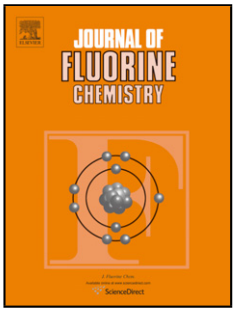

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The Synthesis and Characterization of Highly Fluorinated Aromatic Polyimides

(Chris v. 01 copy edited)

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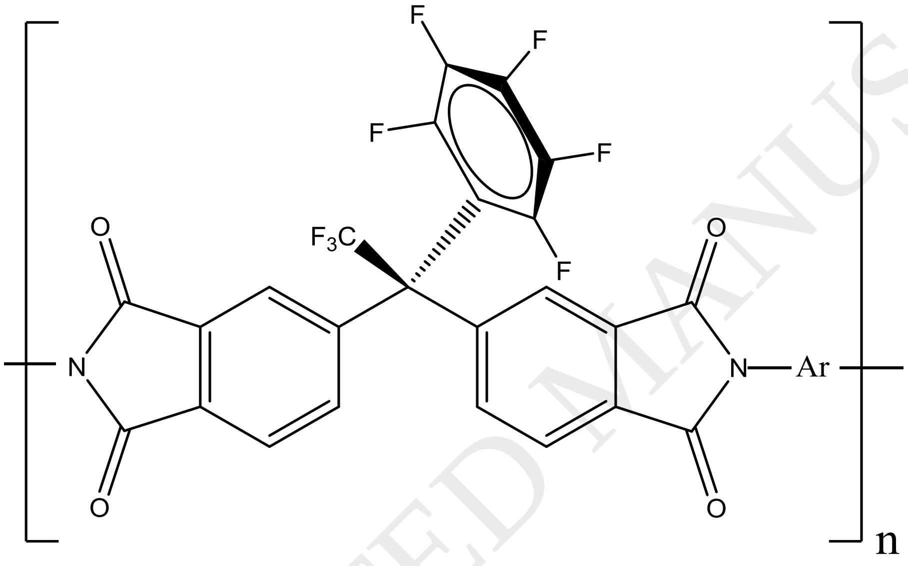
(Additional Supporting information may be found in the online version of this article)

Graphical abstract



8F-POLYIMIDES

HIGHLIGHTS Synthesis and Characterization of Highly-----

- Novel Octafluoro aromatic polyimides with low dielectric constants have been synthesized
- A novel sterically hindered dianhydride, 8FDA, 4,4'-(2,2,2-trifluoro-1-pentafluorophenylethylidene)diphthalic anhydride was synthesized.
- 8FTM, bis(3,4-dimethylphenyl)pentafluorophenyltrifluoromethylmethane was also synthesized.

- The steric requirements for 8FTM synthesis caused the formation by-products resulting in low 8FTM yields.

ABSTRACT

The synthesis and characterization of pendant octafluoro aromatic polyimides (8F-PIs) derived from 4, 4'-(2 ,2, 2-trifluoro-1-pentafluorophenylethylidene)diphthalic anhydride (8FDA) and several aromatic diamines is described. The synthesis of bis(3,4-dimethylphenyl)pentafluorophenyltrifluoromethylmethane (8FTM), and

2-(3, 4-dimethylphenyl)-2-pentafluorophenyl-2-trifluoromethylethanol (8F-OH), the precursors to 8FDA are also discussed. The synthesis of 8FTM is accompanied by two major by-products resulting in a low yield of desired product. The presence of the pentafluorophenyl group in the backbone of the fluorinated polyimides introduces flexibility and free volume manifested by lower Tg's than more rigid analogs. The highly fluorinated polyimides exhibited lower dielectric constants than most fluorinated polyimides. The 8F-PIs cured at a maximum temperature 371°C/1 hr. exhibited thermal stabilities typical of high performance fluorinated polyimides. High temperature (436°C) and pressure (281.2kg/m^2, 4000 psi.) post cure of 8F-PI prepared from 8FDA and p-phenylene diamine exhibited high thermo-oxidative stability, high density and low moisture absorption.

KEYWORDS: fluorinated polyimides, synthesis, thermal stability, dielectric constant, microwave synthesis

1. Introduction

Aromatic polyimides have been important materials in the last thirty years for high technology applications due to their outstanding properties such as thermo-oxidative stability, high glass transition temperatures, selective gas absorption properties, low dielectric constants, good adhesive properties and excellent mechanical properties, among others [1]. Therefore, these materials are used in advanced composites materials, in electronic applications, as membranes for gas separation, and as coatings for optical fibers and copper wires [1, 2]. More recently, sulfonated polyimides have potential applications as proton exchange membranes (PEM's) in fuel cells [3-7].

These materials are generally used in the poly(amic)acid precursor form to form films and bulk specimens. The outstanding thermo-oxidative stability and chemical resistance has been attributed to strong interchain interactions due to the stiffness of the aromatic backbone and associated charge transfer interactions [8]. However, the fabrication of component parts requires high pressure and temperature because of the high melt viscosities resulting from these intermolecular forces. Considerable research has addressed this problem. Within the last thirty years, several fluorinated dianhydrides and fluorinated diamines have been developed from which polyimides with desirable properties have been prepared [9-18]. Our approach to improve relevant properties such as thermo-oxidative stability, processability, moisture resistance, and dielectric constant is by incorporation of fluorine in the polyimide structure and more importantly, the incorporation of fluorine in the form of a bulky pentafluoro group in the repeat unit of the polyimide chain. The synthesis and characterization of a series of fluorinated polyimides from a novel diphthalic dianhydride, 4,4'-(2,2,2-trifluoro-1-pentafluorophenylethylidene)diphthalic anhydride (8FDA) and several aromatic diamines and the synthesis of bis(3,4-dimethylphenyl)pentafluorophenyltrifluoromethylmethane (8FTM) and 2-(3,4-dimethylphenyl)-2-pentafluorophenyl-2-trifluoromethylethanol (8F-OH), precursor monomers to 8FDA are described in this paper.

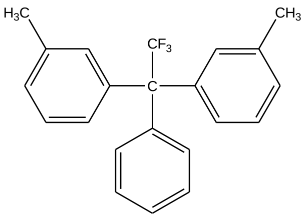
2. Results and Discussion

2.1 *8FTM Synthesis (Scheme 1) INSERT Here*

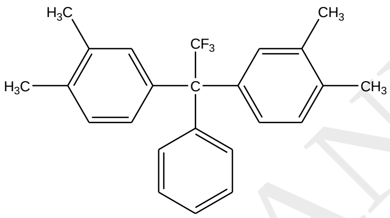
Several conditions were investigated to synthesize 8FTM from octafluoroacetophenone (OFAP) and o-xylene {Scheme1} The procedure described above gave the highest yield of oily product, which contained 8FTM and two major by-products and three minor by-products (GC/MS, Fig.1) Conditions investigated include various acidic catalysts (CF_3SO_3H, HF (48 % solution), H_2SO_4, CH_3COOH, $Sc(CF_3SO_3)_3$, time (16-168 hr.), temperature (10ºC, RT, 60 ºC , 125 ºC) and pressure (atmospheric and autoclave pressure) (Supporting Information, Table S.1). Conversion of the tertiary alcohol, 8F-OH to 8FTM by reaction with o-xylene also gave low yield of product and major by-products

(Scheme 2). The low yields of 8FTM from either OFAP or 8F-OH, both with o-xylene are discussed below. (Insert scheme 2 here)

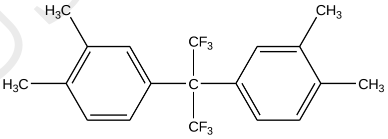
It was expected that procedures for the synthesis of 1-phenyl-1,1-bis(p-tolyl)-2,2,2-trifluoroethane (TTFE) [19], I-trifluoromethyl-1-phenyl-1,1-bis(3,4-dimethylphenyl) methane (3FTM) [20], and 1,1-bis(3,4-dimethylphenyl)-2,2,2,3.3.3-hexafluoropropane (6FTM) [21-24], would be applicable to the synthesis of 8FTM.



TFFE



3FTM



6FTM

For example, in the synthesis of (TTFE), Kray and Rosser [19] used excess trifluoromethanesulfonic acid (TFA) as catalyst and excess toluene with trifluoroacetophenone (TFAP) under reflux conditions to obtain product in 43% yield. In a similar reaction between trifluoroacetophenone (TFAP), *o*-xylene and excess catalyst (TFA), (3FTM) was synthesized at room temperature in 72 hr. in 79% yield [20]. The greater nucleophilicity of the xylyl group over the *o*-tolyl group most likely was responsible for the more moderate conditions required for this reaction relative to the synthesis of TTFE. In contrast, Rogers [21] reports on the synthesis of 6FTM from hexafluoroacetone(HFA) and *o*-xylene in an autoclave at 100ºC using HF acid (48% solution) as Friedel-Crafts catalyst in an unspecified yield. The volatility of HF required the need for pressure in this reaction, but steric hindrance of two CF3 groups in HFA relative to the phenyl group in TFAP may also contribute to the need for harsher conditions for 6FTM synthesis relative to 3FTM. The analogous reaction of octafluoroacetophenone (OFAP) with *o*-xylene presented a new challenge due to steric considerations. The reaction of the bulky 3,4-dimethylphenyl group on the highly electrophilic carbonyl group is not favored due to the bulky CF3 and pentafluorophenyl groups in OFAP, indicating that steric factors outweigh electronic factors. The poor 8FTM yield and multiplicity of products clearly demonstrates that steric factors are dominant.

