

# Synthesis, Characterization, and Properties of Novel Fluorine Containing Aromatic Polyamides

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**ABSTRACT:** A series of novel fluorine containing aromatic polyamides were synthesized by the direct polycondensation of various fluorine containing aromatic diamines and commercially available 5-*t*-butyl isophthalic acid. These polyamides have good solubility in several organic solvents such as dimethylformamide, *N,N*-dimethylacetamide, 1-Methyl-2-pyrrolidone, dimethyl sulfoxide, and tetrahydrofuran. The synthesized polymers exhibited inherent viscosities up to 0.93 dL/g and  $M_w$  up to 1,52,000 with PDI of 2.49. The polyamides exhibited good thermal stability up to 489°C for 10% weight loss in nitrogen and high glass transition temperature up to 273°C. Dynamic mechanical analysis showed a very good retention of storage modulus up to the glass transition temperature. The  $\tan \delta$  peak value at 1 Hz

was used to calculate the  $T_g$  and these values are in good agreement with differential scanning calorimetry data. The polyamide films were flexible with tensile strength up to 72 MPa, elongations at break up to 14%, and modulus of elasticity up to 1.39 GPa depending on the exact repeating unit structure. X-ray diffraction measurements indicate that these polyamides are semicrystalline. Rheology study showed same trend of melt viscosity behavior with different shear rate for all polymers. Water absorption study indicates the hydrophobic nature of the polymer. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1356–1364, 2008

**Key words:** fluorinated polyamide; processability; thermal properties; mechanical properties

## INTRODUCTION

Aromatic polyamides (aramids) exhibit a number of interesting properties, such as high thermal stability, chemical resistance, low flammability, and excellent mechanical properties. Wholly aromatic polyamides are a potential thermoplastic material for different applications because of its attractive combination of chemical, physical, and mechanical properties. Nevertheless, aromatic polyamides of the class are generally difficult to fabricate into fibers and films because of their high melting or softening temperatures and insoluble nature in most organic solvents. Solubilization of polyamides have been targeted by several means, like introduction of flexible linkages,<sup>1–3</sup> addition of bulky side groups,<sup>4</sup> or molecular asymmetry into the backbone,<sup>5,6</sup> which also leads to decrease in the crystallinity. Korshak and co-workers<sup>7,8</sup> demonstrated that the polymer chain having cyclic side cardo group (for e.g., a fluorene group) can cause a significant increase in both glass transition temperature and thermooxidative stability while providing good solubility. Several researchers reported that flexible hexafluoro isopropylidene

groups between rigid phenyl rings in the polymer backbone improved solubility.<sup>9,10</sup> Attention has been made to prepare fluorine-containing condensation polymers because of their unique properties and high performance. Fluorine has a unique set of properties (small size, formation of very strong bonds, strong electronic effects) that make it an extremely valuable substituent in the molecular design of effect-chemicals.<sup>11</sup> In the context of materials, the incorporation of fluorine can be used to affect a variety of properties such as hydrophobicity, thermal stability, solubility, and surface activity, and these changes have been exploited in the design polymers.<sup>12–15</sup> Fluoropolymers have a history dating back to the commercialization of poly(tetrafluoroethylene) (PTFE) over 40 years ago, but it is only in the last few years that a significant growth has been seen in reports of new fluoropolyaromatics.<sup>16–25</sup> It is particularly significant to note the increasing use of the  $\text{CF}_3$  group which is now second in importance only to fluorine itself in pharmacological applications in this context.<sup>16–19,23–25</sup> Researchers reported the first examples of  $\text{CF}_3$ -ring-substituted poly(ether sulfone) (PES) copolymers,<sup>23</sup> which show significant differences from PES itself. People also reported the first examples of  $\text{CF}_3$ -ring-substituted poly(ether ether ketone)s (PEEKs) and compare them with the nontrifluoromethylated homopolymer PEEK as well as with the PES analogues.

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In this study, we have successfully applied phosphorylation<sup>26</sup> reaction to the synthesis of a series of novel polyamides having high molecular weight by the direct polycondensation of 5-*t*-butyl isothalic acid with various synthesized fluorine containing aromatic diamines using triphenyl phosphite (TPP) and pyridine (Py) as condensing agents. The synthesized polymers were well characterized and their properties are reported.

## EXPERIMENTAL

### Materials

1-Methyl-2-pyrrolidone (NMP) (E. Merck, India) was purified by stirring with NaOH and distilled from P<sub>2</sub>O<sub>5</sub> under reduced pressure. Calcium chloride (E. Merck, India) was used after 6 h of oven drying at 140°C. Triphenyl phosphite (E. Merck, Germany) was used as received without further purification. Pyridine (SD Chemicals, India) was purified by stirring with KOH and distilled under reduced pressure. 5-*t*-Butyl isophthalic acid and 4,4'-diaminodiphenyl ether (ODA) (Aldrich Chemical company, USA) was used as received. *N,N*-dimethylacetamide (DMAc) (Spectrochem, India), dimethylformamide (DMF) (SD Chemicals, India), tetrahydrofuran (THF) (SD Chemicals, India), chloroform (CHCl<sub>3</sub>) (E. Merck, India), and dimethyl sulfoxide (DMSO) (E. Merck, India) was used as received. The diamines monomers were prepared as reported earlier.<sup>27</sup>

