

## Fluorinated Polybenzimidazopyrrolones with Excellent Alkaline-Hydrolysis Resistance

Liming Tao,<sup>1,2</sup> Haixia Yang,<sup>2</sup> Jingang Liu,<sup>2</sup> Lin Fan,<sup>2</sup> Shiyong Yang<sup>2</sup>

<sup>1</sup>State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

<sup>2</sup>Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Correspondence to: S. Yang (shiyang@iccas.ac.cn) or H. Yang (yanghx@iccas.ac.cn).

**ABSTRACT:** Two novel aromatic tetraamines containing bulky lateral phenyl unit and multiple trifluoromethyl groups, 1,1-bis[4-(3',4'-diaminophenoxy)phenyl]-1-(3''-trifluoromethylphenyl)-2,2,2-trifluoroethane (6FTA) and 1,1-bis[4-(3',4'-diaminophenoxy)phenyl]-1-[3'',5''-bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane (9FTA) were synthesized and characterized. A series of fluorinated aromatic polybenzimidazopyrrolones (polypyrrolones, PPys) were synthesized via a two-step polycondensation procedure. The inherent viscosities of the precursors, poly(amide amino acid) (PAAA), ranged from 0.39 dL/g to 0.54 dL/g. All the FPPys were amorphous. The freestanding FPPy films could be prepared, which exhibited good thermal stability with the glass transition temperature of 315–389°C, the temperatures of 5% weight loss ( $T_{5\%}$ ) of 497–535°C in nitrogen and residual weight retention at 700°C over 60%. All the FPPy films exhibited excellent alkaline-hydrolysis resistance which retained their original shapes and toughness after boiling 7 days in 10% sodium hydroxide solution. Also after boiling 8 h in 10% sodium hydroxide solution, the tensile strength could retain as high as 56% of the original values. The alkaline-hydrolysis resistance was much better than the polyimides which had similar chemical structures. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40041.

**KEYWORDS:** polyimides; polycondensation; films

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### INTRODUCTION

As a kind of high performance polymer, aromatic polyimides (PIs) are well known for their high thermal stability, excellent mechanical properties, and outstanding dimensional stability.<sup>1–4</sup> PIs have been used as an interlayer dielectric in the electronics industry for several decades due to their outstanding combinational properties as mentioned above. However, PIs are fragile to alkaline hydrolysis. Early researchers<sup>5</sup> have found that Kapton film would be completely hydrolyzed after boiling in hydrazine to produce two initial monomers, pyromellitic anhydride (PMDA) and 4,4'-oxydianiline (ODA), quantitatively. Stephens et al. have studied the kinetics of alkaline hydrolysis of a PI surface.<sup>6</sup> Quantification of the number of carboxylic acid groups formed on the modified PI surface was accomplished by analysis of data from contact angle titration experiments. The alkaline hydrolytic mechanism involved nucleophilic attack of OH<sup>-</sup> on a carbonyl carbon of the imide ring to form a reactive intermediate, followed by decomposition to the observed poly(amic acid). As a result, when PI was used in alkaline environment, the fragility to alkaline hydrolysis must be considered carefully, although it was useful in alkaline etching or surface modification of PI surfaces.<sup>7–10</sup>

On the other hand, polypyrrolones (PPys) are another kind of high performance heteroaromatic polymers. They are typically synthesized by further thermal cyclization of PI backbone with amine groups in the  $\alpha$ -position to the imides groups. They are characterized by many excellent properties: high radiation resistance (above 10<sup>10</sup> rad),<sup>11</sup> heat resistance,<sup>12</sup> ablation resistance,<sup>13</sup> excellent alkaline-hydrolysis stability,<sup>14</sup> and high permeability or selectivity for gases.<sup>15–18</sup> They are also outstanding insulators with high thermal stability and turned to be conductors after pyrolyzed at elevated temperatures. The excellent combinational properties have attracted much attention for applications such as gas/fluid separating membranes, packaging materials in microelectronics and conducting materials.<sup>19–23</sup> More importantly, as compared with PIs, PPys have better alkaline hydrolytic resistance, which has been revealed in our lab.<sup>14</sup> The alkaline hydrolytic resistances together with the excellent combinational properties of PPys mentioned above make them proper alternatives to PIs when used in alkaline environment.

However, the rigidity of PPys resulting from their ladder heteroaromatic backbones restricts their solubility in organic solvents, thus retaining their poor processability, which has been the major limitation for the versatile application of PPys. Till now, only a limited number of PPy derivatives have been prepared in

an effort to enhance the processability of PPys. Formation of semiladder structures<sup>24</sup> and introduction of a flexible segment in PPys' backbones<sup>25–27</sup> have been found to be effective approaches for improving their solubility and processability, as illustrated in a series of research work by Sek D et al. To improve the solubility of PPys, they have introduced single-chain segments with groups such as amide, ether or ester between ladder segments. On the other hand, this modification may influence the thermal and chemical stability of PPys. For example, the poly(esterimidazopyrrolone)s<sup>25</sup> has been synthesized by one-step high temperature polycondensation because of its good solubility in *m*-cresol or *p*-chlorophenol. However, the thermal stability of the polymers was greatly damaged and the temperatures of 10% weight loss ( $T_{10\%}$ ) were less than 350°C. Also we can deduce that the alkaline-hydrolysis resistance of these PPys would be destroyed because the amide or ester groups were frangible to alkaline. Similarly, Wang et al. have designed four aromatic tetraamine monomers possessing flexible ether linkages and the resulting PPys were completely soluble in phenolic solvents.<sup>28</sup>

In our continuous work on microelectronic packaging materials, this laboratory had sought to find novel PPY structures with excellent combinational properties, which can be used as an alternative to PI in alkaline environments. A series of pyridine-bridged PPys were synthesized based on new tetraamines,<sup>14,29,30</sup> but the solubility of these PPys had not been enhanced and the mechanical properties were not so good. We had also introduced asymmetric biphenyl moiety ( $\alpha$ -BPDA) into the backbone of PPys.<sup>31</sup> However, the solubility of PPys had not been enhanced obviously, although the PPys showed excellent thermal stability. It is well known that the introduction of  $-\text{CF}_3$  into PIs can obviously enhance the properties.<sup>32</sup> Therefore, developing a kind of fluorinated PPys containing  $-\text{CF}_3$  groups seems to be a reasonable approach to modify properties of PPys.

In this work, two novel fluorinated tetraamine monomers, 1,1-bis[4-(3',4'-diaminophenoxy)phenyl]-1-(3''-trifluoromethylphenyl)-2,2,2-trifluoroethane (6FTA) and 1,1-bis[4-(3',4'-diaminophenoxy)phenyl]-1-[3'',5''-bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane (9FTA) were synthesized. The thermal, mechanical properties, especially the alkaline resistance of the new PPys derived from the tetraamines were investigated in detail.

## EXPERIMENTAL

### Materials

5-Chloro-2-nitroaniline was purchased from Alfa Aesar and used as received. 1,1-Bis(4'-hydroxyphenyl)-1-(3'-trifluoromethylphenyl)-2,2,2-trifluoroethane (6F-bisphenol) and 1,1-bis(4'-hydroxyphenyl)-1-(3',5'-ditrifluoromethylphenyl)-2,2,2-trifluoroethane (9F-bisphenol) were synthesized in our laboratory according to a previously reported method.<sup>33</sup> 4,4'-Oxydiphthalic anhydride (ODPA, Shanghai Chemspec) was recrystallized from acetic anhydride before use. 2,3,3',4'-Biphenyltetracarboxylic dianhydride ( $\alpha$ -BPDA) was purchased from Beijing POME Corporation and dried in a vacuum oven at 180°C for 12 h before use. 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA, Acros) was recrystallized from acetic anhydride and dried in vacuum at 160°C for 10 h. 2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA) was purchased from Beijing POME Corporation and recrystallized from acetic anhydride before use.

Anhydrous potassium carbonate was purchased from Beijing Chemical Reagents, China and used as received. Commercially available *N,N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidinone (NMP) were purified by vacuum distillation over  $\text{CaH}_2$  and stored over 4Å molecular sieves before use. Other reagents were used as received.