2.2 *Proposed Mechanism of 8FTM formation {Scheme 3}* (Insert here)

The mechanism for the formation of 8FTM and by-products can be explained as follows (Scheme 3): Protonation of the OFAP carbonyl group to form OFAP carbocations 1a and 1b, which can undergo nucleophilic attack by the electron rich *o*-xylyl group to form the tertiary alcohol intermediate 2. Carbocation 1b can also undergo a competitive reaction to yield a more thermodynamically stable product by SN_1 substitution of the pentafluorophenyl group by the *o*-xylyl group to form pentafluorobenzene 3a, and a less hindered carbocation 3b. Since pentafluorophenyl and trifluoromethyl groups are good leaving groups, octafluoroacetophenone (OFAP) is a good substrate for nucleophilic attack. This is supported by the work of Keumi et. al. [25] in studies of trans acetylation of arenes by acylpentamethylbenzene.

The alcohol intermediate 2 is one of the minor by-products identified by GC/MS in this reaction. Protonation of 2 affords a positively charged alcohol 2a, which can dehydrate to the less sterically hindered cation 2b. Cation 2b can react with another *o*-xylyl group to form a highly hindered molecule, 2c, the desired 8FTM product. The second nucleophilic attack on 2b by the *o*-xylyl group appears to be the limiting step in this reaction. Carbocation 2b can also undergo a more favorable transformation by hydride transfer to 2d, a major by-product in this reaction.

Carbocation 3b can undergo nucleophylic attack by another *o*-xylyl group with the elimination of the stable trifluoromethyl anion to form carbocation 4a, which is then protonated to form carbodication 4b, as proposed by Saito et.al. [26, 27] and Olah et.al. [28] in studies of superacid catalyzed reaction of benzaldehyde with benzene. Energetic 4b is proposed to undergo elimination of water with hydride transfer to form 4c [27] or can undergo o-xylyl addition and hydride transfer to form 4d [27]. Both 4c and 4d are major by-products of this reaction. A summary of reaction by-products as identified by GC/MS is shown in Scheme 4. (Insert here)

Synthesis of 8FTM from the tertiary alcohol 8F-OH presents the same steric factors as were encountered in the synthesis of 8FTM from OFAP and *o*-xylene. It requires formation of the carbocation 2b as described above, and bonding of the *o*-xylyl group to the sterically crowded trigonal carbon resulting in a very low yield of 8FTM. Unexpectedly however, was the formation of 8FTM and two other by-products in the synthesis of 8F-OH from OFAP and 4-bromoxylene via a Grignard reaction (Scheme 5). The bonding of two *o*-xylyl groups to a sterically hindered carbonyl group via a Grignard reaction is not easily explained and requires additional study. (Scheme 5 here)

2.3 *Poly (amic-acid) (8F-PAA) and Polyimide (8F-PI) Synthesis (Scheme 6) (Insert here)*

In the synthesis of the polyimides, a two-step procedure [29], the preparation of 8F-PAA followed by imidization to produce PI was selected rather than the one-pot catalytic high temperature method (Scheme 6). Initially, 8F-PAA s were prepared at room temperature for 24 hr. However, according to the GPC method used to determine molecular weights, this produced low molecular weight poly (amic acid) s. This was unexpected because of the highly electrophilic nature of the anhydride group generated by the eight fluorine atoms bundled on the methyl and phenyl groups. Subsequent 8F-PAAs were prepared at 150^{o}C for 3 h but molecular weights were not determined. However, intrinsic viscosities were determined. The intrinsic viscosities of 8F-3, 4'-ODA, 8F-p-PDA and 8F-BDAF poly (amic acid) s in the range 0.28-0.38 dl/g suggest that these molecular weighs are in range 10,000 - 20,000 g/mole [16]. It is not unusual that low inherent viscosities are generated from 6F PAAs [10, 15-16, 30}. The reactivity of fluorinated of fluorinated aromatic diamines was highlighted several years ago by Hougham et al. [10] and Shundrina et al. [15-16} who discuss various process conditions required to effect polymerization. The poor reactivity of 6FDA with ortho substituted –F or –CF_3 diamines resulted in very low viscosity PAA solutions. Therefore, the synthesis of 6F PIs required high temperature polymerization at 350^{o} C, described as solid state chain-extension [10]. The synthesis [16] of fluorinated PIs from 6FDA and ODPA (4,4'-oxydiphalic dianhydride) with 6FTDA (2, 5, 6-trifluoro-4- trifluoromethyl-1, 3-phenylenediamine) required melt processing in benzoic acid to give inherent viscosities of 0.30 dl g^{-1} $^{-}$and 0.28 dl g^{-1} resulting in molecular weights of 19000 g/mole and 14,500 g/mole, respectively as determined by ^{19}F NMR. These polymers required additional solid state chain-extension at 350ºC/1h for final cure [16]. Gibbs [23] reports an inherent viscosity of 0.35 dl g^{-1} for the PAA of 6F-p-PDA, which gave a Tg of 326ºC cured at 371ºC. Therefore, the low poly (amic acid) molecular weights (Table 1) for the room temperature prepared 8F PAA s and low viscosities for the 150ºC prepared 6F PAAs most likely do not reflect the molecular weights of 8F-PIs cured at the elevated temperature. The properties listed in tables 1-4 are an indication that during the high-temperature cure process, chain extension occurs, resulting in much higher molecular weights that are reflected from the poly (amic acid) molecular weight and viscosity data. (Table 1 here)

2.4 Thermal Properties

2.4.1 *Glass Transition Temperature*

The glass transition temperatures (Tg's) (Table 2) of the 8F PI's cured at the final two temperatures, 300ºC and 371ºC clearly show that the elevated cure cycle improves the Tgs by 30-40ºC for most 8F-PI's with 8F-TFMB increased by only 16ºC. The influence of cure temperature on Tg is supported by several studies [10, 23, 24, 31]. For example 3F-p-PDA [24], cured at 371ºC/24 h has a Tg of 371ºC, but increased to 425ºC after cure at 416ºC/8h. Aromatic 6F-p-PDA [23], cured at 350ºC/1 h, yields a Tg of 354ºC, was increased to 371ºC after cure at 370ºC/100 h. The Tg (271ºC) of 6F-2.2'-TFMB cured at

350^{o}C/1 h is raised to 334^{o}C after cure at 371^{o}C/2h [24]. Deshpande et al [30] reports that a thermoplastic PI from pyromellitic dianhydride (PMDA) and 4, 4'-bis (3-aminophenoxy) biphenyl (4, 4'-BAPB) treated at elevated temperatures (375^{o}C -400^{o}C) for 10 minutes raised Tgs from 252 to 260^{o}C. Aromatic 6F PIs [10] prepared from diamines with –F or -CF_3 in the ortho position of the diamine, required high temperature treatment at 350^{o} C for complete cure. The low reactivity of the fluorine substituted diamines required elevated temperature treatment, described as solid state chain-extension for complete cure. This cure process generated high Tgs. These studies are strong evidence that elevated temperature treatment induces solid state chain-extension resulting in an increase in molecular weight and Tg. How this occurs is a matter of speculation, but reaction of residual end groups, and intermolecular crosslinking may be considered for the reasons.

(Table 2 here)

2.4.2 *Thermo-oxidative Stability*

The temperature at which 5% and 10% weight loss occurs in oxygen and nitrogen atmospheres (Table 3) is a measure of the thermal stability and was used to determine the thermal stability of the 8F-PIs. All samples were post cured at 100ºC/1h + 200ºC/1h +300ºC/1h + 371ºC/2h. The data compare favorably with PIs containing the fluorinated 6FDA (6F-PI's) [10, 23-24]. For example, Avimid-N prepared in this study, and 6F-p-PDA10 show Td (10 wt. %) of 525ºC and 541ºC in air respectively, while the value for 8F-p-PDA is 534ºC. The range for 6F-PIs in the Hougham et.al. [10] study is 526ºC - 553ºC.

Fluorinated polyetherimides [14] show Td (10 wt. %) in air ranging 526ºC-563ºC, cured up to 350ºC. (Table 3 here)

2.4.3 *Thermo-oxidative Stability Based on Isothermal Weight Loss at 371ºC*

Isothermal weight loss of 8F-p-PDI -T1, 8F-p-PDA-T2 and Avimid-N was determined at 371ºC in an oven containing ambient air (Figure 2). The maximum cure temperature for the 8F-p-PDI-T1 and Avimid-N samples was 371ºC/2h., while 8F-p-PDI-2 was post cured at 371ºC/1h + 426ºC/4h. Weight loss data show that 8F-p-PDA-T1 is inferior to Avimid-N and 8F-p-PDA-T2. Post curing of 8F-p-PDA-T2 at the higher temperature improves stability and appears equivalent to the stability of Avimid-N. The presence of the pentafluorophenyl group in 8F-p-PDA-T2 relative to the trifluoromethyl group in Avimid-N (6F-PDA 95p/5m) would be expected to improve thermo-oxidative stability. However, steric crowding of pentafluorophenyl group in the 8F-PI repeat unit may be an incentive to relieve strain and cause decreased stability relative to the -CF3 group in Avimid N.. The presence of impurities in the 8FTM starting material might also compromise stability. (Fig.2 here)

2.5 *Density and Moisture Absorption*

The density and moisture absorption data (Table 4) resulting from high- temperature and pressure cure of 8F-p-PDA-T1, 8F-p-PDA-T2 and Avimid-N indicates that increased pressure and temperature has no effect on Avimid-N, a 6F-PDA (95% p/05 % m) polyimide. The density for 6F-p-PDA cured at 350ºC with no pressure is 1.44g/cm^3 and that for Avimid-N [21-24] cured at 350ºC, also with no pressure is 1.40g/cm^3. Apparently, in the 8F-PI polyimide system, the presence of the bulky pentafluorophenyl group is prone to consolidation due to free volume created by the bulky group, leading to increased density and decreased moisture absorption. (Table 4 here)