### Characterization

FTIR spectra were recorded at room temperature by FTIR Thermo Nicolet (NEXUS 870) spectrophotometer using KBr pellets and directly from the thin polyamide samples. Elemental carbon, hydrogen, and nitrogen of the compounds were analyzed by pyrolysis method using Vario EL (Elementar, Germany) elemental analyzer. Differential scanning calorimetry (DSC) analyses were performed on a NETZSCH DSC 200PC differential scanning calorimeter with 10 ± 2 mg samples, at a heating rate of 20°C/min for the determination of the glass transition temperature (*T*<sub>g</sub>) as well as melting temperature. Glass transition temperatures were taken as the midpoint of the change in slope of the baseline on the second DSC heat scan. Thermo gravimetric data were recorded on a NETZSCH TG 209 F1 thermal analyzer to know the decomposition temperature (*T*<sub>d</sub>) at 5% weight loss and 10% weight loss under nitrogen atmosphere. The dynamic mechanical analysis (DMA) was performed on a TA instrument DMA-2980 instrument (USA) under tension mode on thin-film (120–145 μm) samples at a heating rate of 10°C/min and were run at single frequency of 1 Hz for the temperature range of

50–300°C. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were recorded on a Bruker 300 MHz instrument (Switzerland) and Bruker 500 MHz instrument using DMSO-*d*<sub>6</sub> and Pyridine-*d*<sub>5</sub> as solvents, respectively. Tensile strength and elongation at break of thin polyamide films were measured with the help of Hounsfield H10KS-0547 universal tensile testing machine. Test samples with dimension of 10 × 25 mm and a thickness around 0.14 mm were used for the measurement of tensile strength and the percentage of elongation at break. All tests were performed using a cross head speed of 5%/min of the specimen length. Wide angle X-ray diffractograms were recorded by a diffractometer system XPERT-PRO, Goniometer PW3050/60 (Theta/Theta) at 24°C, using Cu K<sub>α</sub> radiation (λ = 1.54 Å), with continuous scan step time 3 s, and generator settings at 25 mA, 40 kV. Inherent viscosities of all these polymers were determined at 0.5 dL/g concentration using an Ubbelohde viscometer in DMAc solvent at 32°C ± 0.5°C. Gel permeation chromatography was performed in Agilent instrument, Model No. Agilent-1100. DMAc/2% H<sub>2</sub>O/(3g/L) LiCl were used as eluant. Flow rate employed 0.5 mL/min, poly(vinylpyridin) was used as standard and RI detector was used for this purpose. Water uptake values were determined by determining the weight change of the polymer films after immersing in distilled water for 120 h. The weight changes were monitored by using a Sartorius-CP225D balance of sensitivity of 10<sup>-6</sup> g. Melt viscosity of the synthesized polyamides were done on a TA Instrument Advanced Rheometer AR1000.

### Polymer preparation

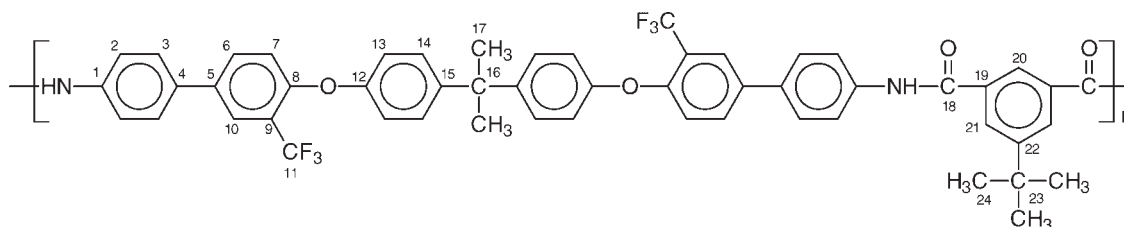
A series of novel fluorinated aromatic polyamides were prepared by the direct polycondensation of various diamines with 5-*t*-butyl isophthalic acid in the mole ratio of 1 : 1 in NMP as solvent and in presence of TPP and pyridine as condensing agent. Typical example of a polycondensation has been shown later.

A mixture of bis2,2-[4{2'trifluoromethyl 4'(4'' aminophenyl) phenoxy}phenyl] isopropylidene (1.51,736 g, 2.171635 mmol), 5-*t*-butyl isophthalic acid (0.48,263 g, 2.171635 mmol), calcium chloride (0.36 g), NMP (5 mL), pyridine (1.4 mL), and TPP (1.4 mL) were weighed into a 50-mL round bottom flask equipped with reflux condenser and nitrogen inlet. The mixture was heated with constant stirring at 95°C for 4 h by a magnetic needle. After 10–15 min of reaction, it was found that viscosity of the reaction goes up. After completion of the reaction the viscous polymer solution was poured drop-wise into a large amount of methanol (600 mL) under constant stirring. The off-white fibrous precipitates were collected by filtration. The fibrous polymer was further washed thoroughly with methanol followed by hot distilled water to

remove any adsorbed  $\text{CaCl}_2$  in polymer mass. The complete removal of  $\text{CaCl}_2$  was checked by adding few drops of the filtrate in  $\text{AgNO}_3$  solution. The polymer mass was dried overnight in oven at  $60^\circ\text{C}$  under vacuum for removal of all traces of solvent. The yield was 1.9013 g ( $\sim 98.93\%$ ). The same procedure was adopted for the other polymers.