### Measurements

The NMR spectra were performed on a Bruker Avance 600 Spectrometer operating at 600 MHz for  $^1\text{H}$  and 150 MHz for  $^{13}\text{C}$  NMR, using  $\text{DMSO}-d_6$  or  $\text{CDCl}_3$  as the solvents. Solid-state  $^{13}\text{C}$  NMR spectra were performed on a Bruker Avance III Spectrometer operating at a frequency of 100 MHz and using cross-polarization/magic angle spinning (CP/MAS). The MAS rate was set at 5.0 kHz to minimize spinning sideband overlap. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer 782 Fourier transform spectrophotometer. Ultraviolet-visible (UV-vis) spectra were recorded on a Hitachi U3210 spectrophotometer at room temperature. Before testing, film samples were dried at 110°C for 1 h to remove the absorbed moisture. Mass spectra were recorded on an AEI MS-50 mass spectrometer. The wide-angle X-ray diffraction (XRD) was conducted on a Rigaku D/max-2500 X-ray diffractometer with  $\text{Cu}/\text{K}\alpha_1$  radiation, operated at 40 kV and 200 mA. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) were recorded on a TA Q series thermal analysis system in nitrogen at a heating rate of 20°C/min. Dynamic mechanical analysis (DMA) was recorded on a TA Q-800 thermal analysis system in nitrogen at a heating rate of 5°C/min. Inherent viscosities ( $\eta_{\text{inh}}$ ) were measured with an Ubbelohde viscometer with 0.5 g/dL NMP solution at 30°C. The absolute viscosities ( $\eta_a$ ) were measured using a Brookfield DV-II+ viscometer at 25°C and the solid content was 12%. The mechanical properties were measured on an Instron-5567 Tensile Apparatus with  $80 \times 10 \times 0.05 \text{ mm}^3$  specimens in agreement with GB/T 1447–2005 at a drawing rate of 2.0 mm/min. Water uptakes were determined by weighing the changes of FPPy film ( $30 \times 10 \times 0.05 \text{ mm}^3$ ) before and after immersion in water at 25°C and 100°C for 24 h.

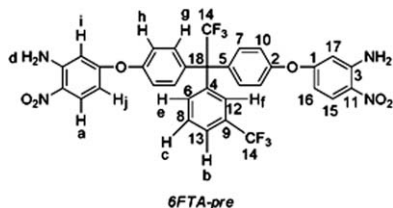
The alkaline-hydrolysis resistance of FPPys was qualitatively investigated according to the following method. The FPPy film sample ( $30 \times 10 \times 0.05 \text{ mm}^3$ ) was immersed in boiling 10% NaOH solution in a 250-mL, round-bottom flask fitted with a condenser. The PI film samples with similar structures were tested with the same procedure for comparison. The time of initial ( $t_i$ ) and complete ( $t_w$ ) hydrolysis was recorded, and  $t_i$  was defined as the time when dregginess appeared in the solution and  $t_w$  was the time when no tested film was left.

Also the mechanical property of the alkaline hydrolyzed FPPy films was investigated as the following method. The FPPy film samples ( $80 \times 10 \times 0.05 \text{ mm}^3$ ) were immersed in boiling 10% NaOH solution for different time and the film samples were rinsed with water and dried with blotting paper. Then the mechanical properties were measured on an Instron-5567 Tensile Apparatus as mentioned above.

### Monomer Synthesis

**1,1-Bis[4-(3'-amino-4'-nitrophenoxy)phenyl]-1-(3''-trifluoromethylphenyl)-2,2,2-trifluoroethane (6FTA-pre).** A mixture of 6F-bisphenol (41.23 g, 0.10 mol), 5-chloro-2-nitroaniline (36.24

g, 0.21 mol), anhydrous potassium carbonate (33.20 g, 0.24 mol) and anhydrous DMAc (400 mL) were added to a four-necked, 1000 mL, round-bottom flask fitted with a nitrogen inlet pipet, a thermometer, a condenser and a mechanical stirrer. The mixture was heated to 130–135°C in nitrogen for 24 h. Then some of the solvent was removed by vacuum distillation. The mixture was poured into an excess amount of ice-water. The yellow precipitate was collected by filtration, washed repeatedly with water, and air dried. Then the crude product was purified by silica gel column with a 1 : 8 (v/v) mixture of ethyl acetate and petroleum ether (60–90°C) as the eluent to give yellow powders: 51.30 g [Yield: 75%; mp: 155.8°C by DSC in N<sub>2</sub>, 10°C/min].

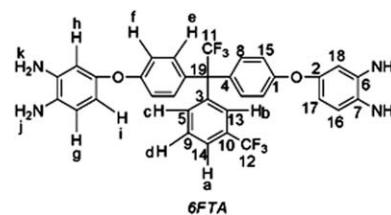


FT-IR (KBr pellet, cm<sup>-1</sup>): 3484, 3374, 3091, 1632, 1605, 1572, 1504, 1434, 1379, 1334, 1257, 1233, 1190, 1153, 1080, 982, 835. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 8.03 (*d*; 2H, H<sub>a</sub>), 7.87 (*d*; 1H, H<sub>b</sub>), 7.75 (*t*; 1H, H<sub>c</sub>), 7.52 (*s*; 4H, H<sub>d</sub>), 7.45 (*d*; 1H, H<sub>e</sub>), 7.33 (*s*; 1H, H<sub>f</sub>), 7.26 (*d*; 4H, H<sub>g</sub>), 7.15 (*d*; 4H, H<sub>h</sub>), 6.50 (*d*; 2H, H<sub>i</sub>), 6.33 (*q*; 2H, H<sub>j</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 162.8(C<sup>1</sup>), 154.8(C<sup>2</sup>), 148.8(C<sup>3</sup>), 140.8(C<sup>4</sup>), 135.1(C<sup>5</sup>), 134.2(C<sup>6</sup>), 131.8(C<sup>7</sup>), 130.5(C<sup>8</sup>), 129.6(*q*, <sup>2</sup>J<sub>C-F</sub> = 31.5 Hz, C<sup>9</sup>), 128.8(C<sup>10</sup>), 127.0(C<sup>11</sup>), 125.9(C<sup>12</sup>), 125.4(C<sup>13</sup>), 124.5(*q*, <sup>1</sup>J<sub>C-F</sub> = 284.2 Hz, C<sup>14</sup>), 120.6(C<sup>15</sup>), 107.4(C<sup>16</sup>), 104.8(C<sup>17</sup>), 64.1(*q*, <sup>2</sup>J<sub>C-F</sub> = 24.0 Hz, C<sup>18</sup>). TOF-MS (electron ionization, *m/e*, percentage of relative intensity): 684(M<sup>+</sup>, 40), 615[(M-69)<sup>+</sup>, 100]. Elem. Anal. Calcd. for C<sub>33</sub>H<sub>22</sub>F<sub>6</sub>N<sub>4</sub>O<sub>6</sub>: C, 57.90%; H, 3.24%; N, 8.18%. Found: C, 57.84%; H, 3.27%; N, 8.13%.

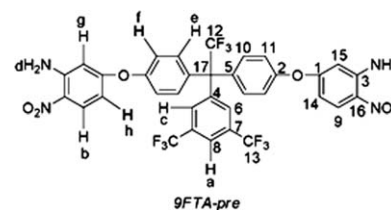
**1,1-Bis[4-(3',4'-diaminophenoxy)phenyl]-1-(3''-trifluoromethylphenyl)-2,2,2-trifluoroethane (6FTA).** A suspension solution of the purified precursor compound 6FTA-pre (20.54 g, 0.03 mol), 5% Pd/C (0.40 g) in ethanol (200 mL), and hydrazine monohydrate (20 mL) was stirred at 70–80°C within 30 min. The mixture was heated at reflux temperature for about 16 h. The reaction solution was filtered hot to remove Pd/C, and the filtrate was then distilled to remove the solvent. The obtained mixture was poured into distilled water to precipitate white powders that were dried in vacuum at room temperature to give 6FTA: 17.43 g [Yield: 93%].