2.6 *Dielectric Constant*

An important parameter related to fluorine content in polymers is dielectric constant, recognized as an important property by Hougham et al. [9-10] and Matsuura et al. [32, 33] and reviewed by Maier et al. [12]. The data (Table 5) show that 8F-PI's exhibit dielectric constants ranging from Є =2.01 to 2.35, which are lower than 6F-PI's listed (Є= 2.63 for Avimid-N) [24]. More recently [16], a polyimide prepared from 6FDA and 2, 4, 6-trifluoro-4-trifluoromethyl-1, 3-phenylenediamine exhibited a dielectric constant of Є =2.68. It is apparent that the pentafluorophenyl group in 8F-PIs is an important influence on the dielectric constant. Factors such as the five C-F bonds in the phenyl substituent appear to reduce polarization, increase free volume due to bulkiness and increased hydrophobicity, which have a greater influence in the dielectric constant than the two CF3 groups in 6F-PI's. (Table 5 here)

3. Conclusions

The synthesis of bis-(3,4-dimethylphenyl)pentafluorophenyltrifluoromethylmethane (8FTM), 2-(3,4-dimethylphenyl)-2-pentafluorophenyl-2-trifluoromethylethanol (8F-OH), 4,4'-(2,2,2-trifluoro-1-pentafluorophenylethylidene)diphthalic anhydride (8FDA) and five new fluorinated polyimides are described in this paper. The five polyimides derived from 8FDA and aromatic diamines contain bulky pentafluorophenyl and trifluoromethyl groups in the polyimide backbone which exhibit low Tgs and low dielectric constants. Thermal stability of the 8F-PIs are equivalent to high performance fluorinated polyimides. Using a high temperature (426°C) and pressure (281kg/cm^2, 4000psi) cure cycle leads to high thermo-oxidative stability, high density, and low moisture absorption. Synthesis of 8FTM, the precursor to 8FDA, is obtained in low yield due initially to steric hindrance of the carbonyl carbon bonded to the bulky pentafluorophenyl and trifluoromethyl groups. Attack of the OFAP carbonyl carbon by a bulky *o*-xylyl group forms another sterically crowded intermediate which must combine with a second bulky *o*-xylyl group to form a more sterically crowded 8FTM molecule, resulting in very low yields.

4. Experimental

4.1 *Materials*

p-phenylenedamine (*p*-PDA) was purchased from Aldrich and recrystallized from absolute ethanol (EtOH). 3,4'-oxydianiline (3,4'-ODA) was purchased from Mitsui Petrochemical Industries, New York, New York, and recrystallized from EtOH. 2,2-bis(3-aminophenyl) hexafluoropropane (3,3'-6FA) and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) was purchased from American Hoechst Corp., Coventry, R.I. 3,3'-6FA was recrystallized from dichloromethane and 6FDA was used as received. 2, 2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane (2,2-BDAF) was purchased from Ethyl Corp., Baton Rouge, La. and used as received. 2, 2'-Bis (trifluoromethyl)benzidine (2,2'-TFMB) was purchased from Wakayama Seika Co. and used without further purification. Avimid-N resin powder was prepared according to a published procedure [20]. Octafluoroacetophenone (OFAP) was purchased from Aldrich and used as received. Trifluoromethane sulfonic acid (TFA), *o*-xylene, (HPLC grade), toluene, (HPLC grade), hexanes, (HPLC grade), acetone, (ACS reagent), acetic acid, (ACS. Reagent) and acetic anhydride (99%), were purchased from Fisher Scientific. Silica gel, (grade 12), and activated carbon (Darco G-6) and Celite 521 were purchased from Aldrich.

4.2 *Characterization of monomers and polyimides*

Fourier Transform Infrared (FT-IR) spectroscopy was carried out on a Nicolet 605X FT-IR spectrometer. Film samples were cast from acetone on pure potassium bromide (KBr) crystals, dried in vacuum to remove solvent before scan. Powdered samples were ground with KBr powder and pressed into thin discs.

Differential Scanning Calorimetry (DSC) was used to determine Tg, and was performed on a Perkin Elmer DSC7 series analysis system, using aluminum pans in nitrogen at a flow rate of 20 cc/min. under nitrogen atmosphere at a flow rate of 20 cm^3 min^{-1}.

A DuPont Model 2950 Thermogravimetric Analyzer (TGA) at a heating rate of 20℃ /min. was used to measure weight loss. Elemental analysis was performed by Gailbraith Laboraties, andwasKnoxville, TN.

Gas Chromatography/Mass Spectroscopy (GC/MS) was performed on a Hewlett-Packard HP-6890 GC/MS system, coupled to a HP 5972 mass selective detector (Agilent), equipped with a J &W DB5-HT COLUMN. GC employed a ResTek Rtx 1-MS column, 30 mm in length, 0.25mm in internal diameter, and 1.0 μm film thickness. The samples were placed into a syringeless injection tube [35] allowing the sample to be injected into the GC injection port. The sample is held for 2 minutes at 35°C, injected into the column which is heated from 35°C to 375°C at 15°C/min. The compounds which eluted from the GC column were transferred directly into the mass spectrometer for identification.

Proton nuclear magnetic resonance spectroscopy (H-NMR) was performed on a Bruker 500 MHz spectrometer. Samples were prepared in $CDCl_3$ or DMSO-d_6.

Gel Permeation Chromatography (GPC) using a Millipore Model 150-C system was applied to determine molecular weight of the poly (amic acid)s. NMP with 0.05 M LiBr was used as the mobile phase. The results were fitted to a calibration curve prepared using poly(methylmethacrylate) standards encompassing a broad molecular weight distribution.

Inherent viscosity was obtained by dissolving the poly (amic acid) in NMP at a concentration of 0.5 (w/v) and measuring the elution time using a Ubbelohbe viscometer in a 25ºC constant temperature water bath.

A variable frequency microwave furnace model LT 502 Xb (Lambda Technologies, Inc, Raleigh, N.C.) with a frequency range from 2.4 to 7.0 GHz was used to perform the microwave synthesis. Temperature was controlled by a Honeywell 3000 process controller with a type K thermocouple inserted into the reaction solution. The maximum output of microwave is 1200 W at 2.45 GHz. For the synthesis, a frequency of 4.69 GHz was used with temperature set to 100ºC for two hours.

Dielectric constants were measured in a Time Domain Dielectric Spectrometer (TDDS) from IMASS, Inc. Polyimide films with 50-75μm thickness were prepared on 2.54 cm (w) x 5.08 cm (l) x 0.32 cm (thickness) stainless steel plates. A guarded cell electrode was used to measure the dielectric constant, where the coated side was connected to the TDDS and to ground, and the bare side was connected to the high voltage. A 10V DC potential was applied over the frequency range of 0.01 to 10 kHz.

Isothermal thermo-oxidative stability was determined by measuring weight loss after exposure of solid polyimide samples at 371ºC in air in a muffle furnace.

Density was measured by the displacement technique (ASTM-D792) in EtOH.

Moisture absorption was measured by first conditioning the solid polyimide samples by drying overnight at 80ºC degrees in vacuum and then weighed. The samples were then completely immersed in distilled water at 25ºC for 24 hours. After soaking, the samples were wiped to remove moisture, and weighed. Absorbed moisture was calculated by the difference in wet and dry weight.

4.3 *Synthesis of Bis(3,4-dimethylphenyl)pentafluorophenyl trifluoromethylmethane (8FTM) by Thermal Autoclave Method (See Scheme 1).*

Octafluoroacetophenone (OFAP), (1.0 g, 3.79 mmol), trifluoromethanesulfonic acid (TFA), (0.55g, 3.68 mmol), and *o*-xylene (0.44 g, 60.6 mmol) were added to a teflon lined 20 ml autoclave. The autoclave was sealed, placed in an oil bath at 125ºC and maintained at this temperature for 24 hr. The autoclave was cooled in an ice bath to room temperature and then opened. The brown oil was dissolved in hexanes (50 ml), extracted with water (20 ml), saturated aqueous sodium carbonate solution (20 ml) and again with water (20 ml), dried over anhydrous magnesium sulfate overnight, filtered, and concentrated to a dark orange oil (1.2g, 69% based on OFAP conversion). GC/MS analysis (Fig. 1) of this oil showed the presence of 8FTM (35%), M/z- 458, two other major peaks identified as 3,4-dimethylphenyl)pentafluorophenyltrifluoromethyl methane (33%), M/z= 354 and bis(3,4-dimethylphenyl) methane (32%), M/z=224, and three very minor peaks, Separation and identification of the major peaks was accomplished by following the column chromatographic and TLC procedures of Still et. al. [36] and Tabur [37]. This oil (1.2 g) was dissolved in hexanes/toluene, (10 ml), (95/5), and poured onto a column (37 cm in length) containing about 60g of silica gel. A constant flow of hexanes/toluene (~60 ml) was added to the column as the mobile phase. The eluent (~50 ml) was collected in 2ml cuts and analyzed by thin layer chromatography (TLC) using UV light on 22.9 cm x 22.9 cm silica plates. The appropriate cuts containing product (8FTM) and the two other by-products were combined separately and then each fraction concentrated on a rotary evaporator to oil yielding 8FTM (0.45 g, 34.5% yield), 3,4-dimethylphenyl) pentafluorophenyltrifluoromethylmethane (0.3g), and bis (3,4-dimethylphenyl)methane (0.2 g). The by-products were analyzed and identified by GC/MS but were not further characterized.