Measured amount of polymer was solubilized in DMAc and casted on to a flat Petri dish and was kept in oven at  $60^\circ\text{C}$  for overnight then heated under vacuum at  $60^\circ\text{C}$  for the complete removal of trapped solvent. Clear and flexible films were obtained for polymer (S1–S3) and brittle film was obtained for polymer S4.

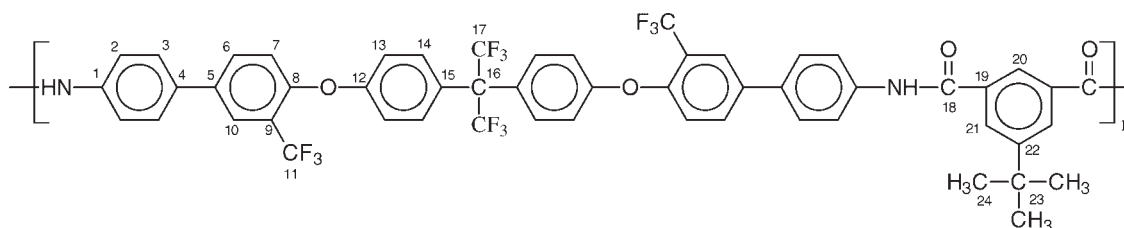
### Polyamide S1



Anal. Calcd for  $(\text{C}_{53}\text{H}_{42}\text{F}_6\text{O}_4\text{N}_2)_n$  (884.933  $\text{g mol}^{-1}$ )<sub>n</sub>: C, 71.94; H, 4.78; N, 3.17. Found: C, 71.88; H, 4.72; N 3.21. FTIR (KBr) ( $\text{cm}^{-1}$ ): 3299.71 (N–H stretching); 3040.24 (aromatic C–H stretching); 2965.90 (aliphatic C–H stretching); 1657 (C=O stretching); 1248.23 (asymmetric C–O–C stretching); 1052.54 (symmetric C–O–C stretching); 1596.59 (C=C ring stretching band); 1133.29 (C–F stretching).  $^1\text{H-NMR}$  (Py- $d_5$ ) (500 MHz)  $\delta$  (ppm): 11.48 (s, 2H, –NH); 9.02 (s, 1H, H<sup>20</sup>); 8.45 (s, 2H, H<sup>21</sup>); 8.30–8.29 (d, 4H,  $J = 7.9$  Hz, H<sup>2</sup>); 8.09 (s, 2H,

H<sup>10</sup>); 7.83–7.81 (d, 2H,  $J = 8.35$  Hz, H<sup>6</sup>); 7.78–7.76 (d, 4H,  $J = 7.8$  Hz, H<sup>3</sup>); 7.42–7.40 (d, 4H,  $J = 7.95$  Hz, H<sup>14</sup>); 7.17–7.15 (d, 2H,  $J = 8.55$  Hz, H<sup>7</sup>); 1.72 (s, 6H, H<sup>17</sup>); 1.214 (s, 9H, H<sup>24</sup>).  $^{13}\text{C-NMR}$  (Py- $d_5$ ) (500 MHz)  $\delta$  (ppm): 166.82 (C<sup>18</sup>); 154.96 (C<sup>12</sup>); 154.71 (C<sup>8</sup>); 152.13 (C<sup>22</sup>); 146.95 (C<sup>1</sup>); 140.05 (C<sup>15</sup>); 136.38 (C<sup>20</sup>); 134.72 (C<sup>4</sup>); 131.99 (C<sup>5</sup>); 128.86 (C<sup>14</sup>); 128.28 (C<sup>6</sup>); 127.62 (C<sup>3</sup>); 125.59 (C<sup>21</sup>); 125.30 (C<sup>10</sup>); 123.00 (C<sup>19</sup>); 121.88 (C<sup>2</sup>); 121.45 (C<sup>9</sup>); 121.10 (C<sup>7</sup>); 120.07 (C<sup>11</sup>); 119.35 (C<sup>13</sup>); 42.43 (C<sup>16</sup>); 34.96 (C<sup>23</sup>); 30.86 (C<sup>17</sup>, C<sup>24</sup>).