FT-IR (KBr pellet, cm<sup>-1</sup>): 3413, 3342, 3050, 1626, 1605, 1504, 1440, 1330, 1293, 1242, 1181, 1153, 1080, 973, 866, 832, 705. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 7.80 (*d*; 1H, H<sub>a</sub>), 7.68 (*t*; 1H, H<sub>b</sub>), 7.42 (*d*; 1H, H<sub>c</sub>), 7.31 (*s*; 1H, H<sub>d</sub>), 6.97 (*d*; 4H, H<sub>e</sub>), 6.91 (*d*; 4H, H<sub>f</sub>), 6.52 (*d*; 2H, H<sub>g</sub>), 6.30 (*d*; 2H, H<sub>h</sub>), 6.15 (*q*; 2H, H<sub>i</sub>), 4.67 (*s*; 4H, H<sub>j</sub>), 4.38 (*s*; 4H, H<sub>k</sub>). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 159.3(C<sup>1</sup>), 146.9(C<sup>2</sup>), 141.6(C<sup>3</sup>), 137.2(C<sup>4</sup>), 134.1(C<sup>5</sup>), 132.4(C<sup>6</sup>), 132.0(C<sup>7</sup>), 131.2(C<sup>8</sup>), 130.4(C<sup>9</sup>), 129.7(*q*, <sup>2</sup>J<sub>C-F</sub> = 31.5 Hz, C<sup>10</sup>), 128.2(*q*, <sup>1</sup>J<sub>C-F</sub> = 284.4 Hz, C<sup>11</sup>), 125.7(C<sup>12</sup>), 125.5(C<sup>13</sup>), 124.5(*q*, <sup>1</sup>J<sub>C-F</sub> = 270.7 Hz, C<sup>14</sup>),

116.8(C<sup>15</sup>), 115.3(C<sup>16</sup>), 108.8(C<sup>17</sup>), 107.0(C<sup>18</sup>), 64.0(*q*, <sup>2</sup>J<sub>C-F</sub> = 23.4 Hz, C<sup>19</sup>). TOF-MS (electron ionization, *m/e*, percentage of relative intensity): 624(M<sup>+</sup>, 100), 555[(M-69)<sup>+</sup>, 23]. Elem. Anal. Calcd. for C<sub>33</sub>H<sub>26</sub>F<sub>6</sub>N<sub>4</sub>O<sub>2</sub>: C, 63.46%; H, 4.20%; N, 8.97%. Found: C, 63.40%; H, 4.22%; N, 8.94%.

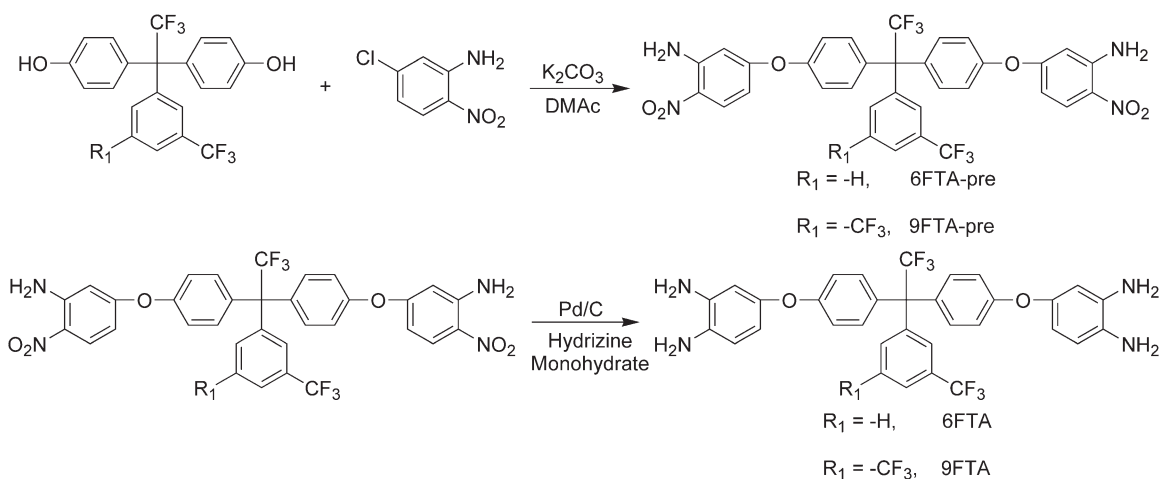


**1,1-Bis[4-(3'-amino-4'-nitrophenoxy)phenyl]-1-[3'',5''-bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane (9FTA-pre).** A mixture of 9F-bisphenol (24.02 g, 0.05 mol), 5-chloro-2-nitroaniline (18.98 g, 0.11 mol), anhydrous potassium carbonate (16.58 g, 0.12 mol) and anhydrous DMAc (260 mL) were added to a four-necked, 500 mL, round-bottom flask fitted with a nitrogen inlet pipet, a thermometer, a condenser and a mechanical stirrer. The mixture was heated to 130–135°C in nitrogen for 20 h. Then some of the solvent was removed by vacuum distillation. The mixture was poured into an excess amount of ice-water. The yellow precipitate was collected by filtration, washed repeatedly with water, and air dried. Then the crude product was purified by silica gel column with a 1 : 9 (v/v) mixture of ethyl acetate and petroleum ether (60–90°C) as the eluent to give yellow powders: 24.24 g [Yield: 70%; mp: 167–169°C by DSC in N<sub>2</sub>, 10°C/min].



FT-IR (KBr pellet, cm<sup>-1</sup>): 3492, 3367, 3083, 1636, 1605, 1578, 1507, 1431, 1367, 1340, 1278, 1233, 1153, 1019, 976, 897, 836, 686. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 8.37 (*s*; 1H, H<sub>a</sub>), 8.03 (*d*; 2H, H<sub>b</sub>), 7.60 (*s*; 2H, H<sub>c</sub>), 7.53 (*s*; 4H, H<sub>d</sub>), 7.28 (*d*; 4H, H<sub>e</sub>), 7.18 (*d*; 4H, H<sub>f</sub>), 6.52 (*d*; 2H, H<sub>g</sub>), 6.32 (*q*; 2H, H<sub>h</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 162.7(C<sup>1</sup>), 155.2(C<sup>2</sup>), 148.8(C<sup>3</sup>), 142.7(C<sup>4</sup>), 134.4(C<sup>5</sup>), 131.9(C<sup>6</sup>), 131.7(*q*, <sup>2</sup>J<sub>C-F</sub> = 33 Hz, C<sup>7</sup>), 129.9(C<sup>8</sup>, C<sup>16</sup>), 129.0(C<sup>9</sup>), 127.2(C<sup>10</sup>), 124.9(*q*, <sup>1</sup>J<sub>C-F</sub> = 287 Hz, C<sup>12</sup>), 123.5(*q*, <sup>1</sup>J<sub>C-F</sub> = 271 Hz, C<sup>13</sup>), 121.1(C<sup>11</sup>), 107.5(C<sup>14</sup>), 104.9(C<sup>15</sup>), 64.6(*q*, <sup>2</sup>J<sub>C-F</sub> = 20 Hz, C<sup>17</sup>). TOF-MS (electron ionization, *m/e*, percentage of relative intensity): 752(M<sup>+</sup>, 32), 683[(M-69)<sup>+</sup>, 100]. Elem. Anal. Calcd. for C<sub>34</sub>H<sub>21</sub>F<sub>9</sub>N<sub>4</sub>O<sub>6</sub>: C, 54.26%; H, 2.81%; N, 7.45%. Found: C, 54.22%; H, 2.83%; N, 7.44%.

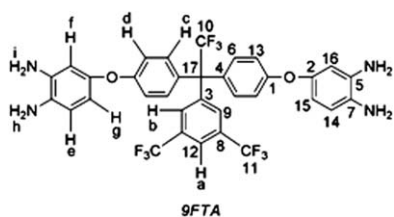
**1,1-Bis[4-(3',4'-diaminophenoxy)phenyl]-1-[3'',5''-bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane (9FTA).** A suspension solution of the purified precursor compound 9FTA-pre (22.58



**Scheme 1.** Synthesis of the fluorinated tetraamine monomers.

g, 0.03 mol), 5% Pd/C (0.40 g) in ethanol (200 mL) and hydrazine monohydrate (20 mL) was stirred at 70–80°C within 30 min. The mixture was heated at reflux temperature for about 16 h. The reaction solution was filtered hot to remove Pd/C, and the filtrate was then distilled to remove the solvent. The obtained mixture was poured into water to precipitate white powders that were dried in vacuum at room temperature to give the tetraamine 9FTA: 18.70 g [Yield: 90%].