8FTM: Melting point (DSC), -40ºC (broad). Elemental analysis, $C_{24}H_{18}F_8$: Calc. C, 62.89; H, 3.95; F, 33.16. Found: C, 59.86; H, 3.80; F, 37.46. FT-IR: 3040 cm^{-1} (aromatic, C-H), 2922 cm^{-1} (CH3), 1525 cm^{-1} (aromatic C-F), 1504 and 762 cm^{-1} (trisubstituted benzene), 1150 cm^{-1} (CF3). ^{1}H-NMR (500 MHz, DMSO-d_6) (Fig.3) 6.87-7.17 ppm (6 H, aromatic), 2.06-2.49 ppm (12 H, 2X3, 4-dimethyl positions). The product contained trace impurity of bis (3, 4-dimethylphenyl) methane. (Figs. 3 here)

4.4 *Synthesis of 8FTM by Microwave Autoclave Heating Method (See Scheme 1).*

A specially designed Teflon autoclave (figure 4) was fitted with a 20 ml. glass tube for the reactants and a thermocouple embedded in an H-HMR tube. Octafluoroacetophenone (OFAP), (1.00 g, 3.79 mmole), o-xylene (7.24g), (68.14 mmole) and trifluoromethanesulfonic acid (TFA), (0.558 g, 3.71 mmole) were added to the glass tube and the reactor was sealed with epoxy adhesive to prevent leakage during the reaction. The loaded Teflon autoclave was placed in the microwave furnace programmed at 100℃ for 2hr. After this process, the unit was removed, cooled to room temperature and opened. Xylene (50ml) was added to the oily product. The solution was washed with water (3x20 ml), with saturated sodium carbonate solution (20 ml) and dried over anhydrous magnesium sulfate overnight. The solution was filtered, and the filtrate concentrated in a rotary evaporator to yield a viscous brown oil (0.483 g), (48.4% based on OFAP conversion). GC/MS of this oil showed 3 major peaks and three minor peaks (Fig 5) The major peaks were identified as bis(3,4-dimethylphenyl)pentafluorophenyltrifluoromethylmethane 8FTM (30.3 %), M/z=458, (3,4-dimethylphenyl)pentafluorophenyltrifluoromethylmethane (45.9 %), M/z= 354, and bis(3,4dimethylphenyl)methane (23.5%), M/z= 224. As above, column chromatographic and TLC procedures as outlined by Still et. al. [36] and Tabur [37] were followed. A chromatographic column (37 cm in length) having a ratio of ~ 50:1 silica gel to oil was used to separate the components. The silica gel (27.5g) was added to the column as a hexanes slurry to reduce the amount of trapped air within the silica gel surface. The oil was dissolved in hexanes (~10 ml) and added to the silica gel column. A constant flow of hexane (67 ml) was added as the mobile phase, collecting the eluent in 3 ml cuts. The cuts were analyzed via thin layer chromatography (TLC) using UV light to identify the products. TLC was performed on 22.9 cm x 22.9 cm silica plates eluting with hexanes for one hr. The appropriate cuts were combined and concentrated via rotary evaporation.

Cuts 1-17 showed no visualization. Cuts 18-26, rf = 0.293 was identified as (3,4-dimethylphenyl)pentafluorophenyltrifluoromethylmethane, M/z =354, cuts 27-43, no spots were visualized, cuts 44-65, rf = 0.119, was identified as bis(3,4-dimethylbenzene)pentafluorophenyltrifluoromethylmethane, M/z=458, 8FTM. The bottom lower portion of the column was removed (~ 7.6 cm) and was washed with acetone. GC/MS (Fig. 5) analysis indicated a species M/z = 224, which was identified as bis (3,4-dimethylphenyl) methane. The appropriate cuts were combined and concentrated for further analysis, 8FTM was collected as a waxy solid, 0.146g, 13.6% yield. FT-IR : 3050 cm^{-1}. (aromatic C-H), 2911 cm^{1} (CH3), 1522 cm^{-1} (aromatic C-H), 1501 cm^{1} and 758 cm^{-1} ,(trisubstituted benzene), 1150 cm^{-1} (CF3). H-NMR (500 MHz D_3CCOCD_3) (Fig. 6), 7,71-7.20 ppm (12H, 2X 3,4'-dimethyl). (figs. 4,5.and 6 here)

4.5 *Synthesis of 8FTM from 8F-OH and o-Xylene (Thermal Autoclave, See Scheme 2)*

4-bromoxylene (1.0707 g, 10.1 mmole) 8F-OH (0.209 g, 0.565 mmole, synthesis described below) and trifluoromethanesulfonic acid (TFA), (0.0829 g, 0.53 mmole), were added to a pre-dried glass vial (10 ml.). The vial was placed in a stainless steel Teflon lined autoclave and maintained at 125ºC for 2 hr. The autoclave was cooled to RT. The reaction mixture was treated and products isolated as described for the synthesis of 8FTM via the microwave autoclave process. A dark oil was isolated (0.09 g,), 34.8 % (includes product mixture). GC/MS analysis (fig.8) of this dark oil revealed the presence of 8FTM, M/Z=458, (48.3%), and three components, bis 2,2-(3,4-dimethylphenyl)methane, M/Z=224 (8.7%), (3,4-dimethylphenyl)-2-pentafluorophenyltrifluoromethane,M/Z=354, (13.9%), starting material, 8F-OH, M/Z=370, (28.9%), and minor components with M/Z=328 and 340. The yield of 8FTM, if isolated would be 16.8 %. (Fig. 7 here)

4.6 *Synthesis of 1-(3,4-dimethylphenyl)-1-pentafluorophenyl-2,2,2-trifluoroethanol (8F-OH) Via the Grignard method (See Scheme 5)*

In a three-neck flask previously dried in an oven at 110ºC/3 hr, equipped with an argon gas inlet and outlet, previously dried addition funnel and reflux condenser was added magnesium powder (0.5618 g. 19.0 mmole), and 5 ml. of sodium dried THF. 4-bromoxylene (2.939 g, 15.9 mmole) in 7.5 ml. of sodium dried THF was added dropwise. After the addition of 0.25 ml. of 4-brom-o-xylene solution, initiation of reaction was observed. Addition was continued to maintain a moderate reflux (~40 min.). Reflux was continued for another 20 minutes after complete addition of 4-bromoxylene. The reaction mixture was cooled to 0ºC, and octafluorophenylacetophenone (OFAP), (3.565 g, 13.5 mmole) in 7.5 ml of dried THF was added dropwise. On completion, the reaction mixture was brought to RT and stirred for 1.5 hrs. Water (15ml) was added with continued stirring. The reaction mixture was extracted with a saturated solution of ammonium chloride (5x50 ml) and water (2x25 ml). The organic phase was concentrated in a rotary evaporator to yield 5.115 g crude reaction product. GC/MS (Fig. 8) of this crude oil showed four major products, bis(3,4-dimethylphenyl)pentafluorophenyltrifluoromethylmethane, 8FTM, M/Z=458, 1-(3,4-dimethylphenyl)-1-pentafluorophenyl-2,2,2-trifluoroethanol, (8F-OH), M/Z = 370, bis (3,4-dimethylphenyl)methane, M/Z = 224 and xylene, M/Z = 106.

Column chromatography as described above for 8FTM was used to separate the reaction products. Fractions (3 ml portions) were collected and monitored via GC/MS to determine the composition of the eluent. Fractions 27-46 were determined to be product, 8F-OH by GC/MS. Concentration of the fractions in a rotatory evaporator yielded oily 8F-OH (2.0 g, 40 % yield). This oil on standing has a tendancy to crystallize. Crystallization yielded white crystals, which were washed with hexanes, and dried at 50ºC in vacuum. Melting point, 104-106ºC (capillary), DSC, m.p. 107.8ºC. GC/MS (Fig. 9) of fraction 27-46, shows M/Z = 370, identified as 8F-OH.

FT-IR : 3595 cm^{-1}, 3510 cm^{-1}, (-OH), 3022 cm^{-1}, (aromatic C-H), 2970 cm^{-1} and 2919 cm^{-1}, (–CH3), 1634 cm^{-1}, 1527 cm^{-1},(aromatic C-F), 1496 cm^{-1}, 774 cm^{-1}., (trisubstituted benzene), 1373 cm^{-1}, (in-plane –OH), 1265 cm^{-1}, (C-O stretch), 1127 cm^{-1}, and 723 cm^{-1} , (-CF3). H-NMR (Fig.10): (CD_2Cl_2): 2.261-2.800 ppm, (2x –CH3 protons), 3.504 ppm., (-OH proton), 7.190-7200 ppm., (3 aromatic protons). (Fig. 8, 9, and 10 here)

4.7 *Synthesis of 4, 4'- (trifluoromethyl-1-pentafluorophenylethylidene) diphthalic tetracarboxylic acid, (8FTA), (See Scheme 1).*

8FTM (1.48g, 3.05mmole), and HNO3, 30% v/v, (8.21g, 39.1mmole) were added to a Teflon lined autoclave. The autoclave was placed in an oil bath at 170℃ and maintained at this temperature for 2.5 hr. The autoclave was cooled in an ice bath, vented and then opened. The clear yellow solution was transferred to a flask, the autoclave was rinsed with water (5x25ml) and combined with the yellow solution. The solution was concentrated at 55ºC in a rotary evaporator to yield a pale yellow solid (1.7g, (98%).The glassy solid was washed with water (5x25ml) and dried at 60ºC overnight. Melting point, (DSC), 160°C (broad). Elemental analysis for $C_{24}H_{10}F_8O_8$, Calc., C, 49.84, H, 1.74, F, 26.28. Found, C, 51.32, H, 1.40, F, 25.20. FT-IR : 3041cm^{-1}, (-OH), 1705 cm^{-1} (C=O), 1506 cm^{-1} (aromatic C-H), 1490^{-1} and 760 cm^{-1}, (trisubstituted benzene), 1128 cm^{-1} and 706 cm^{-1}, (CF3) 1263 cm^{-1}, (C=O), 1003 cm^{-1}, (lone H).

