

# Synthesis and Characterization of Highly Transparent and Hydrophobic Fluorinated Polyimides Derived from Perfluorodecylthio Substituted Diamine Monomers

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**ABSTRACT:** Two new perfluorodecylthio substituted aromatic diamines, namely 2,4-diamino-1-(1*H*,1*H*,2*H*,2*H*-perfluorodecathio)benzene (DAPFB) and 2,2'-Bis((1*H*,1*H*,2*H*,2*H*-perfluorodecyl)thio)[1,1'-biphenyl]4,4'-diamine (BPFBD) were synthesized and polycondensed with 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) to produce two new perfluorinated polyimides (PI2 and PI4). The chemical structures of these polyimides were confirmed by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy and elemental analysis. Two other polyimides (PI1 and PI3) were also synthesized from 6FDA and analogous perfluorodecylthio unsubstituted diamines to investigate the incorporation effect of perfluorodecylthio group on various physical and chemical properties of the synthesized PIs. Compared with PI1 and PI3, PI2 and PI4 exhibited improved solubility, optical transparency, and hydrophobicity, lower moisture absorption, dielectric constant, and thermo-mechanical stabilities owing to

the presence of the perfluorodecylthio side group in the polymer chain. Even though thermo-mechanical properties of PI2 and PI4 ( $T_g^5$ : 413 and 404 °C,  $T_g$ : 220 and 209 °C, tensile strength of 101 and 76 MPa, tensile modulus of 1.7 and 1.5 GPa and elongation at break of 8 and 10%, respectively) were reduced in comparison to PI1 and PI3 but still were good enough for most of the practical applications. Most importantly, the presence of the perfluorodecylthio side group in BPFBD considerably reduced the dielectric constant of PI4 to 2.71 which was quite low as aromatic polyimide. © 2014 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, 53, 479–488

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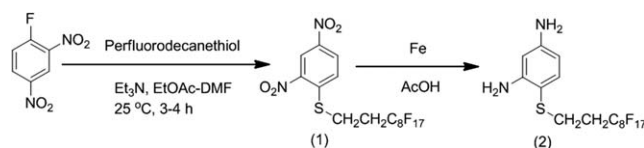
**INTRODUCTION** Polyimides (PIs) are basically composed of alternating electron donating diamines and electron accepting dianhydride moieties. The presences of these alternating donor and acceptor moieties in the main chain induce severe intra- and interchain electronic interaction through charge transfer complex (CTC) formation which increases the interchain packing density and thereby increases the thermomechanical-dimensional stabilities and chemical resistance.<sup>1,2</sup> But these charge transfer interactions also contribute to the poor solution processability, deep reddish-brown coloration, and high dielectric constants of conventional aromatic PIs.<sup>3–5</sup> Various structural modifications such as bulky lateral substituents,<sup>6–8</sup> flexible linkages,<sup>9–11</sup> noncoplanar biphenyl moieties<sup>12,13</sup> as well as unsymmetrical structures<sup>14–16</sup> have been made to decrease the coloration and enhance the solubility of conventional aromatic PIs by decreasing the CTC formation. On the other hand, introducing fluorinated substituents such as hexafluoroisopropylidene linkages,

perfluoroalkyl groups and pendent trifluoromethyl groups have also been recognized as one of the most promising method to synthesize processable and colorless PIs.<sup>17–29</sup> The high electronegativity along with low molar polarization of the fluorinated groups could ultimately lead to the synthesis of organo-soluble and optically transparent aromatic PIs having low dielectric constants and low water absorptions.

In this study, two new aromatic diamines with perfluorodecylthio side group 2,4-diamino-1-(1*H*,1*H*,2*H*,2*H*-perfluorodecathio)benzene (DAPFB) and 2,2'-Bis((1*H*,1*H*,2*H*,2*H*-perfluorodecyl)thio)[1,1'-biphenyl]4,4'-diamine (BPFBD)) were synthesized and polycondensed with 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) to produce two new perfluorinated PIs. Two other PIs were also synthesized by the condensation of 6FDA and two analogous diamines, namely 2,4-diamino-1-fluorobenzene (DAFB) and 4,4'-diamino-2,2'-diiodobiphenyl (DAIB) to investigate the incorporation effect of perfluorodecylthio side group on

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**SCHEME 1** Synthesis of DAPFB.

the solubility, optical transparency, thermomechanical stability, dielectric constant, water absorption, and surface properties of the synthesized PIs.