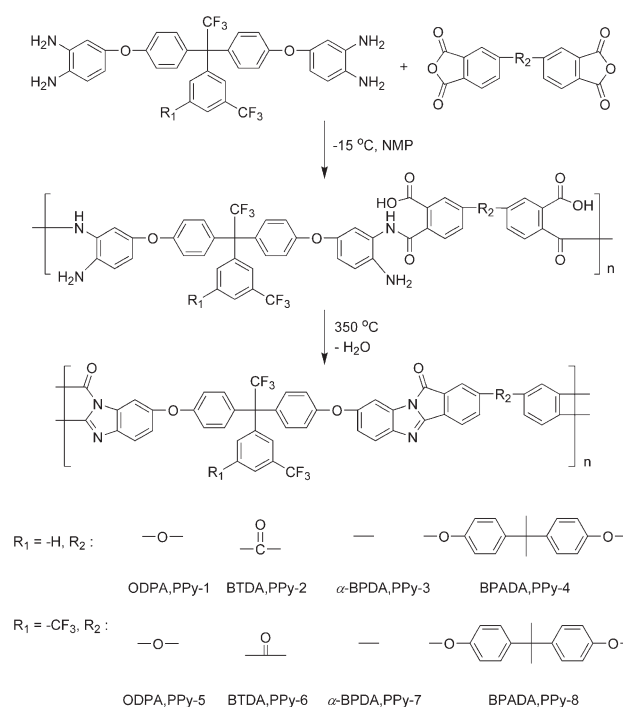
FT-IR (KBr pellet,  $\text{cm}^{-1}$ ): 3413, 3342, 3052, 1627, 1607, 1505, 1443, 1370, 1281, 1244, 1181, 1150, 972, 895, 836, 683.  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ , ppm): 8.28(*s*; 1H,  $\text{H}_a$ ), 7.56(*s*; 2H,  $\text{H}_b$ ), 6.98(*d*; 4H,  $\text{H}_c$ ), 6.92(*d*; 4H,  $\text{H}_d$ ), 6.50(*d*; 2H,  $\text{H}_e$ ), 6.28(*d*; 2H,  $\text{H}_f$ ), 6.13(*q*; 2H,  $\text{H}_g$ ), 4.66(*s*; 4H,  $\text{H}_h$ ), 4.38(*s*; 4H,  $\text{H}_i$ ).  $^{13}\text{C}$  NMR (600 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ , ppm): 159.5( $\text{C}^1$ ), 146.7( $\text{C}^2$ ), 143.3( $\text{C}^3$ ), 137.1( $\text{C}^4$ ), 132.4( $\text{C}^5$ ), 131.1( $\text{C}^6$ ), 131.0( $\text{C}^7$ ), 131.06(*q*,  $^2J_{\text{C-F}} = 32.7$  Hz,  $\text{C}^8$ ), 129.8( $\text{C}^9$ ), 127.8(*q*,  $^1J_{\text{C-F}} = 284.4$  Hz,  $\text{C}^{10}$ ), 123.4(*q*,  $^1J_{\text{C-F}} = 271.2$  Hz,  $\text{C}^{11}$ ), 123.2( $\text{C}^{12}$ ), 116.8( $\text{C}^{13}$ ), 115.2( $\text{C}^{14}$ ), 108.7( $\text{C}^{15}$ ), 106.9( $\text{C}^{16}$ ), 63.9(*q*,  $^2J_{\text{C-F}} = 23.7$  Hz,  $\text{C}^{17}$ ). TOF-MS (electron ionization, *m/z*, percentage of relative intensity): 692( $\text{M}^+$ , 100), 623( $(\text{M}-69)^+$ , 17). Elem. Anal. Calcd. for  $\text{C}_{34}\text{H}_{25}\text{F}_9\text{N}_4\text{O}_2$ : C, 58.96%; H, 3.64%; N, 8.09%. Found: C, 58.89%; H, 3.67%; N, 8.03%.



### Polymer Synthesis and Film Preparation

A series of FPPys were synthesized by polycondensation of 6FTA and 9FTA with various aromatic dianhydrides, including ODPA, BTDA,  $\alpha$ -BPDA and BPADA, respectively. The synthesized FPPys were abbreviated as PPy-1 to PPy-8, successively, as shown in Scheme 2.

PPy-1 is given as an example. 6FTA (1.8737 g, 3.0 mmol) was added with stirring to freshly distilled NMP (9 mL) held in a 50-mL, three-necked flask equipped with a mechanical stirrer, a dropping funnel, a dry nitrogen inlet, and a thermometer. The reaction system was cooled with an ice-acetone bath and the temperature was maintained at  $-15^\circ\text{C}$  to  $-10^\circ\text{C}$ . ODPA (0.9306 g, 3.0 mmol) dissolved in freshly distilled NMP (12 mL) was added dropwise to the system over a period of 1 h. The reaction mixture was stirred at  $-10^\circ\text{C}$  for 5 h and then 12 h at room temperature to yield a viscous homogeneous PAAA-1 solution. The deep brown solution was then filtered through a 0.2-mm Teflon syringe filter to eliminate any undissolved impurities.



**Scheme 2.** Synthesis of the FPPys.

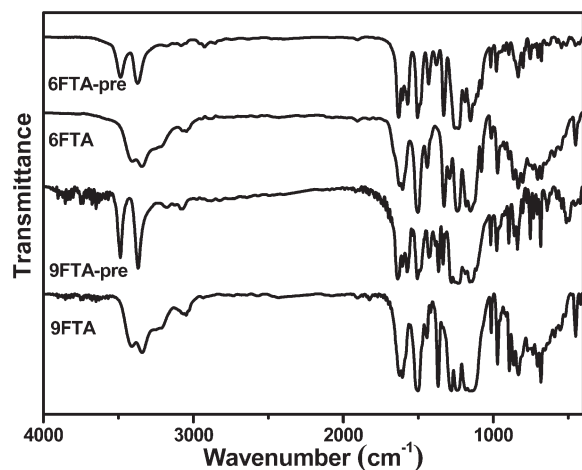


Figure 1. Comparison of the FT-IR spectra of precursors and tetraamines.

Part of the solution poured into excess of ethanol to produce silky precipitate, which was collected, thoroughly washed with ethanol, and dried at 100°C under vacuum for 24 h to get brown PAAA-1 resin, which was used to measure the inherent viscosity. The rest of the solution was cast onto a clean glass plate, and the solvent was removed at 80°C for 4 h, 120°C for 1 h, 150°C for 1 h, 200°C for 1 h, 250°C for 1 h, 300°C for 1 h and 350°C for 1 h. Freestanding FPPy films with deep brown in color was obtained.

The other FPPys were synthesized in the same procedure as mentioned above, except ODPA and 6FTA were replaced by the corresponding tetraamines and dianhydrides, as shown in Scheme 2.

## RESULTS AND DISCUSSION

### Monomer Synthesis

The two novel fluorinated tetraamine monomers were prepared by the reaction sequence as shown in Scheme 1. First, the inter-

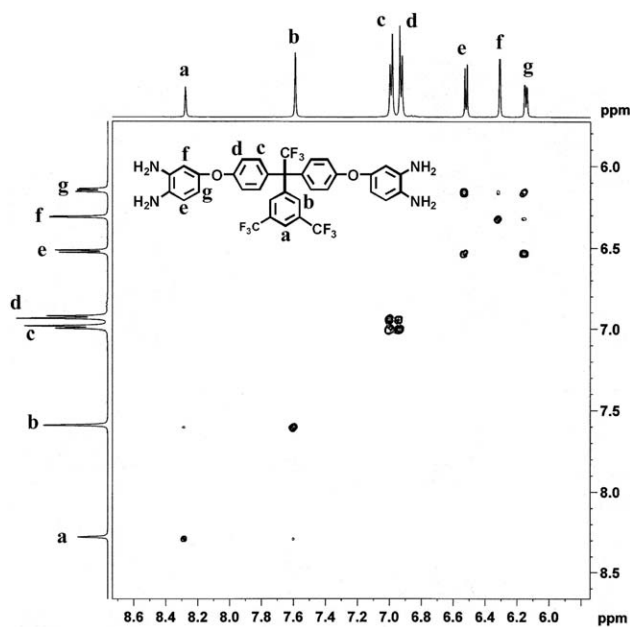


Figure 2.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of 9FTA (600 MHz,  $\text{DMSO}-d_6$ ).

