms of the copolyimides under air and nitrogen atmospheres are given in Figure S5 and Figure S6 respectively. It can be seen from the results that all copolyimides exhibited high thermo-oxidative stability and high char yields.

When compared to the BTDA/ODA homopolyimide films, a decrease was observed in the initial decomposition and the maximum weight loss temperatures which can be attributed to the early decomposition of these copolyimides which in turn exhibited high char yields than BTDA/ODA homopolyimides.

Glass transition temperatures (Tg) of the polyimides and copolyimides are given in Table 2 and Table 3 respectively. It can be clearly seen from these results that the fluorinated pendant alkyl groups containing homopolyimides exhibit low Tg values. Pendant fluoro alkyl groups decreased the chain packing and thus increased the free volume of the polyimides. The highest Tg value was found as 233 °C for PMDA containing polyimides and it is attributed to the rigid backbone of this polyimides.

For the copolyimides it was found that the glass transition temperatures were decreased as the amount of mDA13FAPO increased in the copolymer composition. The glass

transition temperature for BTDA/ODA was found as 297 °C while the Tg of BTDA/ mDA13FAPO homopolyimide was 203 °C. All copolyimides exhibited single Tg values and thus we compared the experimental Tg values with the calculated Tg values obtained from the well-known Fox equation:

$$\frac{1}{Tg} = \frac{W_1}{Tg_1} + \frac{W_2}{Tg_2}$$

where  $W_1$  and  $W_2$  are the weight fractions and  $Tg_1$  and  $Tg_2$  are the glass transition temperatures of homopolyimides.

Weight fractions were calculated according to the following equation:

$$Wi = \frac{miMi}{\sum miMi}$$

where m<sub>i</sub> and M<sub>i</sub> are the molar fraction and the molecular weight of the repeating unit [46].

Calculated and experimental results were found to be very close for 50 and 75 percent mDA13FAPO containing copolymers. However, the calculated Tg value for 25 percent mDA13FAPO containing copolymers was highly deviated from the experimental value. The positive deviation from the Fox equation indicates additional interactions in the polymer matrix. Thus, this deviation for 25 percent mDA13FAPO containing copolymers can be attributed to the interactions between phosphine oxide groups and it can be said that the fluorous tail was not as efficient as expected to increase the free volume particularly for these copolyimides. When the amount of mDA13FAPO increases, the experimental and calculated Tg values start to get closer. Therefore it can be said that at higher amounts of mDA13FAPO, the flexibilizing effect of the perfluorinated alkyl chain is much more dominant than the interactions caused by the phosphine oxide groups.

#### **3.6.** Flame retardancy properties

LOI test is a common method for the determination of the flame retardancy of polymeric materials. Due to the poor film forming properties of mDA13FAPO containing polyimides, we could not be able to determine the flammability characteristics of these homopolyimides. But the flame retardancy of these homopolyimides were calculated theoretically according to the following equation by van Krevelen [47] :

$$CP = \frac{H}{C} - o.65 \left(\frac{F}{C}\right)^{1/3} - 1.1 \left(\frac{Cl}{C}\right)^{1/3}$$

where H/C, F/C and Cl/C are the atomic ratios of the respective elements in the polymer composition and "cp" is composition parameter. And the LOI value can be derived from the following correlations:

For CP  $\leq$  1: LOI  $\approx$  0.175 or 17.5 %

For CP  $\geq$  1: LOI  $\approx$  0.60 – 0.425 CP

Calculated LOI values are given in Table 2. The calculated LOI values were found to change between 54 and 62. LOI values of the copolyimides are given in Table 3. All copolyimides exhibited high flame retardancy and exhibited LOI values between 32 and 44. The LOI values of copolyimide films were found to increase as the amount of mDA13FAPO was increased due to the increase in the inorganic content and due to presence of both fluorine and phosphine oxide groups. When previous studies on the flame retardant polyimides are taken into consideration, it can be seen that the LOI values of several different neat polyimides and their composites range from 28 to 60 [41, 48-53]. There are only few papers that report the LOI values for the phosphorous containing polyimides [51, 52] or fluorinated polyimides [41, 53]. For instance bis(3-aminophenyl) phenylphosphine oxide (m-BAPPO) containing fluorinated copolyimides displayed high LOI values of 46 and 48, respectively [51]. In

another work the LOI value of the only 7 mole percent (DAPPO) containing copolyimide fibers were found as 43 [52].

#### 3.7. Mechanical properties of the copolyimides

Since the homopolyimides in this work were brittle and exhibited poor film forming properties only the mechanical properties of the copolyimides were determined. Tensile strength, elongation at break and tensile modulus of copolyimides are displayed in Table 4. As can be seen from the results due to the presence of flexible perfluoroalkyl group, modulus of the copolyimides decreased while elongation at break values increased. Thus it can be said that 25 and 50 percent mDA13FAPO containing copolyimides exhibited tough and flexible character with better film forming properties. 75 % mDA13FAPO containing copolyimide was slightly higher than 50 percent mDA13FAPO containing films. On the other hand its elongation at break values dramatically decreased which reflects its brittle character. Overall it can be concluded that we successfully prepared copolyimide films with good mechanical properties in line with our goal to improve the film quality of mDA13FAPO containing polyimides.