## EXPERIMENTAL

### Materials

1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (97%), 2,4-dinitro-1-fluorobenzene ( $\geq 99\%$ ) and 1-iodo-3-nitrobenzene (99%) were purchased from Aldrich and were used as received. 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA, Aldrich, 99%) was dried at 120 °C for 1 day under vacuum before use. All the other chemicals used in this study were supplied from Aldrich and were used as received.

### Synthesis of 2,4-Dinitro-1-(1*H*,1*H*,2*H*,2*H*-perfluorodecathio)benzene (DNPFB)

The synthetic route of DNPFB is outlined in Scheme 1. 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (PFDT) (1 mmol) and  $\text{Et}_3\text{N}$  (1.1 mmol) were dissolved in 15 mL of 33% dimethylformamide (DMF) solution in ethyl acetate (EtOAc) under  $\text{N}_2$  atmosphere. 2,4-Dinitro-1-fluorobenzene (0.8 mmol) dissolved in minimum volume of DMF was added drop wise into the PFDT solution under vigorous stirring at 25 °C. The stirring was continued for another four hours which results a light yellow precipitate to appear. The precipitate was filtered and the filtrate was further concentrated by rotary evaporator which results more precipitate to appear. Both of these two precipitates were washed with minimum volume of hexane and dried in vacuum at 80 °C for 12 h. Yield (isolated): 90%. Light yellowish solid, Mp 140–141 °C (EtOAc : hexane = 1:5),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.11 (d,  $J = 2.8$  Hz, 1H, Ph-*H*), 8.44 (dd,  $J = 9.2$  and 2.4 Hz, 1H, Ph-*H*), 7.53 (d,  $J = 9.2$  Hz, 1H, Ph-*H*), 3.30 (m, 2H,  $-\text{SCH}_2-$ ), 2.57–2.51 (m, 2H,  $-\text{CH}_2\text{CF}_2$ ) (Supporting Information Fig. S1);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.0, 149.1, 138.4, 106.5, 104.3, 100.8, 31.8 (m) and 25.9 (Supporting Information Fig. S2); Anal. calcd. for  $\text{C}_{16}\text{H}_7\text{F}_{17}\text{N}_2\text{O}_4\text{S}$ : C, 29.74; H, 1.09; N, 4.33. Found: C, 29.59; H, 1.17; N, 4.40; FTIR (KBr,  $\text{cm}^{-1}$ ): 3085, 1588, 1520, 1470, 1369, 1366, 1206, and 1149 (Supporting Information Fig. S3).

### Synthesis of 2,4-Diamino-1-(1*H*,1*H*,2*H*,2*H*-perfluorodecathio)benzene (DAPFB)

DNPFB (1 mmol) was dispersed under  $\text{N}_2$  atmosphere in 5 mL of glacial acetic acid and 0.5 mL of water in a 20 mL of round bottomed flask. With vigorous stirring, 670 mg of Fe powder (100 mesh) was added slowly in a small portion over a period of 10 min keeping the temperature at 25 °C. The reaction mixture after stirring for an additional 6 h was diluted with 15 mL of EtOAc and filtered through Cellite.

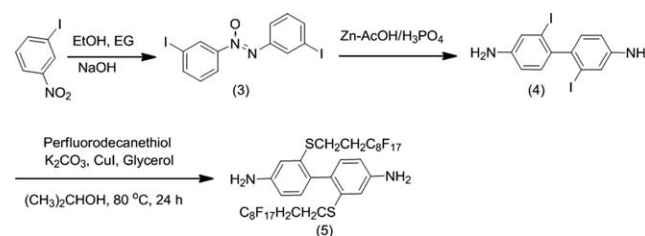
The filtrate after washing successively with water and 10%  $\text{NaHCO}_3$  solution was evaporated under vacuum. The crude product was purified further by flash chromatography using 6% EtOAc solution in hexane as eluent and silica gel as stationary phase. Yield (isolated): 65%. Off white solid, Mp 95–96 °C (EtOAc: hexane = 1:5),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.14 (d,  $J = 8.4$  Hz, 1H, Ph-*H*), 6.06–6.02 (m, 2H, Ph-*H*), 4.28 (s, 2H,  $-\text{NH}_2$ ), 3.66 (s, 2H,  $-\text{NH}_2$ ), 2.81–2.76 (m, 2H,  $-\text{SCH}_2-$ ), 2.38–2.20 (m, 2H,  $-\text{CH}_2\text{CF}_2$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.2, 144.6, 144.4, 127.6, 126.1, 122.0, 29.9 (m), and 23.4;  $^{19}\text{F}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  -80.87 (t,  $J = 10.5$  Hz, 3F), -113.95 (m, 2F), -121.79 to -121.97 (m, 6F), -122.78 (s, 2F), -123.33 (s, 2F), and -126.18 (s, 2F) (Supporting Information Fig. S3); Anal. calcd. for  $\text{C}_{16}\text{H}_7\text{F}_{17}\text{N}_2\text{O}_4\text{S}$ : C, 29.74; H, 1.09; N, 4.33. Found: C, 29.59; H, 1.17; N, 4.40; FTIR (KBr,  $\text{cm}^{-1}$ ): 3085, 1588, 1520, 1470, 1369, 1366, 1206, and 1149 (Supporting Information Fig. S4).