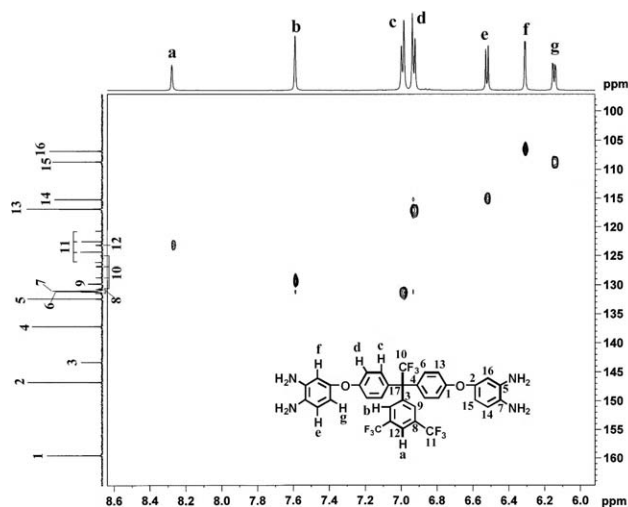


Figure 3. HSQC spectrum of 9FTA (600 MHz,  $\text{DMSO}-d_6$ ).

mediate 6FTA-pre and 9FTA-pre were synthesized by the aromatic chloro-displacement reaction of 5-chloro-2-nitroaniline with the bisphenols (6F-bisphenol and 9F-bisphenol) in the presence of potassium carbonate in DMAC, and then purified by silica gel column. Second, the two tetraamines, 6FTA and 9FTA were readily obtained by the catalytic reduction of the intermediates with hydrazine monohydrate and Pd/C catalyst in refluxing ethanol with high yields and high purity.

The structures of the obtained dinitro compounds (6FTA-pre and 9FTA-pre) and tetraamines (6FTA and 9FTA) were confirmed by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FT-IR, elemental analysis, MS spectrometry and two-dimensional NMR experiments. Figure 1 compares the FT-IR spectra of the intermediates and tetraamines. Obviously, the absorption bands presented at 1570–1580 and 1360–1370  $\text{cm}^{-1}$  resulting from asymmetric and symmetric stretching vibration of nitro groups ( $-\text{NO}_2$ ) disappeared after the dinitro intermediates were reduced. This should be evidence which indicates that the nitro group was changed into the amino group. The strong absorption at 1145 and 1250  $\text{cm}^{-1}$  assigned to the C–F stretching vibration was also observed, both in the intermediates and in the tetraamines.

Figures 2 and 3 give representative  $^1\text{H}$ - $^1\text{H}$  COSY and HSQC spectrum of 9FTA in  $\text{DMSO}-d_6$ . The  $^1\text{H}$  NMR spectrum confirms that the nitro groups have been completely converted into amino groups by the high field shift of the aromatic protons and by the signals changes of the primary amine protons. For example, in the  $^1\text{H}$  NMR spectra of 9FTA-pre, the strong single peak at 7.53 ppm should present the primary amine protons. It appeared farthest downfield of the spectrum because of the strong-withdrawing nitro group in the *ortho* position. After reduced to 9FTA, the signals of primary amine protons high field shift to be in the range of 4.0–5.0 ppm. All the other protons in the structure could be assigned easily according to the integral values of intensity. The protons in trifluoromethyl-substituted phenyl moiety appeared farthest downfield of the spectrum because of the strong electron-withdrawing trifluoromethyl group. In the  $^{13}\text{C}$  NMR spectrum of 9FTA, most of the carbon atoms resonated in the region of 106–160 ppm.  $\text{C}^8$  and

**Table I.** Physical Properties and Elemental Analysis of the FPPys

Code	$\eta_a$ (mPa s) <sup>a</sup>	$\eta_{inh}$ (dL/g) <sup>b</sup>	Formula (formula weight)	Elemental analysis (%) <sup>c</sup>			
				C	H	N	
PPy-1	2500	0.43	(C <sub>49</sub> H <sub>24</sub> F <sub>6</sub> N <sub>4</sub> O <sub>5</sub> ) <sub>n</sub> [(862.73) <sub>n</sub> ]	Calcd	68.22	2.80	6.49
				Found	67.63	3.01	6.56
PPy-2	2800	0.47	(C <sub>50</sub> H <sub>24</sub> F <sub>6</sub> N <sub>4</sub> O <sub>5</sub> ) <sub>n</sub> [(874.74) <sub>n</sub> ]	Calcd	68.65	2.77	6.40
				Found	66.07	2.77	6.12
PPy-3	4300	0.39	(C <sub>49</sub> H <sub>24</sub> F <sub>6</sub> N <sub>4</sub> O <sub>4</sub> ) <sub>n</sub> [(846.73) <sub>n</sub> ]	Calcd	69.51	2.86	6.62
				Found	67.22	2.77	6.34
PPy-4	9600	0.54	(C <sub>64</sub> H <sub>38</sub> F <sub>6</sub> N <sub>4</sub> O <sub>6</sub> ) <sub>n</sub> [(1073.00) <sub>n</sub> ]	Calcd	71.64	3.57	5.22
				Found	69.55	3.19	5.32
PPy-5	4300	0.48	(C <sub>50</sub> H <sub>23</sub> F <sub>9</sub> N <sub>4</sub> O <sub>5</sub> ) <sub>n</sub> [(930.73) <sub>n</sub> ]	Calcd	64.52	6.02	2.49
				Found	62.32	6.49	2.52
PPy-6	2200	0.39	(C <sub>51</sub> H <sub>23</sub> F <sub>9</sub> N <sub>4</sub> O <sub>5</sub> ) <sub>n</sub> [(942.74) <sub>n</sub> ]	Calcd	64.98	5.94	2.46
				Found	63.47	6.22	2.53
PPy-7	7100	0.59	(C <sub>50</sub> H <sub>23</sub> F <sub>9</sub> N <sub>4</sub> O <sub>4</sub> ) <sub>n</sub> [(914.73) <sub>n</sub> ]	Calcd	65.65	6.12	2.53
				Found	64.67	6.44	2.61
PPy-8	1200	0.40	(C <sub>65</sub> H <sub>37</sub> F <sub>9</sub> N <sub>4</sub> O <sub>6</sub> ) <sub>n</sub> [(1141.00) <sub>n</sub> ]	Calcd	68.42	4.91	3.27
				Found	65.68	5.57	2.87

<sup>a</sup> Absolute viscosity measured with PAAA solution in NMP at 15% solid content at 25°C.

<sup>b</sup> Inherent viscosity measured with PAAA solution in NMP at a concentration of 0.5 g/dL at 30°C.

<sup>c</sup> All the samples were thermally baked at 200°C for 3 h prior to test.