#### 3.8. Optical properties of copolyimide films

Generally fluorine containing polyimides are characterized by their high optical transparencies and they are suitable for optical devices. The optical transparencies of mDA13FAPO containing copolyimide films were characterized by UV-vis. spectroscopy. Fig. 6 shows the transmission spectra of novel copolyimide films in the range between 300 and 800 nm. It was found that the optical transmittance of copolyimides increased with increasing amount of mDA13FAPO. However, even at 100% mDA13FAPO containing polyimide films, the optical transparency was found to be lower than the transparency of

BTDA/ODA homopolyimides. This situation could be related to contribution of the phosphine oxide group to the total UV absorption.

#### 3.9. Surface energy and contact angle values of mDA13FAPO containing copolymers

The hydrophobicity and the oleophobicity of the hybrid coating materials were investigated by water and diiodomethane contact angle measurements. The results are shown in Table 5. All contact angle measurements were obtained from the air side of the polyimides and the reported values are at least the average of five different measurements. The results showed that the addition of fluorine significantly increases both the water and the diiodomethane contact angles. This behavior of fluorine containing materials is related with the segregation of the fluorinated segment on the surface of the coatings and as a result the surface energy of the coatings decreases [54]. Thus the fluorine enriched surface of the polyimides showed increased hydrophobicity. Water contact angle images of the copolyimides are presented in Figure 7. The increase in both the water and diiodomethane contact angles may not seem as high as expected. Although mDA13FAPO contains high amounts of fluorine, it also possesses a phosphine oxide unit which is a polar group. Moreover the obtained results are in accordance with the results reported in literature [19]. The monomer designed by Laurence et al., contains the same molar amount of fluorine with mDA13FAPO and the highest water and diiodomethane contact angles reported by them are 90.1° and 65.5°, respectively.

Furthermore the surface energy values of the copolyimides can be seen in Table 5. As can be seen from the table the surface energy of the polyimides decrease with increasing amount of mDA13FAPO. The surface energy of the BTDA/mDA13FAPO was found as 30 mN/m. This result is also in accordance with the results given by Laurence et. al. [19] and ref. [20].

#### 3.7. Morphology

Figure 8 shows the surface morphology of BTDA-mDA13FAPO homopolyimides. It can be seen from the SEM images that several crater like structures were formed on the surface of the BTDA- mDA13FAPO homopolyimides. At higher magnifications several bulges were detected on the surface of these mDA13FAPO containing polyimides. These structures were attributed to phase separation between the polymer main chain and the fluorous pendant groups. Thus the poor filming properties of these homopolyimides can also be attributed to this incompatible system. Moreover the elemental composition of the polymer surface was determined by energy dispersive X-ray spectroscopy (EDS). According to the EDS results the weight percentages of C, O, F and P were found as 57%, 9%, 22% and 10% respectively.

Fluorine and phosphor mapping images of BTDA-mDA13FAPO homopolyimides are given in Figure 9. As can be seen from this figure the surface of these polyimide films were completely covered with fluorine and phosphorous.

#### 4. Conclusions

In this study a novel diamine monomer; mDA13FAPO was prepared. First, an Arbuzov type of reaction was performed between triphenyl phosphine and 2-perfluorohexyl ethyl iodide and the resulting phosphonium salt was then dephenylated to give (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) diphenyl phosphine oxide (13FADPPO). mDA13FAPO was obtained after nitration and subsequent reduction of 13FADPPO. Then mDA13FAPO containing homo and copolyimides were synthesized. These polyimides exhibited moderate Tg values (194-233 °C), good thermal stability and excellent solubility. On the other hand, homopolyimides displayed poor film forming properties. Copolymerization improved the film forming properties of homopolyimides obtained from

mDA13FAPO and various dianhydrides. Moreover results showed that these copolyimides have low surface energies and high contact angle values.

Fluorine and phosphorous containing mDA13FAPO has the potential to be used for the synthesis of many other polymers like polyamides, polyureas and polyamide-imides, etc. It can also be used a hardener for epoxy resins or as a chain extender for polyurethanes. This new diamine compound can be functionalized with acrylic groups and can be used in photocurable coatings.

We are currently working on the preparation mDA13FAPO containing sulfonated polyimides for fuel cell applications. Our future work will focus on the investigation of the effects of this diamine on the properties of epoxy resins and UV curable coatings.

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**Figure 2**. <sup>1</sup>H-NMR spectra of a) 13FADPPO b) mDN13FAPO c) mDA13FAPO. All spectra were recorded in CDCl<sub>3</sub>.



**Figure 3**. <sup>31</sup>P-NMR spectra of a) 13FADPPO b) mDN13FAPO c) mDA13FAPO. All spectra were recorded in CDCl<sub>3</sub>.



**Figure 4**. <sup>19</sup>F-NMR spectra of a) 13FADPPO b) mDN13FAPO c) mDA13FAPO. All spectra were recorded in CDCl<sub>3</sub>.