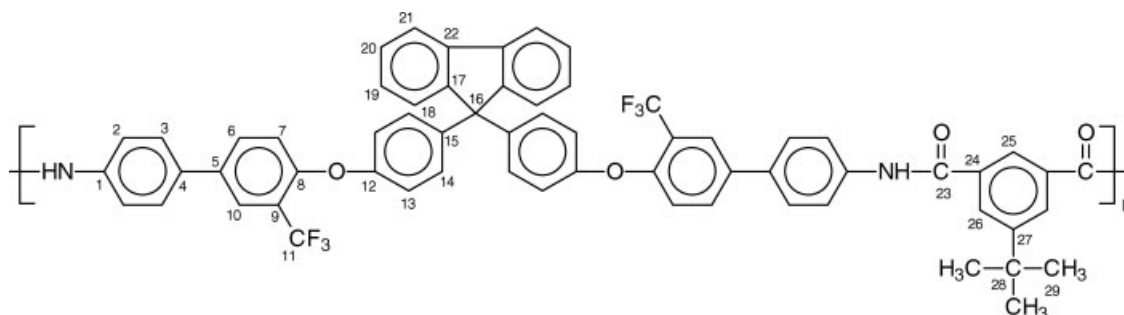
### Polyamide S2



Anal. Calcd for  $(\text{C}_{53}\text{H}_{36}\text{F}_{12}\text{O}_4\text{N}_2)_n$  (992.885  $\text{g mol}^{-1}$ )<sub>n</sub>: C, 64.11; H, 3.65; N, 2.82; F, 22.96; O, 6.44. Found: C, 63.92; H, 3.63; N 2.80. FTIR (KBr) ( $\text{cm}^{-1}$ ): 3316.02, (N–H stretching); 3048.63 (aromatic C–H stretching); 2964.57, (aliphatic C–H stretching); 1677 (C=O stretching); 1249.05 (asymmetric C–O–C stretching); 1053.60 (symmetric C–O–C stretching); 1604.28 (C=C ring stretching band); 1135.05 (C–F stretching).  $^1\text{H-NMR}$  (Py- $d_5$ ) (500MHz)  $\delta$  (ppm): 11.48 (s, 2H, –NH); 9.03 (s, 1H, H<sup>20</sup>); 8.46 (s, 2H, H<sup>21</sup>); 8.32–8.31 (d, 4H,  $J = 8.25$

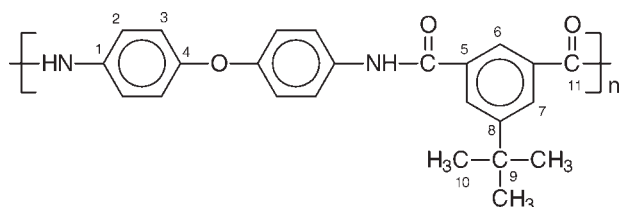
Hz, H<sup>2</sup>); 8.12 (s, 2H, H<sup>10</sup>); 7.90–7.89 (d, 2H,  $J = 8.25$  Hz, H<sup>6</sup>); 7.81–7.79 (d, 4H,  $J = 8.25$  Hz, H<sup>14</sup>); 7.62–7.61 (d, 4H,  $J = 8.3$  Hz, H<sup>3</sup>); 7.30–7.28 (d, 6H,  $J = 8.35$  Hz, H<sup>13</sup>, H<sup>7</sup>); 1.15 (s, 9H, H<sup>24</sup>).  $^{13}\text{C-NMR}$  (Py- $d_5$ ) (500MHz)  $\delta$  (ppm): 166.83 (C<sup>18</sup>); 158.02 (C<sup>12</sup>); 153.35 (C<sup>8</sup>); 152.13 (C<sup>22</sup>); 140.24 (C<sup>1</sup>); 137.10 (C<sup>15</sup>); 136.38 (C<sup>19</sup>); 134.50 (C<sup>4</sup>); 132.40 (C<sup>11</sup>); 132.24 (C<sup>17</sup>); 128.57 (C<sup>6</sup>); 128.28 (C<sup>5</sup>); 127.72 (C<sup>14</sup>); 125.71 (C<sup>10</sup>); 125.31 (C<sup>20</sup>); 125.17 (C<sup>9</sup>); 123.00 (C<sup>3</sup>); 122.35 (C<sup>7</sup>); 122.10 (C<sup>16</sup>); 121.88 (C<sup>2</sup>); 121.56 (C<sup>21</sup>); 34.97 (C<sup>23</sup>); 30.86 (C<sup>24</sup>).

## Polyamide S3



Anal. Calcd for  $(C_{63}H_{44}F_6O_4N_2)_n$  (1007.059 g mol<sup>-1</sup>)<sub>n</sub>: C, 75.13; H, 4.4; N, 2.78; F, 11.32; O, 6.35. Found: C, 75.05; H, 4.37; N 2.76. FTIR (KBr) (cm<sup>-1</sup>): 3326.67, (N—H stretching); 3039.24, (aromatic C—H stretching); 2962.38, (aliphatic C—H stretching); 1676.8 (C=O stretching); 1246.44 (asymmetric C—O—C stretching); 1133.70; 1052.85 (symmetric C—O—C stretching); 1596.13 (C=C ring stretching band); 1133.70 (C—F stretching). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>) (300MHz) δ (ppm): 10.58 (s, 2H, —NH); 8.49 (s, 1H, H<sup>25</sup>); 8.21 (s, 2H, H<sup>26</sup>); 7.99 (s, 10H, H<sup>10</sup>, H<sup>6</sup>, H<sup>3</sup>, H<sup>21</sup>); 7.65 (s, 4H, H<sup>14</sup>); 7.50 (s, 2H, H<sup>20</sup>); 7.40 (s, 2H, H<sup>18</sup>); 7.34 (s, 2H, H<sup>19</sup>); 7.23 (s, 4H, H<sup>2</sup>); 7.03 (s, 6H, H<sup>7</sup>, H<sup>13</sup>); 1.14 (s, 9H, H<sup>29</sup>). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>) (300MHz) δ (ppm): 165.47 (C<sup>23</sup>); 162.27 (C<sup>12</sup>); 154.82 (C<sup>8</sup>); 153.48 (C<sup>17</sup>); 151.45 (C<sup>22</sup>, C<sup>27</sup>); 150.44 (C<sup>1</sup>); 141.43 (C<sup>25</sup>); 139.49 (C<sup>15</sup>); 139.01 (C<sup>4</sup>); 135 (C<sup>19</sup>); 133.31 (C<sup>6</sup>); 131.97 (C<sup>5</sup>); 129.48 (C<sup>14</sup>); 127.98 (C<sup>18</sup>); 126.91 (C<sup>20</sup>, C<sup>21</sup>); 125.99 (C<sup>26</sup>); 125.20 (C<sup>23</sup>); 124.63 (C<sup>10</sup>); 121.59 (C<sup>24</sup>); 120.94 (C<sup>2</sup>); 120.49 (C<sup>9</sup>); 120.10 (C<sup>11</sup>, C<sup>7</sup>); 118.76 (C<sup>13</sup>); 63.94 (C<sup>16</sup>); 34.87 (C<sup>28</sup>); 30.97 (C<sup>29</sup>).