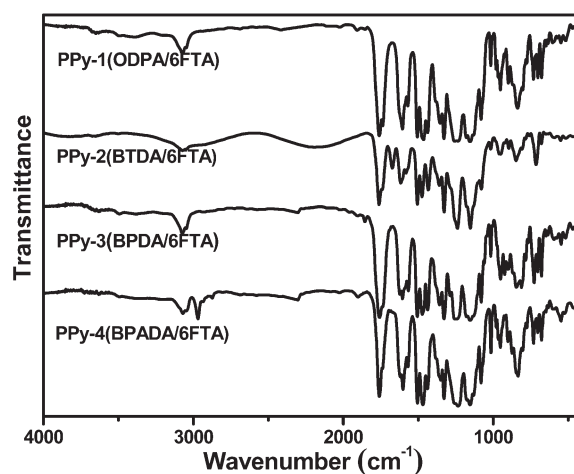
C<sup>11</sup> showed clear quartet absorption at 131.1 and 123.4 ppm, respectively, probably because of the <sup>2</sup>J<sub>C-F</sub> and <sup>1</sup>J<sub>C-F</sub> coupling of the carbons with fluorine atoms in the tetraamine. The coupling effect between C and F atoms decreased with the increase of the distance between the C and F atoms. For instance, C<sup>11</sup> showed a stronger coupling effect with F than that of C<sup>8</sup>. A full assignment of the resonances of the aromatic protons and carbons was assisted by the two-dimensional COSY spectra, and these spectra agree well with the proposed molecular structures. The elemental analysis values were also in well accordance with the calculated ones. All the analysis results confirmed that we obtained the compounds what we designed.

### Polymer Synthesis and Characterization

In this work, FPPys were prepared from the two novel tetraamines with various aromatic dianhydrides via a two-step condensation polymerization as shown in Scheme 2. That is, the formation of a poly(amide amino acid) (PAAA) via low-temperature solution polycondensation and then thermal cyclization of PAAAs to give FPPys. Because of the inductive or electronic effects, the reactive activity of the two amine groups in the tetraamines was different, and the *m*-amino showed the higher activity than that of the *p*-amino.<sup>14</sup> The reaction was strongly affected by the stoichiometry, adding sequence and adding velocity of the monomers. To avoid gelling and yield a PAAA solution with reasonable viscosity, exact stoichiometry of the dianhydride and tetraamine and low addition velocity was chosen in the synthesis of the PAAAs. Thus, fibrous PAAA resins with light brownish red in color could be obtained by pouring the polymer solution into excess of ethanol. Strong and freestanding FPPy films were obtained by casting the PAAA

solutions on clean glass plate followed by thermally baking with the final temperature of 350°C.

Table I shows the physical features of the FPPys. The inherent viscosities of the PAAAs ranged from 0.39 to 0.54 dL/g, which were determined by an Ubbelohde viscometer with 0.5 g/dL NMP solution at 30°C, demonstrating that PAAAs with moderate to high molecular weights were obtained. The formation of FPPys was confirmed by FT-IR and Solid-state <sup>13</sup>C NMR spectroscopy. FT-IR spectroscopic characterization was performed on thin films, which were about 10–15 μm in thickness. Figure 4 shows the FT-IR spectra of FPPys based on 6FTA. All the



**Figure 4.** FT-IR spectra of PPy-1~PPy-4 (film samples, 10–15 μm in thickness).

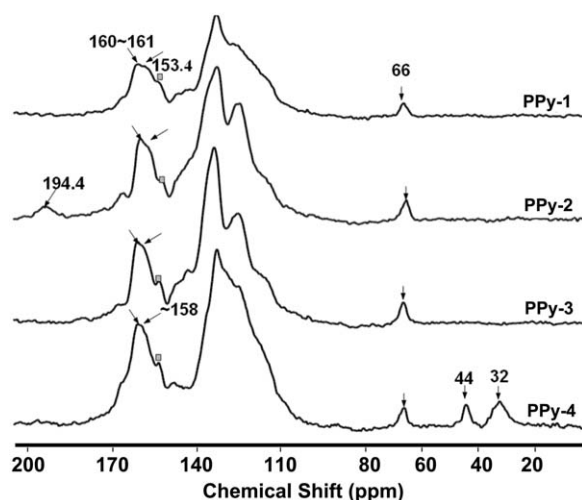


Figure 5. Solid-state  $^{13}\text{C}$  NMR spectra of PPY-1~PPY-4.

FPPys showed characteristic absorption bands at  $1760\text{ cm}^{-1}$  as a result of C=O stretching vibration and  $1620\text{ cm}^{-1}$  as a result of C=N stretching vibration in the pyrrolone ring.<sup>34,35</sup> As expected, C–F multiple stretching absorptions were also found at  $1250$  and  $1145\text{ cm}^{-1}$ . The characteristic N–H stretching vibrations at around  $3400\text{ cm}^{-1}$  were seldom observed in FT-IR spectroscopy, which suggested that the tetraamines possessed sufficient reactive activity when it reacted with aromatic dianhydrides in spite of the presence of electron-withdrawing trifluoromethyl substituents.

Because all the FPPys did not dissolve in any organic solvents, solid-state  $^{13}\text{C}$  NMR was used to determine the structure of FPPys obtained here. Figure 5 exhibits the solid-state  $^{13}\text{C}$  NMR spectra of the FPPys and the detailed assignment were tabulated in Table II. The peak around 160–161 ppm was attributed to the chemical shifts of carbon atom of carbonyl groups in the pyrrolone ring (C=O). The peak around 152–153 ppm was attributed to the chemical shift of carbon attached the nitrogen atoms in the pyrrolone ring (N=C–N). The strong, broad, and overlapped peaks in the region of 100–145 ppm were attributed to the chemical shifts of aromatic carbon atoms. In the high field region, the small, weak peak around 66 ppm was attributed to the chemical shifts of quarternary aliphatic carbons from the tetraamines, which is also in well accordance with the  $^{13}\text{C}$  NMR of 6FTA and 9FTA. As expected, from the spectra of PPY-4, we can see the signals of quarternary aliphatic carbons and methyl carbons in the bisphenol-A units (44.5 and 32.6 ppm,

respectively). Meanwhile, from the spectra of PPY-2, we can also see the signal of the benzophenone carbonyl carbon from BTDA units at 194.4 ppm.<sup>36,37</sup> It is noted that no characteristic chemical shifts of residual NMP (around 176, 50, 30, 19 ppm)<sup>38</sup> were found in all FPPys' spectra, indicating the final baking temperature of  $350^\circ\text{C}$  was high enough to remove all the residual solvents. The elemental analysis data of the FPPys (Table I) were also in well accordance with the calculated ones. The characterization by FT-IR, solid-state  $^{13}\text{C}$  NMR, and elemental analysis confirmed that all the polymers have the expected chemical structures.

#### Morphology and Mechanical Properties of the FPPys

Figure 6 is the wide-angle XRD patterns of the FPPys. It can be seen that all of the synthesized FPPys are completely amorphous in morphologic structure, which could also be illustrated by the DSC measurements (Figure 7), in which none melting endothermic peak was observed except glass transition temperatures ( $T_g$ s) of the polymers. The results indicated that the backbones with multiple trifluoromethyl groups and bulky aromatic side moieties increased the disorder along the polymer chains, decreased the intermolecular interactions and reduced the efficiency of chain packing. Such efforts were essential to hinder the polymer crystallization.

All the FPPys could be cast into freestanding films with moderate to good quality. These films were subjected to tensile tests and the results were included in Table III. They showed an ultimate tensile strength of 72–97 MPa, an elongation at break of 4.2–7.4%, and a tensile modulus of 2.38–2.83 GPa, indicating strong and tough polymeric film materials.

The electrical insulating properties of the FPPy films were also shown in Table III. The FPPy films showed good electrical insulating properties with surface resistance of  $2.7\text{--}7.3 \times 10^{14}\ \Omega$  and volume resistance of  $3.6\text{--}8.3 \times 10^{15}\ \Omega\cdot\text{cm}$ , respectively.

The water adsorptions for the FPPys ranged in 0.7–1.7% at  $25^\circ\text{C}$  and 2.0–4.4% at  $100^\circ\text{C}$  for 24 h. Compared with the fluorinated PIs which have similar chemical structures,<sup>39</sup> the FPPys obtained here showed relatively higher water adsorptions, maybe because the great rigidity of the pyrrolone moieties and the kinked quaternary carbon links in the tetraamine units greatly reduced the efficiency of chain packing.