H-NMR (Fig11), *d*$_6$-DMSO, 7.65-8.02 ppm., (6 H aromatic). (Fig. 11 here)

4.8 *Synthesis of 4, 4'-(2, 2, 2-trifluoro-1-pentafluorophenylethylidene) diphthalic anhydride (8FDA),(See Scheme 1).*

4,4'-(2,2,2-Trifluoro-1-pentafluorophenylethylidene) diphthalic tetracarboxylic acid (8FTA), (1.0 g, 1.74 mmole) was heated at 100℃ in a vacuum oven for 16 hr. The yellow glassy solid which formed was recrystallized from acetic anhydride to yield a white crystalline solid, 0.89 g. (95% yield). Melting point, (DSC), 240°C(sharp). Elemental analysis for $C_{24}H_6F_80_6$, Calc, C, 53.16, H, 1.11, F, 28.03. Found, C, 51.05, H, 1.51, F, 27.15. FT-IR: 1855 cm^{-1} and 1782 cm^{-1}, (C=O), 1506 cm^{-1}, (aromatic C-F), 1250 cm^{-1}, (C=O), 1143 cm^{-1} and 706 cm^{-1}, (CF_3).

H-NMR (Fig.12), (*d*$_6$-DMSO): 7.57-8.27 ppm, (6 H, aromatic). (Fig. 12 here)

4.9 *Synthesis of 8F- Poly (amic-acid) s, and 8F-Polyimides (See Scheme 6).*

Monomers were dried in vacuum at 25ºC overnight prior to using. Equal molar amounts of 8FTA and aromatic diamines were dissolved in DMAC at 15% solids in different flasks. The amine solution was added to the dianhydride solution in a nitrogen atmosphere while stirring at room temperature for 24 hr. The reaction progress was monitored by FT-IR during this time sequence. Since this process gave poly (amic-acid) with low molecular weights (Table 1), the 8F-PAA's were then prepared at 150ºC for 3 hr. The poly (amic-acid) solution was used to prepare polyimide films on glass slides and on stainless steel coupons (2.54 cm x 5.08 cm x 0.26 cm) for dielectric constant measurements and to prepare polyimide powder and polyimide specimens for DSC, TGA, moisture absorption, density and thermal stability studies. The cure cycle for films, powder and polyimide disks is described below. Avimid-N poly (amic acid) was synthesized as described above from 6FDA and p-PDA/m-PDA (95/5).

4.10 *Preparation of Polyimides Films (See Scheme 6).*

Polyimide films (2-3 mil thickness, ~75µ) for FT-IR and dielectric constant measurements were prepared by pipetting poly (amic-acid) solution (5-10 ml) onto pre-cleaned glass slides or stainless steel coupons (2.54 cm x 5.08 cm x 0.26 cm). The glass and stainless steel specimens were placed in a glass chamber containing a gas inlet and outlet. Solvent was evaporated at room temperature under a nitrogen flow. The specimens were cured at 100ºC /1h + 200ºC /1h + 300ºC /1h raising the temperature slowly (20ºC /min) to each temperature interval.

4.11 *Preparation of Polyimide Powder.*

A solution of poly (amic acid) prepared from 8FDA and p-phenylene diamine was poured into a 50/50 water/methanol mixture (50 ml) under high shear in a laboratory blender. The precipitated poly(amic acid) was filtered, dried at 60 ºC / 3 hr. and then imidized using the following two cure cycles: 100 ºC /1 h + 200 ºC /1 h + 300 ºC /1 h and 100 ºC /1 h + 200 ºC /1 h + 300 ºC /1h +370ºC/2h for thermal analysis measurements.. The resulting polyimide powder was used to fabricate 8F-PDA disks. Avimid-N powder was prepared from the poly (amic acid) in the same manner.

4.12 *Preparation of Polyimide Discs*

4.12.1 *8F-PDA-1 and Avimid-N Disks*

8F-PDA polyimide powder (2.2g) was placed in a stainless-steel mold (2.54 cm diameter). The mold was placed in a press preheated at 300℃.and held at this temperature at a pressure of 281.2 kg.cm^2 (4000 psi) for 3 hr. The press was cooled to RT, the pressure was released to yield a specimen 2.5 cm. in diameter x 0.3 cm thick. The same process was used to prepare the Avimid-N disk.

4.12.2 *8F-PDA-2 Disk*

8F-PDA polyimide powder (2.2 g,) was loaded into a stainless mold, and placed in a programmable Tetrahedron: Initially, the cycle (300℃/3h, at 281.2kg/cm2, 4000 psi) described above for 8F-PDA-1 was used. In addition, the sample was treated at 316℃ at 281.2kg/cm^2, (4000 psi) for 2.5 h, then raised to 371℃ and held at this temperature and pressure for 2 h. The temperature was raised to 426℃ at 2℃/min, and held for 4 h.

The sample was cooled to 287℃ under pressure (281.2kg/cm^2, 4000 psi) and held at this temperature for I minute. The press was cooled to RT and the pressure was released at RT. A dark brown, dense specimen was produced.

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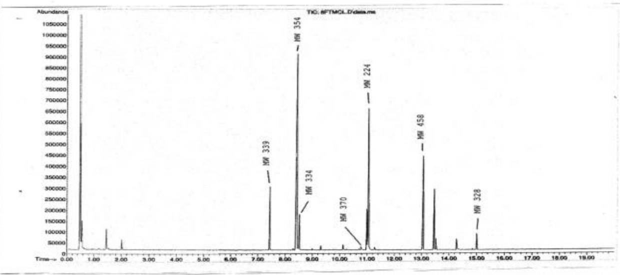

Fig. 1. GC/MS of Crude 8FTM Oil from Thermal Autoclave Reaction

Fig. 1. GC/MS of Crude 8FTM Oil from Thermal Autoclave Reactor.

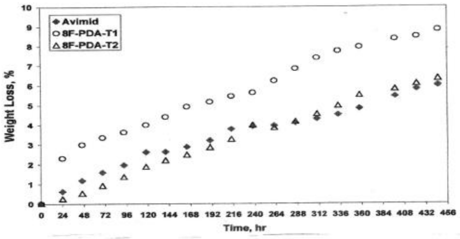

Fig. 2. Isothermal Weight Loss of 8F-p-PDA-T1, 8F-p-PDA-T2 and Avimid-N after Aging at 371°C in an Oven in Ambient Air.

Fig. 2. Isothermal Weight Loss of 8F-p-PDA-T1, 8F-p-PDA-T2 and Avimid-N after Aging at 371^{o}C in an Oven in Ambient Air.

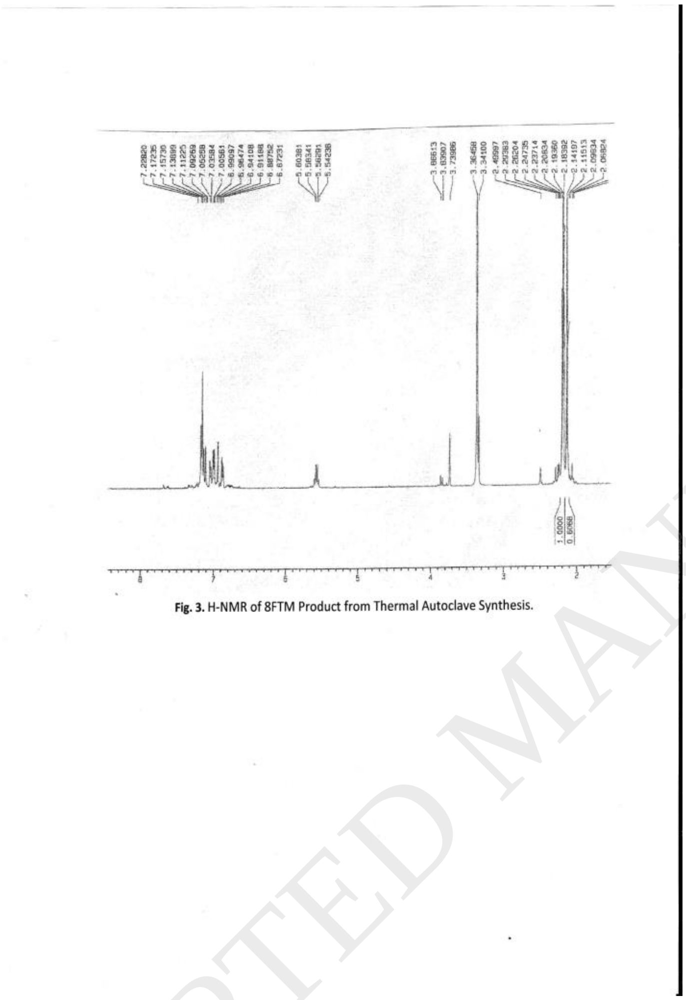

Fig. 3. H-NMR of 8FTM Product from Thermal Autoclave Synthesis.

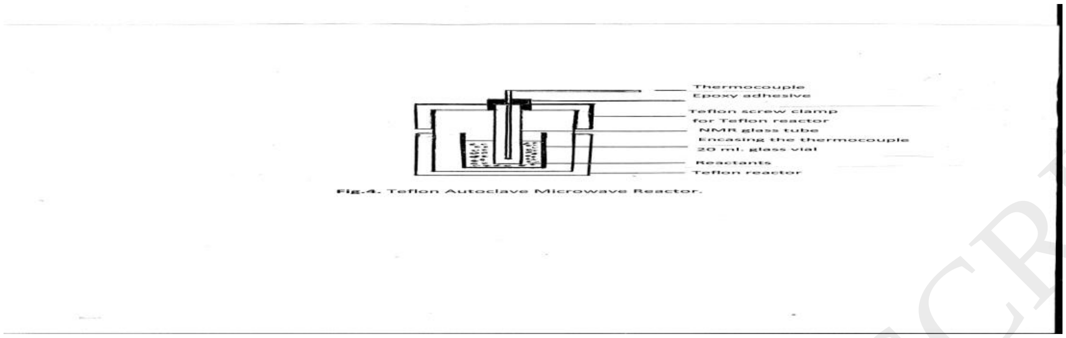

Fig.4. Teflon Autoclave Microwave Reactor.