### Synthesis of 2,4-Diamino-1-fluorobenzene (DAFB)

2,4-Dinitro-1-fluorobenzene (1 mmol) was dispersed under  $\text{N}_2$  atmosphere in 5 mL of glacial acetic acid (AcOH) and 0.5 mL of water in a 20 mL of round bottomed flask. With vigorous stirring, 670 mg of Fe powder (100 mesh) was added slowly in a small portion over a period of 10 min keeping the temperature at 25 °C. The reaction mixture after stirring for an additional 6 h was diluted with 15 mL of EtOAc and filtered through Cellite. The filtrate after washing successively with water and 10%  $\text{NaHCO}_3$  solution was evaporated under vacuum. The crude product was purified further by chromatography using 4% EtOAc solution in hexane as eluent and neutral alumina as stationary phase. Yield (isolated): (82%). Light yellow liquid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.74 (dd,  $J = 8.8$  and 8.0 Hz, 1H, Ph-*H*), 6.09 (dd,  $J = 7.6$  and 2.8 Hz, 1H, Ph-*H*), 5.99–5.95 (m, 1H, Ph-*H*), 3.60 (s, 2H,  $-\text{NH}_2$ ), 3.41 (s, 2H,  $-\text{NH}_2$ ) (Supporting Information Fig. S5); Anal. calcd. for  $\text{C}_6\text{H}_7\text{FN}_2$ : C, 57.13; H, 5.59; N, 22.21. found: C, 56.99; H, 5.67; N, 22.27; FTIR (neat,  $\text{cm}^{-1}$ ): 3379, 3304, 3201, 1601, 1492, 1259, 814, and 698.

### 4,4'-Diamino-2,2'-Diiodobiphenyl (DAIB)

The compound was prepared from 1-iodo-3-nitrobenzene (Scheme 2) following a reported procedure of the synthesis of 4,4'-diamino-2,2'-dibromobiphenyl.<sup>30</sup> 21.20 g (530.00 mmol) of sodium hydroxide was placed in a 250 mL, three-neck, round-bottom flask equipped with a mechanical stirrer, a condenser, and a stopper and 60 mL of ethanol. The reaction mixture was heated at 70 °C for 0.5 h to dissolve most of sodium hydroxide. After adding 12.38 g (49.50 mmol) of

**SCHEME 2** Synthesis of BPFBD.

1-Iodo-3-nitrobenzene dissolved in 80 mL of ethylene glycol, the reaction mixture was heated at reflux for 3 h. The hot reaction mixture was poured slowly into 500 mL of ice to form precipitate. The deep brown precipitate was collected by filtration and washed several times with cold water. The compound was dried in vacuum at 60 °C for 24 h to yield 3,3'-diiodoazoxybenzene (3). The crude product was used in the next procedure without further purification. Yield: 6.75 g (60.0%).