#### Thermal and Optical Properties of the FPPys

The thermal properties of the FPPys were tabulated in Table IV. DSC was used to determine the glass transition temperature ( $T_g$ ) values of the FPPys with a heating rate of  $20^\circ\text{C}/\text{min}$  under

Table II. Solid-State  $^{13}\text{C}$  NMR Assignment of FPPys Based on 6FTA

Code	Pyrrolone carbonyl	Pyrrolone C=N	Tertiary central phenyl	Quaternary central phenyl	Bound to ether oxygen	N-substituted phenyl	Aliphatic
PPY-1	161.0	153.5	143.8 142.0	133.1	158.6	127.3 125.6	66.6
PPY-2	161.1	153.5	143.5	133.8	158.7	126.9 125.7	66.6
PPY-3	161.1	153.4	143.1	133.8	157.4	125.5	66.8 66.4
PPY-4	161.0	153.5	-	132.8	158.0	125.2	44.5,32.6

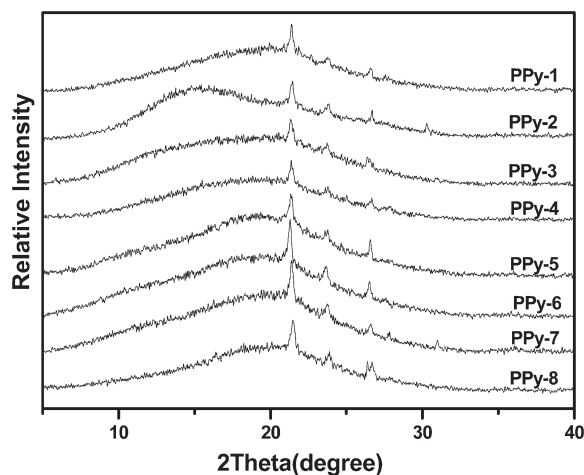


Figure 6. Wide-angle XRD patterns of the FPPys.

nitrogen atmosphere. All the eight kind of FPPys did not show very clearly glass transition on the DSC thermograms, maybe because of the great rigidity of the polymer chains. The  $T_g$  values of the polymers were found to be in the range of 302–343°C, depending on the structure of the dianhydride component and decreasing with the increasing flexibility of the polymer backbones. All the FPPys showed relatively high  $T_g$  values, could be mainly attributed to the strong inter- and intramolecular interactions in the polymer backbone. In general, the 6FTA-based PPy-s showed 15–35°C higher  $T_g$  value than the 9FTA-based ones (PPy-1,2,3,4) was more rigid than that of the 9FTA-based ones (PPy-5,6,7,8). As expected, PPy-2 (BTDA/6FTA) exhibited the highest  $T_g$  maybe due to the rigid benzophenone units.

DMA was also used to determine the  $T_g$  values of the FPPys with a heating rate of 5°C/min under nitrogen atmosphere and Figure 8 shows a typical DMA curve (PPy-4). All the data were tabulated in Table IV. The  $T_g$  values obtained from DMA were quite different. The  $T_g$  values of the polymers were found to be in the range of 315–389°C. As shown in Figure 8, although

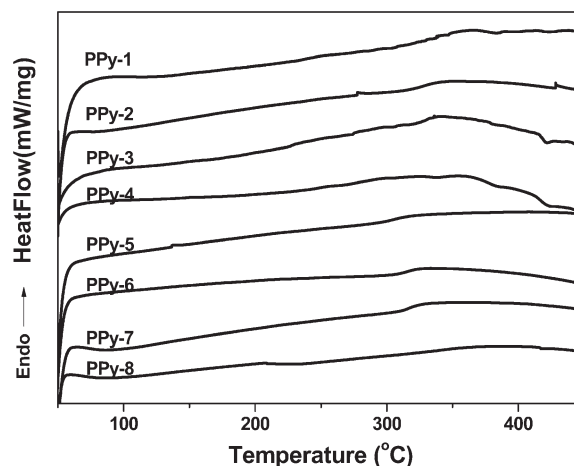


Figure 7. DSC thermograms of the FPPys.

PPy-4 was derived from BPADA, which has an isopropyl segment in the structure, the  $T_g$  value was still measured as 319°C, indicating the excellent thermal property of this kind of polymeric materials.

The thermal stability of the FPPys was evaluated by TGA measurements under nitrogen and air. Figure 9 shows the TGA curve of PPy-1. No notable weight loss was observed below 500°C to all of the FPPys from the TGA curves, except PPy-4 and PPy-8, which contained bisphenol-A units in the backbone. However, as the temperature over 500°C, all FPPys showed more rapid thermal decomposition, which probably was attributed to the presence of multiple  $-\text{CF}_3$  groups in the backbones. The thermal decomposition temperatures ( $T_d$ ) of the FPPys in nitrogen were in the range of 502–540°C. The 5% ( $T_{5\%}$ ) and 10% ( $T_{10\%}$ ) weight loss temperature of the FPPys reached 496–535°C and 531–558°C in nitrogen, respectively. Meanwhile, the char yields at 700°C under nitrogen were all above 59%. The data mentioned above indicated that the FPPys based of 6FTA and 9FTA possessed excellent thermal stability, which could be interpreted by the stable conjugated pyrrolone rings in the polymer backbones.

Table III. Mechanical, Electrical Insulating, and Water Uptakes of the FPPys

Code	TS <sup>a</sup> (MPa)	TM <sup>a</sup> (GPa)	EB <sup>a</sup> (%)	Rv <sup>b</sup> × 10 <sup>-15</sup> (Ω cm)	Rs <sup>c</sup> × 10 <sup>-14</sup> (Ω)	WU <sup>d</sup> (%)	
						25°C	100°C
PPy-1	97	2.38	7.4	8.3	4.2	0.7	2.0
PPy-2	82	2.83	4.7	4.5	5.0	1.1	4.4
PPy-3	84	2.39	5.6	6.5	4.6	1.4	2.3
PPy-4	78	2.27	4.6	3.6	4.7	1.7	4.1
PPy-5	72	2.25	4.8	6.4	4.7	1.3	3.8
PPy-6	76	2.33	4.2	5.2	2.7	1.1	4.0
PPy-7	79	2.28	5.2	5.9	7.3	1.3	4.0
PPy-8	82	2.25	4.8	5.5	6.0	1.4	3.2

<sup>a</sup>TS: tensile strength; EB: elongation at break; TM: tensile modulus.

<sup>b</sup>Volume resistance.

<sup>c</sup>Surface resistance.

<sup>d</sup>Water uptakes at 25°C and 100°C, respectively.



**Table IV.** Thermal Properties of the FPPys

Code	$T_g$ (°C)		In nitrogen				In air		
	DSC <sup>a</sup>	DMA <sup>b</sup>	$T_d^c$ (°C)	$T_{5\%}^c$ (°C)	$T_{10\%}^c$ (°C)	$R_w^d$ (%)	$T_d^c$ (°C)	$T_{5\%}^c$ (°C)	$T_{10\%}^c$ (°C)
PPy-1	338	360	538	533	558	69.4	534	498	521
PPy-2	343	342	532	530	551	68.8	587	508	532
PPy-3	331	342	540	535	558	71.5	593	515	538
PPy-4	- <sup>e</sup>	319	502	497	531	69.0	538	483	518
PPy-5	302	315	535	531	554	66.0	549	506	529
PPy-6	313	336	522	529	551	66.1	551	508	530
PPy-7	316	336	536	529	552	59.7	560	510	533
PPy-8	- <sup>e</sup>	389	508	505	536	66.9	562	475	507

<sup>a</sup> $T_g$ : midpoint of baseline shift on the DSC curve.

<sup>b</sup>Peak temperature of  $\tan \delta$ .

<sup>c</sup> $T_d$ , onset decomposition temperature;  $T_{5\%}$ ,  $T_{10\%}$ , temperatures at 5% and 10% weight loss, respectively.

<sup>d</sup>Residual weight retention ( $R_w$  %) at 700°C.

<sup>e</sup>No apparent  $T_g$  in the measurement.

The optical transparency of the FPPys was measured by UV-visible spectra and the results of cutoff wavelength and transmittance at 450 nm, 500 nm, and 600 nm were listed in Table V. All the FPPy films were deep brown in color with cutoff wavelength in the range of 415–461 nm. The light transmittance values at 450 nm were all lower than 12%. At 600 nm, all the FPPys showed transmittances over 83%. Generally, the strong conjugation interactions between the fused benzene and pyrrole ring were propitious for the formation of charge-transfer complexes (CTC),<sup>40</sup> which resulted in strong absorption by the polymer in the visible light region. The good light-absorbing properties of the present FPPy films make them potential candidates for high performance light-shielding materials in some fields.