**Figure 5.** ATR-FTIR spectra of polyimides a) BTDA- mDA13FAPO b) 6FDAmDA13FAPO c) ODPA- mDA13FPO and d) PMDA- mDA13FAPO)



**Figure 6.** UV transmittance of copolyimide films a) BTDA-ODA b) BTDA- mDA13FAPO c) BTDA- mDA13FAPO75 d) BTDA- mDA13FAPO50 and e) BTDA- mDA13FAPO25

#### BTDA-ODA

BTDA-mDA13FAPO25



BTDA-mDA13FAPO50



BTDA-mDA13FAP075





BTDA- mDA13AFAPO



Figure 7. Water droplets on novel copolyimide films



**Figure 8.** SEM micrographs of BTDA-mDA13FAPO homopolyimides a) 1000X b) 10000X and 50000X



Figure 9. Fluorine (a) and phosphorous (b) mapping images of BTDA-mDA13FAPO homopolyimides



Scheme 1: The synthetic route to mDA13FAPO



**R**:  $CF_3CF_2CF_2CF_2CF_2CF_2CH_2CH_2$  —

Scheme 2: The procedures for preparing poly(amic acid) and polyimides



Scheme 3: The procedures for preparing copolyimides via thermal imidization

Polyimides	DMAc	DMF	DMSO	NMP	m-Cresol	CHCI <sub>3</sub>	THF	Toluene
ODPA- mDA13FAPO	+	+	$+\Delta$	+	+	$+\Delta$	$+\Delta$	-
6FDA- mDA13FAPO	+	+	$+\Delta$	+	+	$+\Delta$	$+\Delta$	-
BTDA- mDA13FAPO	+	$+\Delta$	$+\Delta$	+	+	$+\Delta$	-	-
PMDA- mDA13FAPO	+	+	$+\Delta$	+	$+\Delta$	$+\Delta$	$+\Delta$	-

 Table 1. Solubility of mDA13FAPO containing polyimides

+: soluble  $+\Delta$ : soluble upon heating -: insoluble

Homopolyimides	P F		N Tg	Tg	Tg LOI <sup>a</sup>	Air Nitrogen					
	(%) (%) (%) (°C	(°C)	(°C)	T5 (°C)	T <sub>max</sub> (°C)	Char (%)	T5 (°C)	T <sub>max</sub> (°C)	Char (%)		
ODPA- mDA13FAPO	3.63	28.94	3.28	194	56	429	557	16	430	520	32
6FDA- mDA13FAPO	3.14	36.55	2.84	204	62	432	542	7	439	530	25
BTDA- mDA13FAPO	3.58	28.54	3.24	203	54	448	576	12	435	610	46
PMDA- mDA13FAPO	4.07	32.44	3.68	233	61	427	497	7	427	502	23

**Table 2.** Thermal properties of the homopolyimides under air and nitrogen atmospheres, their glass transition temperatures and LOI values

<sup>a</sup>Calculated LOI values.

Н	<b>Tg</b> (°C) <sup>a</sup>	Tg (°C) <sup>b</sup>	LOI	Air			Nitrogen		
				<b>T</b> 5	T <sub>max</sub> (	Char	<b>T</b> 5	T <sub>max</sub> (	Char
				(°C)	°C)	(%)	(°C)	°C)	(%)
BTDA-ODA	297	-	28	484	619	1,5	550	620	49
BTDA- mDA13FAPO25	270	256	32	450	607	5	473	646	48
BTDA- mDA13FAPO50	224	219	37	437	597	8	457	608	40
BTDA- mDA13FAPO75	211	213	44	443	606	10	437	556	45
BTDA- mDA13FAPO	203	-	49	448	576	12	435	610	46

**Table 3.** Thermal properties of the copolyimides under air and nitrogen atmospheres, their experimental and calculated Tgs and LOI values

<sup>a</sup>Experimental Tg values

<sup>b</sup>Calculated Tg values

Sample	Tensile Modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
BTDA-ODA	1.34	132	6.3
BTDA-	1.27	129	12.2
mDA13FAPO-25			
BTDA-	1.05	121	13.9
mDA13FAPO-50			
BTDA-	1.1	106	7.5
mDA13FAPO-75			
BTDA-	-	-	-
mDA13FAPO *			

**Table 4.** Mechanical properties of mDA13FAPO containing copolyimides

\* 100 percent mDA13FAPO containing films were too brittle to be tested.

			-				
Sample	Contact Angles (°)*		Owens-Wendt Method				
	Water Diiodomethane		Surface Energy mN/m	Disperse	Polar		
BTDA-ODA	63	45	59.2	2.2	57.0		
BTDA-	72	47	37.5	12.9	24.6		
mDA13FAPO25							
BTDA-	89	52	33.6	10.4	23.2		
mDA13FAPO50							
BTDA-	94	58	31.6	24.6	7.0		
mDA13FAPO75							
BTDA-	102	65	30	17.2	12.8		
mDA13FAPO							

**Table 5.** Contact angles and surface free energies of the copolyimides

\*The reported contact angle values are average of five different measurements.