6.0 g (13.3 mmol) of compound (3) was placed in a 250 mL, three-neck, round-bottom flask equipped with a mechanical stirrer, a condenser, a thermometer, 60 mL of tetrahydrofuran and 80 mL of glacial acetic acid. 8.0 g of Zn dust (<10  $\mu\text{m}$ ) was added slowly over a period of 0.5 h maintaining the reaction temperature below 40 °C. Once the addition of zinc dust was over, 12 mL of 85% phosphoric acid was added slowly maintaining the reaction temperature below 55 °C. After stirring for 30 min, the reaction mixture was filtered to remove zinc dust and the filtrate was poured into 150 mL of cold water. The aqueous phase was extracted twice with 50 mL of dichloromethane (DCM). The combined organic phase was concentrated to 50 mL and added dropwise to 30 mL of conc. hydrochloric acid at 0 °C under stirring. The stirring was continued for 1 h to allow off white precipitate to appear. The precipitated salt was filtered, washed several times with DCM, and dissolved in 100 mL of water. The aqueous solution was made alkaline by 10% aqueous sodium hydroxide solution and organic content was extracted with DCM. The DCM extract was evaporated to dryness to give off white solid. The benzidine monomer was further purified by recrystallization from 50% EtOAc solution in hexane. The product yield was 2.4 g (42.0%). Off white solid, Mp 170–171 °C (Lit.<sup>31</sup> Mp 169–170 °C), <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  7.11 (d, *J* = 2.0 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 6.58 (dd, *J* = 8.4 and 2.4 Hz, 2H), 5.20 (s, 4H, -NH<sub>2</sub>) (Supporting Information Fig. S6); FTIR (KBr, cm<sup>-1</sup>): 3413, 3304, 3201, 1621, 1594, 1471, 1279, 842, 684, and 575 (Supporting Information Fig. S7).

### 2,2'-Bis((1H,1H,2H,2H-perfluorodecyl)thio) [1,1'-Biphenyl]4,4'-diamine (BPFBDD)

CuI (380 mg, 2 mmol) and K<sub>2</sub>CO<sub>3</sub> (2.76 g, 20 mmol) were added to a glass vial equipped with a mechanical stirrer (Scheme 2). The vial was evacuated and backfilled with N<sub>2</sub> by three times. DAIB (2.18 g, 5 mmol), PFDT (5.28 g, 11.00 mmol), 2-propanol (40 mL), and ethylene glycol (10 mL) were added at room temperature and the tube was heated to 80 °C and stirred for 24 h. The use of both 2-propanol and ethylene glycol was helpful to result good yield with controllable viscosity. The reaction mixture was then allowed to cool to room temperature, before diluting with DCM (100 mL). The DCM extract obtained after filtration was concentrated *in vacuo*. The crude product was purified further by flash chromatography using 5% EtOAc solution in hexane as eluent and silica gel as stationary phase. Yield (isolated): 3.14 g (55%). White solid, Mp 72 °C (EtOAc : hexane = 1:5), <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.36 (d, *J* = 2.0 Hz, 2H, Ph-H),

7.12 (dd, *J* = 8.5 and 2.5 Hz, 2H, Ph-H), 6.68 (d, *J* = 8.5 Hz, 2H, Ph-H), 4.35 (s, 4H, -NH<sub>2</sub>), 2.95 (t, *J* = 8.3 Hz, 4H, -SCH<sub>2</sub>), 2.39–2.28 (m, 4H, -CH<sub>2</sub>CF<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  147.1, 135.2, 130.6, 122.6, 117.0, 116.1, 31.8 (m), and 25.3; <sup>19</sup>F NMR (500 MHz, CDCl<sub>3</sub>): -80.87 (t, *J* = 10.5 Hz, 3F), -113.95 (m, 2F), -121.79 to -121.97 (m, 6F), -122.78 (s, 2F), -123.33 (s, 2F), and -126.18 (s, 2F) (Supporting Information Fig. S8); Anal. calcd. for C<sub>32</sub>H<sub>18</sub>F<sub>34</sub>N<sub>2</sub>S<sub>2</sub>: C, 33.70; H, 1.59; N, 2.46. Found: C, 33.56; H, 1.65; N, 2.54; FTIR (KBr, cm<sup>-1</sup>): 3475, 3373, 1605, 1475, 1203, 1146, 814, and 662 (Supporting Information Fig. S7).