## Polyamide S4

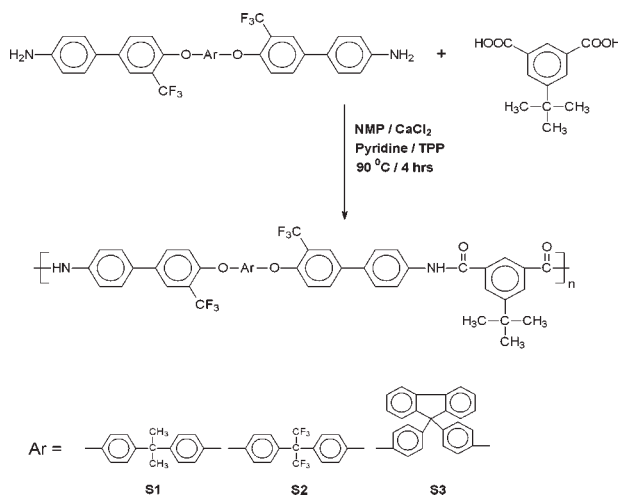


Anal. Calcd for  $(C_{24}H_{22}O_3N_2)_n$  (386.454g mol<sup>-1</sup>)<sub>n</sub>: C, 74.59; H, 5.73; N, 7.24; O, 12.41. Found: C, 74.42; H, 5.70; N 7.19. FTIR (KBr) (cm<sup>-1</sup>): 3294, (N—H stretching); 3060.74 (aromatic C—H stretching); 2961.09 (aliphatic C—H stretching); 1657 (C=O stretching); 1230.16 (asymmetric C—O—C stretching); 1165.95 (symmetric C—O—C stretching); 1599.10 (C=C ring stretching band); <sup>1</sup>H-NMR

(DMSO-*d*<sub>6</sub>) δ (ppm) 10.49 (s, 2H, —NH); 8.43 (s, 1H, H<sup>6</sup>); 8.17 (s, 2H, H<sup>7</sup>); 7.84 (d, 4H, H<sup>2</sup>); 7.08 (d, 4H, H<sup>3</sup>); 1.42 (s, 9H, H<sup>10</sup>). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>) (300MHz) δ (ppm): 165.31 (C<sup>11</sup>); 153.09 (C<sup>8</sup>); 151.46 (C<sup>4</sup>); 135.06 (C<sup>1</sup>); 134.62 (C<sup>5</sup>); 127.50 (C<sup>7</sup>); 124.43 (C<sup>6</sup>); 122.45 (C<sup>3</sup>); 118.73 (C<sup>2</sup>); 34.92 (C<sup>9</sup>); 30.95 (C<sup>10</sup>).

## RESULTS AND DISCUSSION

The polyamides were prepared by the typical phosphorylation reaction.<sup>26,28</sup> Equimolar amount of various synthesized diamines were reacted with 5-*t*-butyl isophthalic acid in NMP in presence of pyridine and TPP as condensing agent. CaCl<sub>2</sub> was added to control the molecular weight by forming the complex like CaCl<sub>2</sub>.*n*Py. Scheme 1 describes the synthesis of the polyamides and their structure. A model polymerization was also carried out by the reaction of ODA with 5-*t*-butyl isophthalic acid under same experimental condition to compare the properties of this new series of polymers.



**Scheme 1** The synthesis step of the polymers (S1-S3).

**TABLE I**  
Molecular Weight (GPC) and Inherent Viscosity of the Polymers

Polymer	Yield (%)	$M_n$	$M_w$	PDI	$\eta_{inh}$ (dL g <sup>-1</sup> )
S1	99	61,000	1,52,000	2.49	0.93
S2	95	60,000	1,46,000	2.43	0.80
S3	99	42,000	1,14,000	2.71	0.88
S4	99	17,000	45,000	2.65	0.41

The polyamides were obtained in almost quantitative yields Table I. The inherent viscosities of the synthesized polyamides (S1–S4) are within the range of 0.41–0.93 dL/g. This viscosity data indicates that the high molecular weight polymer is formed. The molecular weight is high enough, judging from the high viscosity of the polymer and toughness of the polymer membrane. The lower viscosity of the synthesized polymer S2 is due to the increasing number of electro withdrawing trifluoromethyl groups present in the 4,4'-(Hexa fluoro isopropylidene)diphenol moiety. The trifluoromethyl group decreases the inter-chain interaction with increasing fluorine atom.<sup>27</sup> The bulky fluorene moiety increases the hydrodynamic volume, because of which polymer S3 shows higher inherent viscosity than S2. Because of the good solubility of the polymers in DMAC/2% H<sub>2</sub>O/ (3g/L) LiCl, GPC measurement has been done to estimate the molar masses of the polymers as well as polydispersity index. PDI values of all these polymer was in the range expected for a condensation polymer.