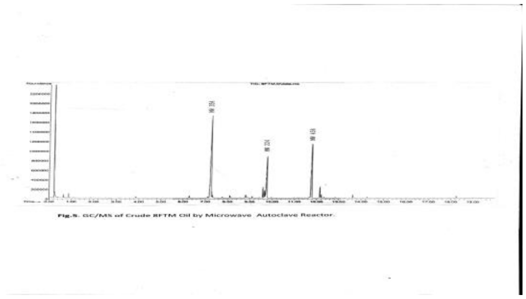

Fig.5. GC/MS of Crude 8FTM Oil by Microwave Autoclave Reactor.

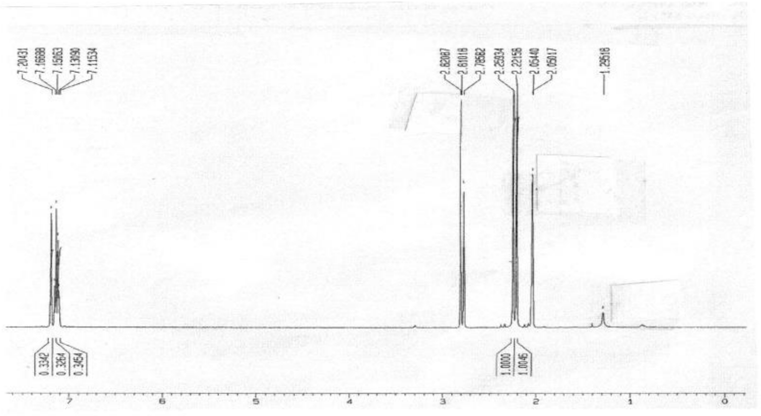

Fig.6. H-NMR of 8FTM Product by Microwave Autoclave Reactor.

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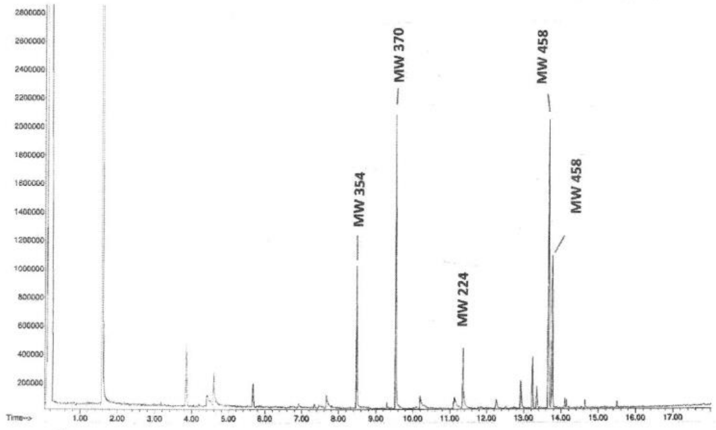


Fig.7.GC/MS Spectrum of Crude 8FTM Oil for the Synthesis of 8FTM from 8F-OH and o-Xylene.

Fig.7.GC/MS Spectrum of Crude 8FTM Oil for the Synthesis of 8FTM from 8F-OH and o-Xylene.

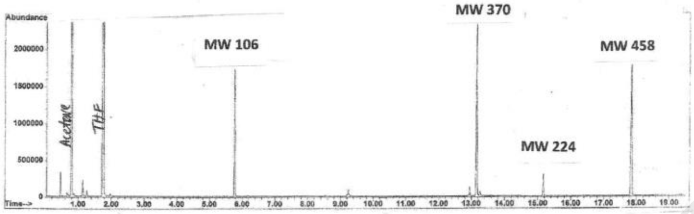


Fig.8. GC/MS Spectrum of Crude 8F-OH Oil for the Synthesis of 8F-OH from OFAP and 4-Bromo-o-xylene Via the Grignard Reaction.

Fig.8. GC/MS Spectrum of Crude 8F-OH Oil for the Synthesis of 8F-OH from OFAP And 4-Bromo-o-xylene Via the Grignard Reaction.

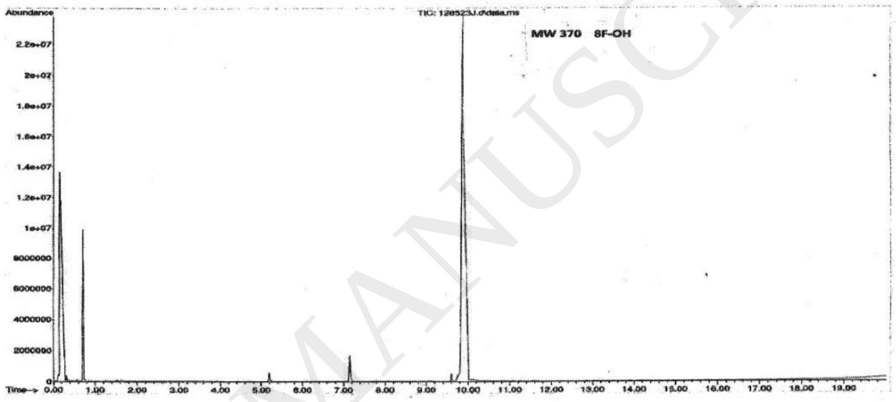


Fig.9. GC/MS Spectrum of Purified 8F-OH Oil (fraction cuts 27-46) from the Synthesis of 8F-OH from AFAP and 4-Bromo-o-xylene.

.**Fig.9.** GC/MS Spectrum of Purified 8F-OH Oil (fraction cuts 27-46) for the Synthesis of 8F-OH from AFAP and 4-Bromo-o-xylene**.**

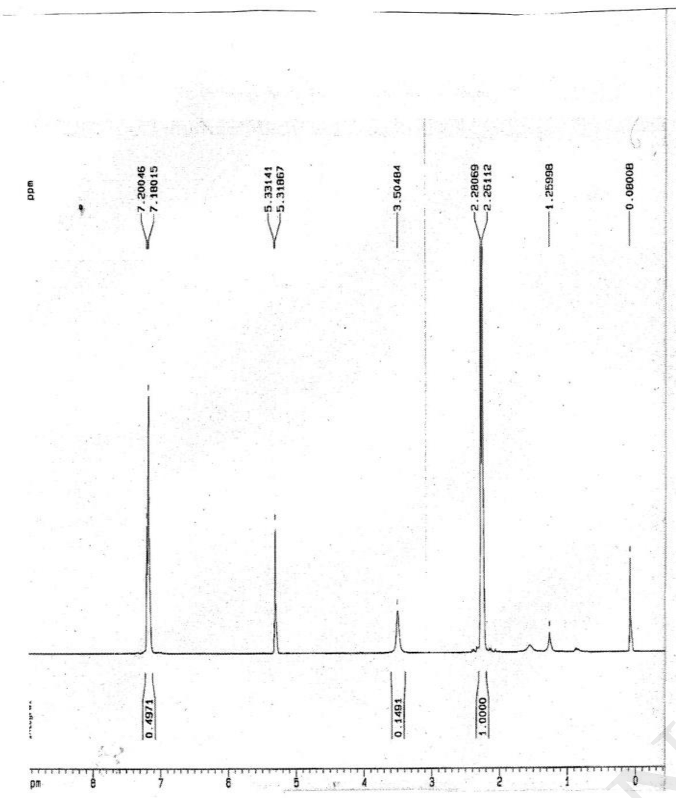


Fig.10. H-NMR of 8F-OH.

Fig.10. H-NMR of 8F-OH.

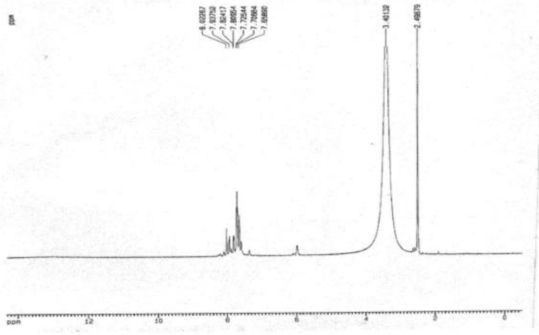


Fig.11. H-NMR of 8FTA.