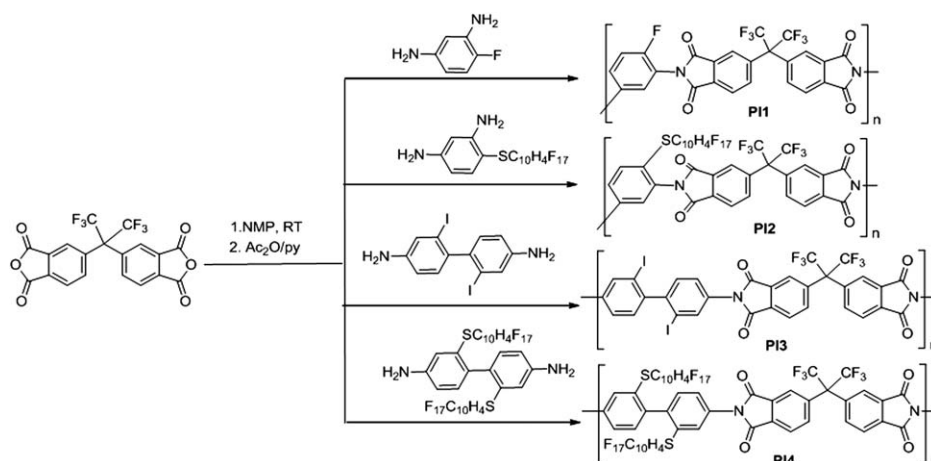
### The General Procedure for the Preparation of the Perfluorinated PIs

To a solution of diamine (1.0 mmol) in CaH<sub>2</sub> dried *N*-methyl-2-pyrrolidone (NMP) (15 wt % of solid content), 6FDA (1 mmol) was added in one portion (Scheme 3). The reaction mixture was stirred for 7 days (24 h for DAFB and DAIB) to form poly(amic acid) (PAA) precursor. An extra NMP (3 mL) was then poured into the reaction flask and *in situ* chemical cyclodehydration was carried out by adding an equimolar mixture of acetic anhydride (1 mL) and pyridine (0.5 mL) into the PAA solution with stirring at room temperature for 12 h under a nitrogen flow. The solution was then heated at 120 °C for 6 h to perform a complete imidization (for DAFB and DAIB, this step was skipped). The reaction mixture was then allowed to cool to room temperature, before being poured into large excess of methanol. The resulted precipitate was filtered, washed thoroughly with methanol and hot water, and dried at 100 °C under vacuum to yield PIs. The PI films were prepared with the casting solutions of 15 wt % of the polyimides in NMP solutions. The PI solutions were spin-coated onto 3 inch diameter fused silica (amorphous SiO<sub>2</sub>) substrates and dried at 80 °C for 8 h, 150 °C for 2 h, 200 °C for 2 h and 250 °C for 1 h under nitrogen flow. After drying, the glass plates were immersed in water to facilitate removal of the flexible, free-standing polyimide films.

### Characterization

<sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were recorded on a Varian Unity Plus NMR spectrometer (both 400 and 500 MHz). Elemental analysis was conducted with an elemental analyzer (EA, Vario EL, Elementar Analysen Systeme). The attenuated total reflection-Fourier transform infrared (ATR-FTIR, JASCO FT/IR-4100) spectra were obtained with 32 scans per spectrum at a 2 cm<sup>-1</sup> resolution. A robust single reflection accessory (JASCO ATR Pr0450-S) with a germanium IRE (*n* = 4.0, incidence angle = 45°) was used for the ATR measurements. Average molecular weight (*M*<sub>w</sub>) and polydispersity index (PDI) of the soluble PIs were estimated by gel permeation chromatography (GPC) using a Waters 515 differential refractometer with Waters 410 HPLC Pump and two Styrogel HR 5E columns in DMF (0.1 mg L<sup>-1</sup>) solvent at 42 °C, calibrated with polystyrene standards. To investigate the thermal stability of the PIs, thermogravimetric analyses (TGA) were performed under N<sub>2</sub> using a TGA Q50 Q Series thermal analyzer at a heating rate of 10 °C min<sup>-1</sup> from room temperature to 700 °C. Measurements of glass transition





SCHEME 3 Synthesis of fluorinated polyimides.