The structural characterizations of the polymers were carried out by means of FTIR spectroscopy and elemental analysis. The N–H stretching frequencies around 3320–3140 cm<sup>-1</sup> of the clearly indicate the formation of polyamides. The absence of IR stretching band above 3400 cm<sup>-1</sup> indicates there is no free amine. In polymer, because of hydrogen bonding interaction, the N–H stretching band shows around 3320–3140 cm<sup>-1</sup> instead of ~ 3430 cm<sup>-1</sup>. The stretching band observed around 1650–1680 cm<sup>-1</sup> corresponds to the –C=O stretching of amide bond; 1230–1250 cm<sup>-1</sup> to the characteristic to the ether band (asymmetric C–O–C stretching). The result of elemental analyses (C, H, and N) of all the polyamides (S1–S4) strongly supports the structure.

**TABLE III**  
Mechanical Properties of the Polymers

Polymer	Tensile strength (MPa)	Elongation at break (%)	Modulus (GPa)
S1	58	10	1.39
S2	72	14	1.32
S3	69	09	1.30
S4	66	04	1.35

<sup>1</sup>H- and <sup>13</sup>C-NMR spectra also support the structure of the polymers. All polymers showed a singlet above 10 ppm in proton NMR spectra corresponds to amide proton that generates due to polymer forming reaction. Detail spectral characterization is given in experimental section.

#### Polymer solubility

The solubility of the polyamides was tested qualitatively in various organic solvents. The solubility properties of the polyamides are reported in Table II. Some of the polyamides exhibited excellent solubility at the ambient temperature in polar solvents such as NMP, DMF, DMAc, and DMSO, whereas some are partially soluble and some are insoluble. The insolubility of the polyamides in CHCl<sub>3</sub> is attributed to the low value of dielectric constant of the solvent. From Table II, it was noticed that the introduction of trifluoromethyl group and the bulky group in the polymer backbone are especially effective for the high solubility, irrespective of the diacid component. The higher solubility of these polymers may be attributed to the bulky CF<sub>3</sub> groups, and fluorene moiety which increased the disorder in the chain and hindered dense chain packing, thereby reducing dense chain interactions to enhance solubility.<sup>15,27</sup>

#### Mechanical properties

The mechanical properties of all the polyamide films are shown in Table III. These polyamides showed tensile strength up to 72 MPa, elongation at break up to 14%, and Young modulus up to 1.39 GPa which depended on the exact repeating unit structure. The polyamide derived from diamine containing

**TABLE II**  
Solubility of the Polymers in Different Solvents

Polymer	NMP	DMF	DMAc	Pyridine	DMSO	THF	DCM	Chloroform
S1	+	+	+	+	±	+	±	–
S2	+	+	+	+	±	+	±	–
S3	+	+	+	+	+	+	±	–
S4	+	+	±	+	+	–	±	–

Solubility: (+) Soluble at room temperature; (±), partially soluble; (–), insoluble.

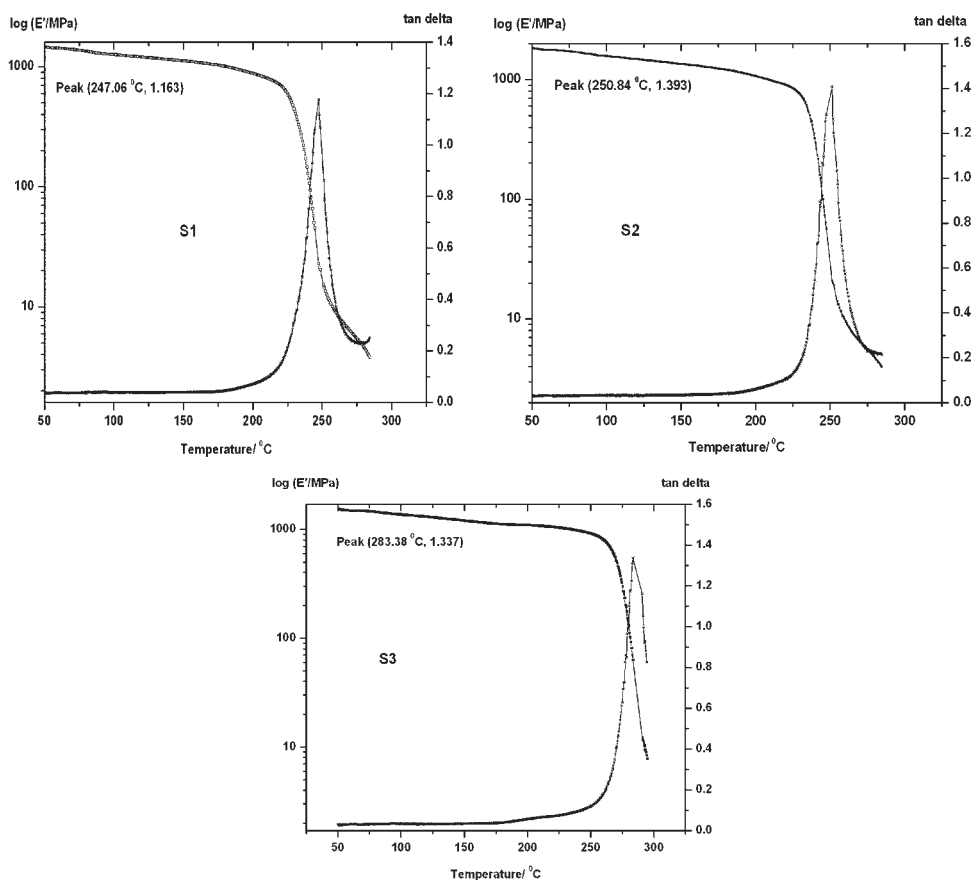


Figure 1 DMA plots of the polymers S1, S2 and S3.