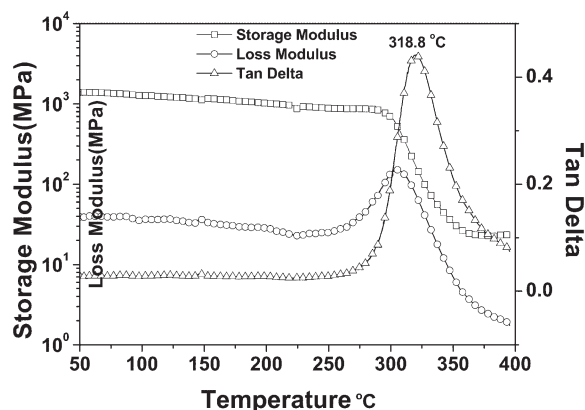
#### Alkaline-Hydrolysis Resistance Properties of the FPPys

Experimental results had demonstrated that PPys containing pyridine segments possessed good hydrolysis resistance in alkaline aqueous solution,<sup>14</sup> so we tested the alkaline-hydrolysis resistance of FPPys synthesized here by a similar method. And the PI film sample derived from ODPa and 12FDA (PI-3),<sup>39</sup> which had a similar chemical structure, was tested with the same procedure for comparison. As seen in Table VI, the PI-ref

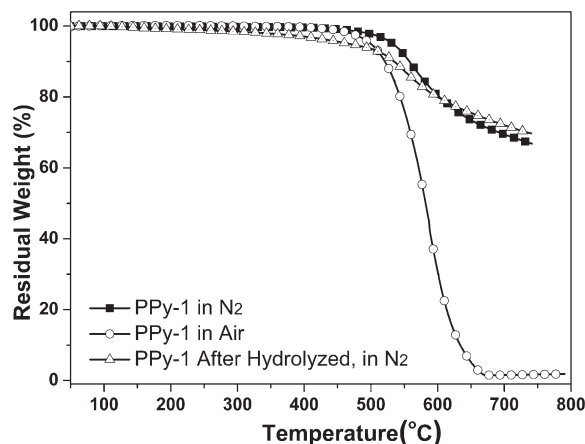
started to hydrolyze in the 10% boiling alkaline solution for 7 h and completely dissolved in the alkaline solution within 13 h to give some white floccules in the solution. However, all the FPPy films could stand about 30 h in the 10% boiling alkaline solution before hydrolysis was initially observed. After boiling in 10% aqueous sodium hydroxide for 7 days, all the FPPy films could remain most of their original shapes except some shrinkage. At the same time, the FPPys synthesized here showed better alkaline-hydrolysis resistance than the reported pyridine-bridged PPys, maybe because of the hydrophobicity of trifluoromethyl groups in the polymer backbone.

The TGA results measured under nitrogen indicated that PPy-1 showed acceptable thermal resistance even after boiling in 10% NaOH solution for 7 days; the residual weight at 700°C was 72%, very close to that of unhydrolyzed film (69%), demonstrating that the thermally stable chemical structures remained in the polymer backbones after hydrolyzed.

Also we tested the mechanical properties retention rate after alkaline-hydrolysis for a period of time. The films were cut into specific shapes and size in order for the mechanical testing. All



**Figure 8.** DMA curve of PPy-4.



**Figure 9.** TGA thermograms of PPy-1.

**Table V.** Optical Properties of the FPPys

Code	d ( $\mu\text{m}$ ) <sup>a</sup>	F (%) <sup>b</sup>	Cutoff (nm) <sup>c</sup>	T <sub>450</sub> (%) <sup>d</sup>	T <sub>500</sub> (%) <sup>d</sup>	T <sub>600</sub> (%) <sup>d</sup>
PPy-1	13	13.21	454	0	56.1	90.0
PPy-2	9	13.03	456	0	41.5	85.4
PPy-3	11	13.46	461	0	57.5	90.0
PPy-4	8	10.62	415	12.0	55.7	87.1
PPy-5	9	18.37	421	8.7	69.6	91.6
PPy-6	12	18.14	457	0	51.6	90.0
PPy-7	10	18.69	435	4.5	72.4	94.0
PPy-8	9	14.99	416	10.5	45.3	83.6

<sup>a</sup>Film thickness.<sup>b</sup>Fluorine content.<sup>c</sup>Cutoff wavelength.<sup>d</sup>Transparency at 450, 500 and 600 nm respectively.

Water uptake.

the samples were boiling in the 10% alkaline solution for 2 and 8 hours, then rinsed with deionized water and wiped with blotting paper. The mechanical properties were tested and the results were summarized in Table VII. After alkaline hydrolyzed for 2 h, the tensile strength can be retained as high as 79%. PPy-1 and PPy-8 show relatively better alkaline-hydrolysis resistance. Even after 8 hours alkaline-hydrolysis, the tensile strength still remained as high as 56% of the original values.

The excellent alkaline-hydrolysis resistance for FPPys could probably be attributed to the more fused multiaromatic structures of pyrrolone moieties as compared with PIs. When attacked by OH<sup>-</sup>, the imide rings were easily broken; the product was amide groups, which were even more frangible to OH<sup>-</sup>. Thus the hydrolyzing can be enhanced. It was reported that Kapton film would be completely hydrolyzed after boiling in hydrazine to produce two initial monomers, PMDA and ODA, quantitatively.<sup>5</sup> However, when attacked by OH<sup>-</sup>, the carbonyls of pyrrolone rings were also broken and the products were benzimidazole groups with carboxylic groups in the *ortho* position. The benzimidazole groups also showed excellent

alkaline-hydrolysis resistance which obstructed further decomposition.<sup>41</sup>

## CONCLUSIONS

Two novel fluorinated aromatic tetraamines 6FTA and 9FTA were synthesized and characterized, which were employed to react with various aromatic dianhydrides to yield a series of fluorinated aromatic polypyrrolones (FPPys). The inherent viscosities of the PAAAs ranged from 0.39 to 0.54 dL/g. All the FPPys were amorphous. The freestanding FPPy films could be prepared, which exhibited good thermal stability. All the FPPy films exhibited excellent alkaline-hydrolysis resistance which retained their original shapes and toughness after boiling 7 days in 10% sodium hydroxide solution. Also after boiling 8 h in 10% sodium hydroxide solution, the tensile strength could retain as high as 56% of the original values. The outstanding

**Table VI.** Hydrolysis-Resistance Properties in Alkaline Aqueous Solution of the FPPy Films

Code	t <sub>i</sub> <sup>a</sup> (h)	t <sub>w</sub> <sup>b</sup> (h)
PPy-1	30	>168 (7 days)
PPy-2	31	>168 (7 days)
PPy-3	31	>168 (7 days)
PPy-4	33	>168 (7 days)
PPy-5	30	>168 (7 days)
PPy-6	31	>168 (7 days)
PPy-7	33	>168 (7 days)
PPy-8	31	>168 (7 days)
PI-ref <sup>c</sup>	7	13

<sup>a</sup>Initial hydrolyzing time of PPy.<sup>b</sup>Wholly hydrolyzing time of PPy.<sup>c</sup>PI-ref: see ref 39 PI-3.**Table VII.** Mechanical Properties Retention After Hydrolyzed in Alkaline Aqueous Solution

Code	Hydrolyzed time(h)	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
PPy-1	0	2.38	96.5	5.2
	2	2.52	68.0	3.6
	8	2.07	53.8	3.6
PPy-2	0	2.83	82.2	4.7
	2	1.57	33.2	3.8
	8	- <sup>a</sup>	-	-
PPy-6	0	2.33	75.6	4.2
	2	1.87	56.8	4.0
	8	- <sup>a</sup>	-	-
PPy-8	0	2.25	81.7	4.8
	2	1.66	64.8	4.6
	8	2.3	55.6	4.1

<sup>a</sup>Not measured because the samples were wrinkled after boiling.

combinational properties make them proper alternatives to PIs when used as protecting materials in alkaline environment.

#### ACKNOWLEDGMENTS

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