Fig.11. H-NMR of 8FTA**.**

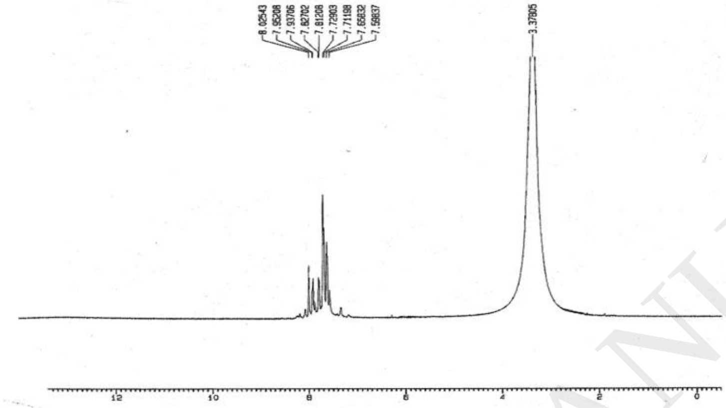
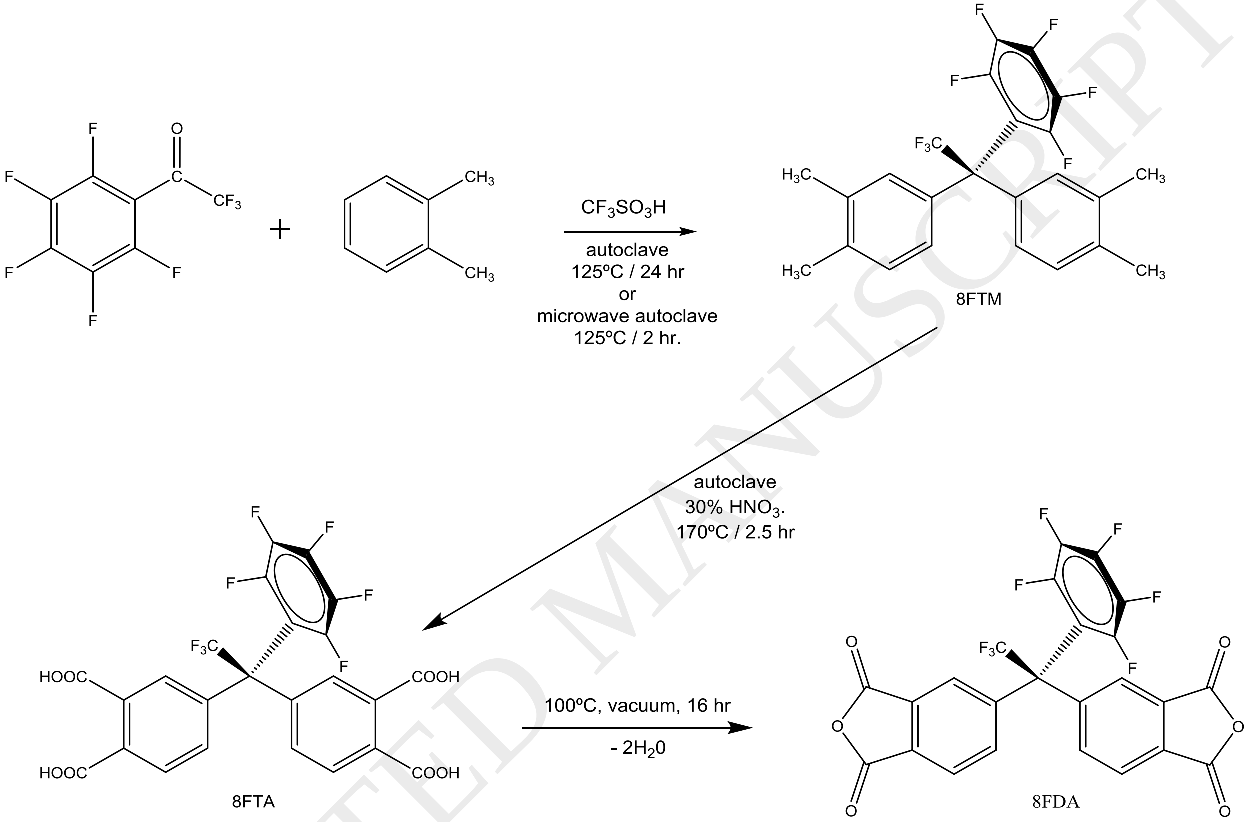
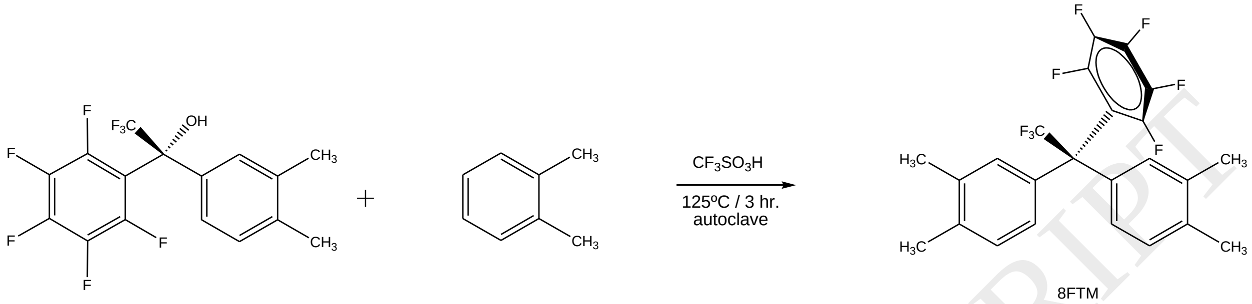


Fig.12. H-NMR of 8FDA.

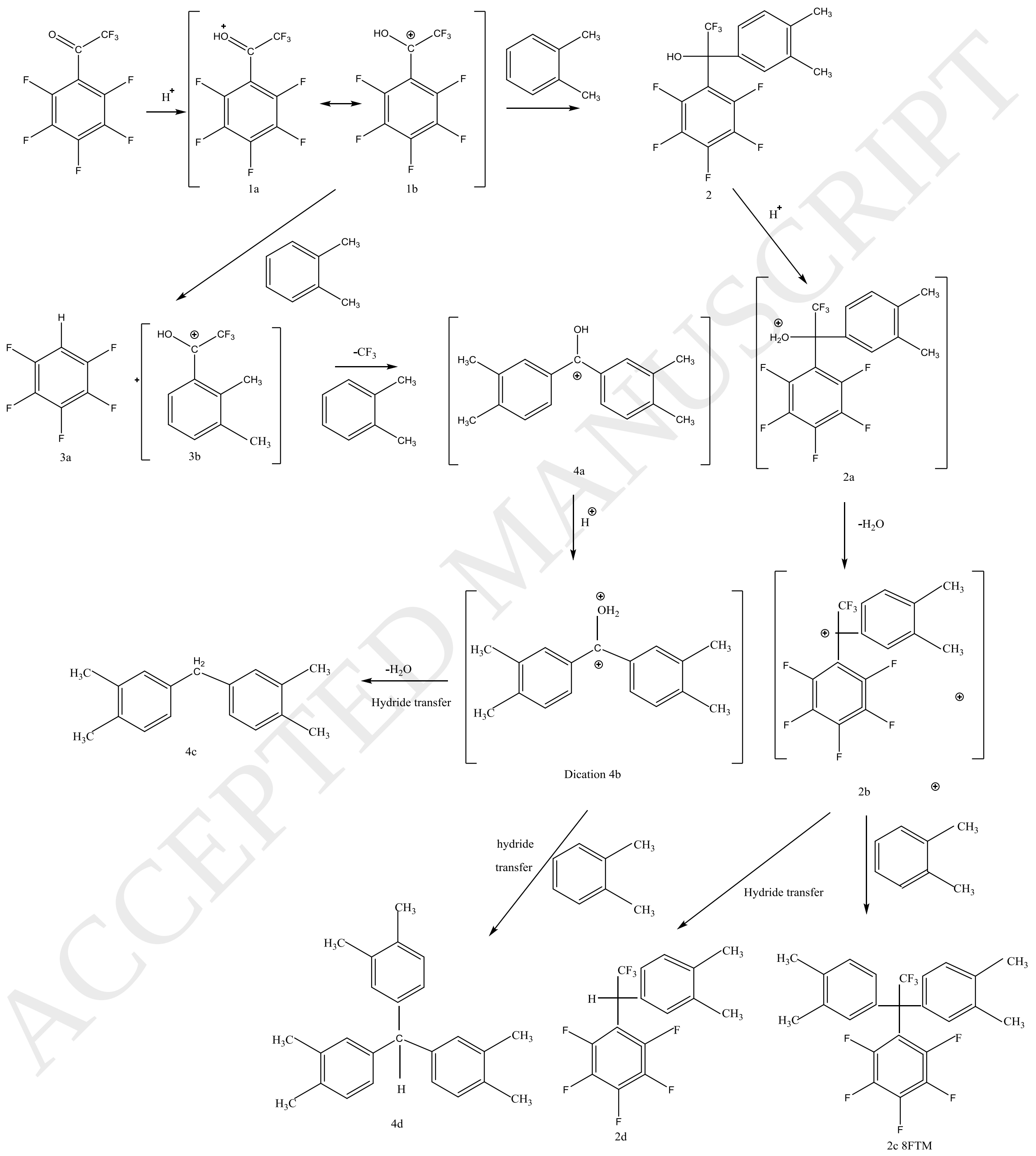
Fig.12. H-NMR of 8FDA.



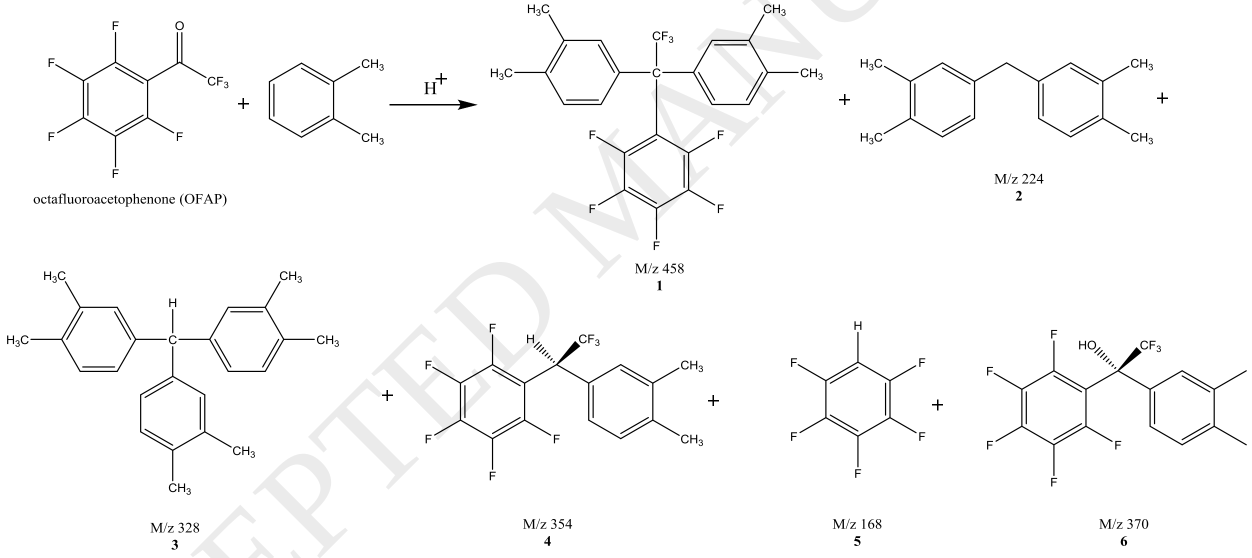
Scheme 1: Synthesis of 8FTM, 8FTA, and 8FDA