fluorene unit showed less elongation at break (9%) in the series. This may be due to the rigid nature of the fluorene groups. The polyamide S4 exhibit least elongation and break this may be due to less no of flexible ether linkage in the polymer repeating unit structure.

DMA analysis is the technique to know about the polymer properties during dynamic application. It tells about  $T_g$  as well as storage modulus values of the polymers and its change with temperature. The  $\tan \delta$  peak at 1 Hz of these polymers was used to calculate the  $T_g$ . The DMA analysis of all these polymers reported in this investigation is showed in

Figure 1. It was found that very good retention of storage modulus of the polymer up to the glass transition temperature.

#### Thermal behavior

The thermal stability and  $T_g$  of the polymers were evaluated by thermogravimetric analysis (TGA) and DSC, respectively. The polymer showed excellent thermal stability as expected in case of aromatic polyamides. The values are summarized in Table IV. The TGA results indicated that the decomposition temperature, at which 5 and 10% loss of mass was

TABLE IV  
Thermal Properties of the Polymers

Polyamide	$T_g$ (°C)		$T_d$ (°C) <sup>a</sup>		$T_m$ (°C)	Char yield <sup>b</sup>
	DSC	DMA	5% Mass loss	10% Mass loss		
S1	250	247	363	475	352	68.89
S2	252	251	421	489	356	58.81
S3	273	283	369	481	349	70.64
S4	268	–	273	415	–	63.86

<sup>a</sup> Temperature was recorded with TGA.

<sup>b</sup> Char yield at 700°C under nitrogen.

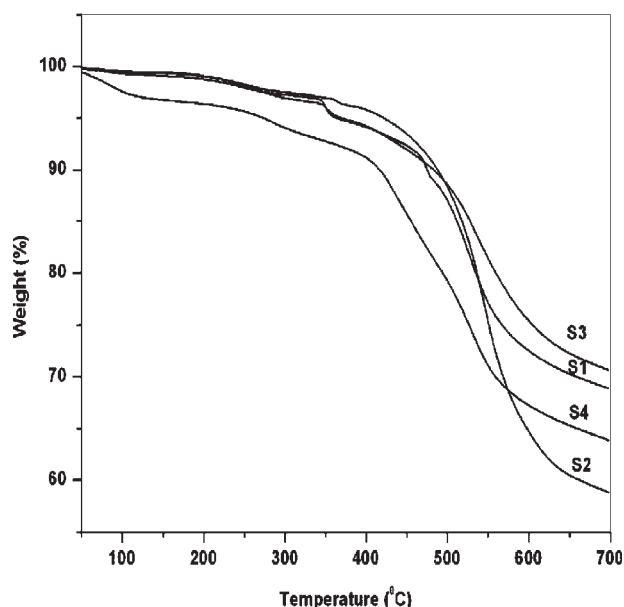


Figure 2 TGA thermogram of the polymers.

observed, for these polymers are in the range 273°C–421°C and 415°C–489°C. The higher thermal stability of 4,4'-(hexa fluoro isopropylidene)diphenol containing polyamides obtained from TGA thermograms has been shown in Figure 2, is due to excess trifluoromethyl groups, their rigid structure and may be due to their higher degree of aromaticity. The char yield at 700°C for all the polymers under nitrogen atmosphere exceeds 58%. The high char yield is due to the anaerobic heating of the polymers that produce carbonaceous material. The lower thermal stability of the polymer S4 is attributed to the low molecular weight of this polymer.

The glass transition temperatures ( $T_g$ ) of the polyamides were evaluated by DSC and DMA. The  $T_g$ 's of

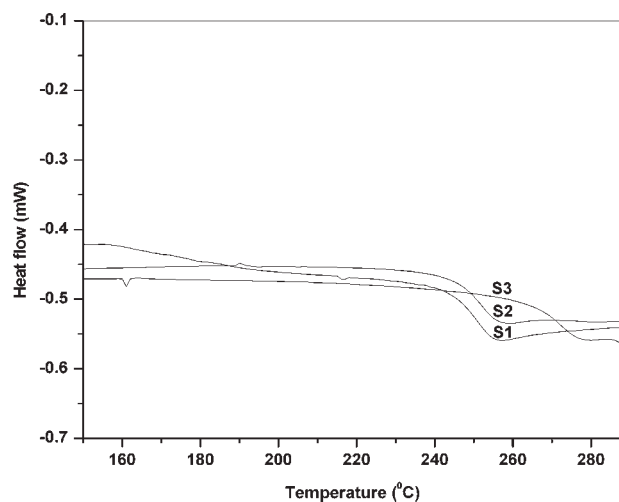


Figure 3 DSC thermogram of the polymers (S1-S3).