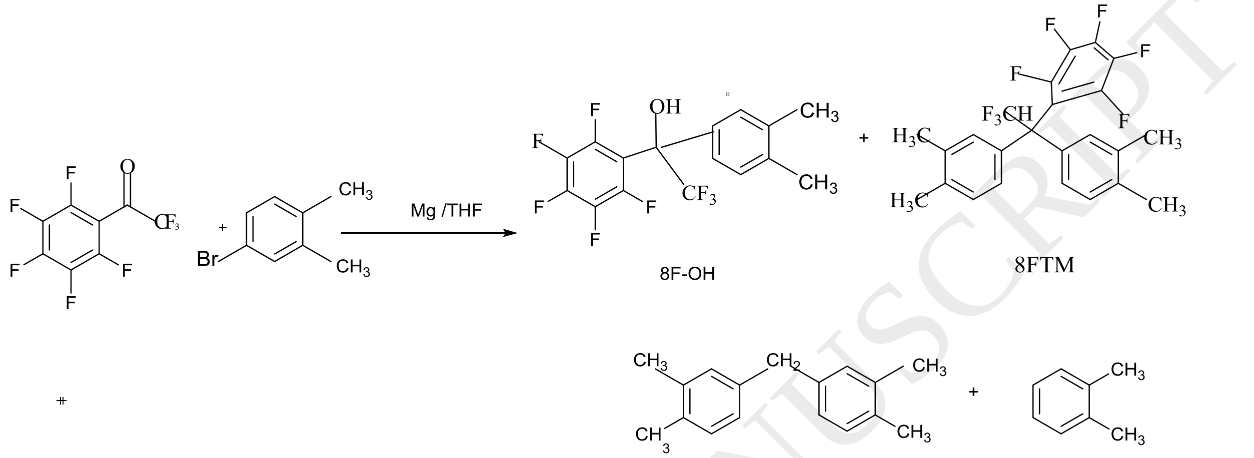
Scheme 2: Synthesis of 8FTM from 8F-OH and o-Xylene


H+
1a
1b
2
H+
3a
3b
-CF3
4a
2a
H⊕
-H2O
-H2O
Hydride transfer
4c
Dication 4b
2b
hydride
transfer
Hydride transfer
4d
2d
2c 8FTM

Scheme 3. Proposed Mechanism for By-Product Formation in 8FTM Synthesis

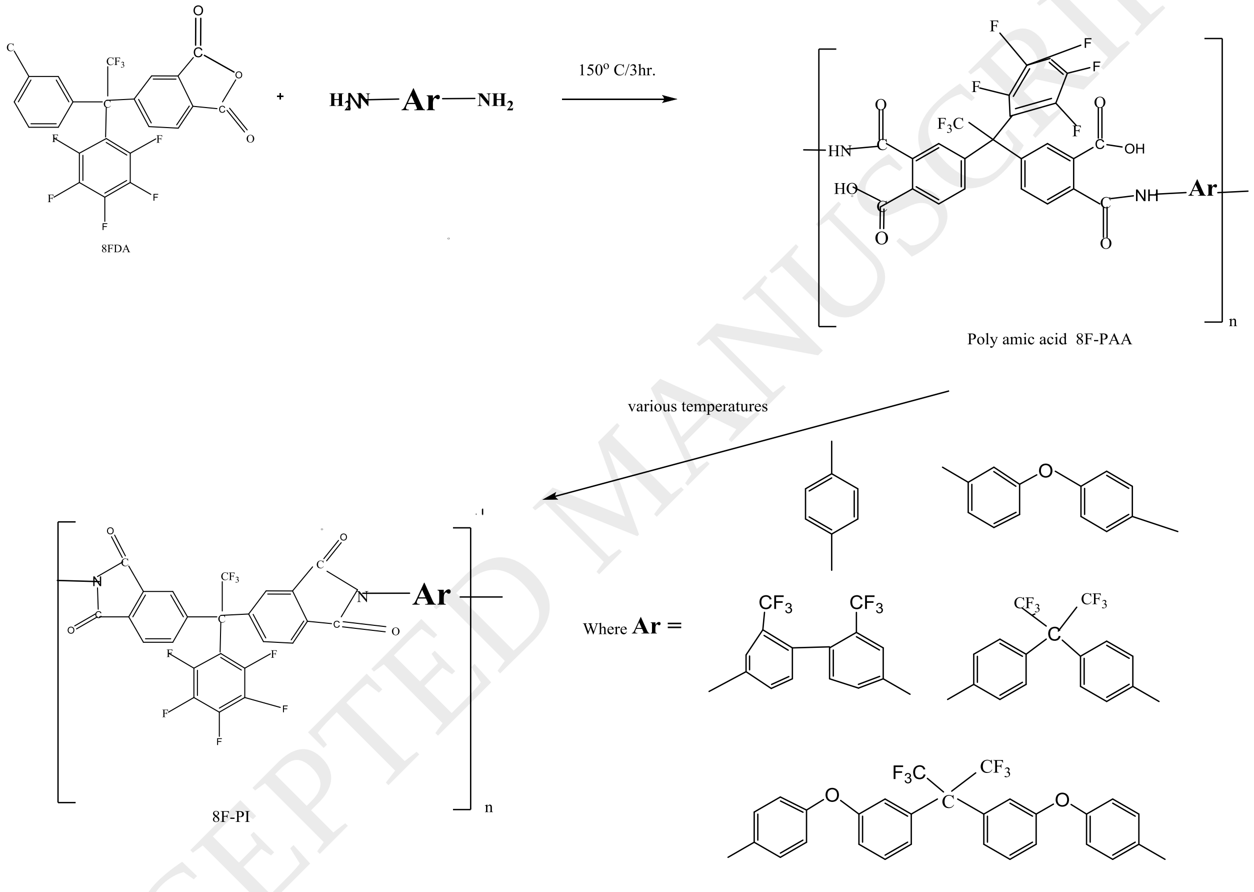


Scheme 4: Products formed in the reaction between octafluoroacetophenone (OFAP) and *o*-xylene



Scheme 5 Synthesis of 8F-OH via showing 8FTM formation and Two other Products
the Grignard Reaction

Scheme 5. Synthesis of 8F-OH via the Grignard Reaction showing 8FTM formation and two other products



Scheme 6. Synthesis of 8F-PAA and 8F-PI

Table 1. Molecular Weights of Poly (amic acids)[a]

Poly (amic acid)	M_w (g/mol)	M_n (g/mol)	M_w/M_n	η_{inh}[b]
8F-3,4'-ODA	8397	1973	4.20	0.28
8F-p-PDA	544	344	1.58	0.38
8F-6FA	1805	795	2.29	-----
8F-BDAF	4875	1125	4.33	0.29
8T-TFMB	1099	569	1.93	0.19

a. GPC method.

b. ASTM D2857-16

Table. 2 Glass Transition Temperatures (T_g) of 8F-PI's

Polyimide	Tg[a], °C After final cure, 300°C / 1 h	Tg[b], °C After final cure, 371°C / 2 h r
8F-3,4'-ODA	234	270
8F-p-PDA	291	323
8F-p-PDA	----	330
8F-6FA	215	250
8F-BDAF	265	305
8F-TFMB	275	291

a. Cure cycle: 100°C/1h + 200°C/1h + 300°C/1h
b. Cure cycle: 100°C/1h + 200°C/1h +300°C/1hr +371°C/2 h

Table 3. Temperature at 5% and 10% Weight Loss by TGA Method[a]

Polyimide	In Oxygen		In Nitrogen	
	Td (5%), °C	Td (10%), °C	Td (5%), °C	Td (10%), °C
8F-3,4'-ODA	456	501	463	573
8F-p-PDA	505	534	535	581
8F-3,3'-6FA	477	510	524	548
8F-BDAF	475	505	516	537
8F-TFMB	493	527	545	576
Avimid-N[b]	501	525	522	545

a. Cure cycle. : 100°C/1h + 200°C/1h +300°C/1h +371°C/2 h

b. Ref.20

Table.4 Density and Moisture Absorption of 8F-PDAs and Avimid-N

Polyimide	Density[a] (g/cm^3)	Moisture Absorption[b] (Wt. %)
8F-p-PDA-1[c]	1.71	0.98
8F-p-PDA-2[d]	1.78	0.85
Avimid-N[c]	1.44	1.23

a. ASTM-D792b.
b. After exposure to RT distilled water for 24 hr.
c. Cure cycle: 100°C/1 h + 200°C/1 h + 300°C/1 h +300°C/3h (281.2 kg/cm^2, 4000 psi)
d. *Cure cycle:* 100°C/1 h + 200°C/1 h + 300°C/1 h + 316°C/2.5h (281.2 kg/cm2, 4000 psi) + 371°C/2h (281.2 kg/cm^2, 4000psi), +426°C/4h, (281.2 kg/cm^2, 4000psi)

Table 5. Dielectric Constants of 8F-PIs and 6F-PIs

Polyimide	Є[a]	Polyimide	Є[b]
8F-3,4’-ODA	2.34	6F-3,3’-ODA	2.73[c]
----------		6F-4,4’-ODA	2.79[c]
8F-p-PDA	2.01	6F-p-PDA	2.73[c]
8F-3,3’-6FA	2.35	6F-3,3’-6FA	2.39[c]
8F-BDAF	2.07	6F-BDAF	2.50[c]
8F-TFMB	2.11	6F-TFMB	2.89[d]
----------		Avimid-N[e]	2.63[a]

a. 1kHz, 40-60 % RH
b. Ref. 34, 1kHz
c. Ref. 34, 25-35 % RH
d. Ref. 10, 40% RH
e. Ref. 20