all polymers followed the same trend both in DSC and DMA. The glass transition temperature values are summarized in Table IV. DSC measurements were conducted at 20°C/min in N<sub>2</sub> atmosphere, and second heating scans were used to evaluate the  $T_g$ . The glass transition temperature of these polymers were in the range of 250–273°C obtained from DSC measurement has been shown in Figure 3. It is well known that with the increase in rigidity  $T_g$  increases.<sup>29</sup> Polymer derived from 4,4'-(hexa fluoro isopropylidene)diphenol containing diamine exhibited a little bit higher  $T_g$  compared to the analogous 4,4'-isopropylidenediphenol containing diamine, may be attributed due to the bulky nature of 4,4'-(hexa fluoro isopropylidene)diphenol (covalent radii of F = 0.064 nm, covalent radii of H = 0.037 nm).<sup>30</sup> The fluorene moiety could result in highest  $T_g$  among the series because of highest steric strain and that gives a higher barrier to chain rotation than that with a smaller one.<sup>29,31</sup> The higher barrier to rotation in the polymer membranes inhibits the local segmental motion.

Crystalline melting  $T_m$  in these polymers has been studied. The flexibility of polymer chains and bulkiness of the side chains is an important factor in determining the melting point of the polymers.  $T_m$  is related to heat of fusion  $\Delta H_m$  and entropy of fusion  $\Delta S_m$ . In general, in case of polyamides molar cohesion cannot account for high value of  $T_m$ .<sup>32</sup> These results from low liquid state entropy ( $\Delta S_m$ ), which arises from partial retention of hydrogen bonding in the melt and from chain stiffening due to the tendency for resonance. Out of polymers S1–S3; S2 shows highest melting temperature (356°C) because of extra hydrogen bonding in the melt and higher van der Waals volume.<sup>33</sup> The melting temperature of polymer S1 shows slightly lower melting temperature (352°C) than S2 but higher than S3. This might be due to higher van der Waals force in S1 for the presence of methyl substituent in the polymer backbone.

### X-ray analysis

The characterizations of molecular packing for the synthesized polyamides were measured by using X-ray diffractometer. X-ray measurements of the polymer films indicated that all the aromatic polyamides

TABLE V  
Percent Crystallinity of the Polymer Membranes

Sample	$d$ -Spacing (Å)	Film quality	Crystallinity (%)
S1	2.10	Clear, flexible	5.31
S2	2.10	Clear, flexible	7.63
S3	2.10	Clear, flexible	9.07
S4	2.10	Clear, brittle	10.19

were essentially semicrystalline in nature, which has been shown in Table V. *d*-spacing (Å) values and film quality of these polyamide membranes indicates that these are quite dense even in the presence of bulky units in the polymer backbone and homogeneous in nature. The van der Waals volumes of the groups attached to the polymer backbone chain has been shown in the Table VI.<sup>33</sup> Though in the polyamides S2 and S3 groups attached having van der Waals volumes are approximately same 88.5 and 87.7, but due to  $\Pi$  interaction of the chains in S3 makes it more crystalline. S1 is less crystalline though van der Waals volume is less. This might be due to the more hydrogen bonding interaction in S2 in comparison to S1. Polyamide S4 is most crystalline, most crystalline nature of S4 is attributed to the absence of bulky units.

### Rheology study

We have measured the melt viscosity of the synthesized polymer samples S1–S3 at their melting temperature. It has been observed that the polymer melts exhibits non-Newtonian (pseudoplastic) behavior and shows how the viscosity decreases with increasing the applied shear rate. Molecular weight data of the polymers as obtained from GPC supports the initial melt viscosity data of the polymers; melt viscosity increases with increase in molecular weight (S1 > S2 > S3).

### Water absorption study

The water absorption data of the synthesized polyamide films was measured at 30°C  $\pm$  1°C and has been shown in Table VII. The water absorption value of the synthesized polyamides lies between 0.15% and 1.47%. The lowest water absorption data of sample S2 can be due to the presence of more fluorine atoms as  $-\text{CF}_3$  groups (having hydrophobic nature) compared to the other polymers. The polyamide S4 having no fluorine absorbs maximum % of water compared to the other synthesized polymers.<sup>34</sup>

## CONCLUSIONS

Several novel processable fluorine containing aromatic polyamides having high molecular weights were successfully prepared by the direct polycon-

TABLE VI  
van der Waals Volume of Different Groups

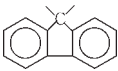
Group	$V_w$	$\Pi$ -Interaction	H-Bonding
$\text{C}(\text{CH}_3)_2$	30.7	No	No
$\text{C}(\text{CF}_3)_2$	88.5	No	Yes
	87.7	Yes	No

TABLE VII  
Water Absorption Values of the Polymers

Polyamide	Water absorption (%)	
	72 (h)	120 (h)
S1	0.27	0.31
S2	0.15	0.15
S3	0.60	0.62
S4	1.47	1.47

densation of 5-*t*-butyl isophthalic acid with various synthesized aromatic diamines containing pendent trifluoromethyl groups. These polyamides showed good thermal stability, excellent solubility in polar organic solvents. Film casted in DMAc showed very good mechanical properties. The films exhibit low water absorption rate. These synthesized polyamides can be applied for pervaporation separation of alcohol and water mixtures and may find application in gas separation. The studies are under progress. Thus, the synthesized aromatic polyamides are considered as new candidates for processable high-performance polymeric materials.

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