temperatures were performed using a DSC Q 100 TA instrument at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  under  $\text{N}_2$  atmosphere. The transparencies of the PI films were measured from ultraviolet-visible spectra recorded from one accumulation on a OPTIZEN 3220UV spectrometer optimized with a spectral width of 200–800 nm, a resolution of 0.5 nm, and a scanning rate of  $200\text{ nm min}^{-1}$ ; the thickness of each film was  $\approx 20\text{ }\mu\text{m}$ . Wide-angle X-ray diffraction (WXAD) measurements of the pulverized samples were conducted at room temperature in the reflection mode using a Rigaku diffractometer (Model Rigaku Miniflex). The Cu K $\alpha$  radiation ( $\lambda = 1.54\text{ }\text{\AA}$ ) source was operated at 50 kV and 40 mA. The  $2\theta$  scan data were collected at  $0.01^{\circ}$  intervals over the range  $1.5^{\circ}$ – $40^{\circ}$  and at a scan speed of  $0.58^{\circ} (2\theta)\text{ min}^{-1}$ . Tensile properties were determined from stress–strain curves obtained with Kyungsang Universal Testing Measurement (UTM) Materials Testing System (Model KSU.05) at a strain rate of  $10\text{ mm min}^{-1}$  at room temperature. Measurements were performed with film specimens (50 mm in gauge length, 10 mm wide and 0.1 mm thick). Each reported value is the average of five different measurements. The dielectric constant ( $\epsilon$ ) was obtained at 1 MHz using an impedance-gain phase analyzer (HP4194A) and the formula  $\epsilon = C d / A \epsilon_0$ , where  $C$  is the observed capacitance,  $d$  is the film thickness,  $A$  is the area, and  $\epsilon_0$  is the free permittivity. The thickness of each film was  $1.0 \pm 0.05\text{ }\mu\text{m}$ . Plasma treatment of the indium-tin oxide (ITO) plates were done using Plasma cleaner; Harrick Plasma PDC-32A. Each reported value is the average of three different measurements. Water absorptions ( $W_A$ ) were determined by weighing the changes of PI films ( $3.0 \times 1.0 \times 0.005\text{ cm}^3$ ) before and after immersion in water at  $25\text{ }^{\circ}\text{C}$  for 24 h. Each reported value is the average of five different measurements. The static contact angle (SCA) was measured using a drop shape analysis system (DSA 100, Krüss GmbH, Germany) with a  $500\text{ }\mu\text{L}$  syringe and a needle, 0.5 mm in diameter, and 38 mm in length. The liquid flow used for the SCA measurements was  $6\text{ }\mu\text{L}$  at a flow rate of 600 rpm. Each reported value is the average of three different measurements. The melting points (uncorrected) were measured with a BUCHI Melting Point B-545 apparatus.

## RESULTS AND DISCUSSION

### Monomer Synthesis and Characterization

The syntheses of the diamine monomers DAPFB and BPFBD are depicted in Schemes 1 and 2, respectively. As shown in Scheme 1, the perfluorinated diamine monomer DAPFB was obtained through a two-step synthetic route. The first step involved in the synthesis of DNPFB (1) by *S*-arylation of PFDT with 2,4-dinitro-1-fluorobenzene using triethylamine ( $\text{Et}_3\text{N}$ ) as a base. DNPFB was reduced in the second step by  $\text{Fe}/\text{AcOH}$  to obtain DAPFB (2). The same procedure was also followed to reduce 2,4-dinitro-1-fluorobenzene to 2,4-diamino-1-fluorobenzene (DAFB). A three step synthetic procedure was adapted for the synthesis of BPFBD (Scheme 2). Treatment of 1-iodo-3-nitrobenzene with sodium hydroxide in a mixture of ethanol and ethylene glycol gave the azoxy compound (3) in 60% yields. The reaction of (3) with zinc dust in acetic acid and phosphoric acid led to the intermediary formation of hydrazobenzene that instantly underwent the benzidine rearrangement reaction by concentrated hydrochloric acid to yield DAIB (4) in 42% yields. The diamine monomer BPFBD was obtained after the CuI catalyzed cross-coupling reaction of DAIB with PFDT in 55% isolated yields.

The structures of the synthesized diamine monomers and of the intermediates were confirmed by FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and  $^{19}\text{F}$  NMR spectroscopy, and elemental analyses. Supporting Information Figure S4 shows the FTIR spectra of DNPFB and DAPFB. DNPFB gave characteristic bands at  $1540$ – $1342\text{ cm}^{-1}$  ( $\text{NO}_2$  asymmetric and symmetric stretching). After reduction, the characteristic absorptions of the nitro group disappeared in DAPFB, and the amino group exhibited N–H stretching bands in the region of  $3474$ – $3331\text{ cm}^{-1}$ . Both DNPFB and DAPFB show very sharp stretching band at  $1204$ – $1149\text{ cm}^{-1}$  for C–F bonds. The appearance of a very strong band at  $1204$ – $1143\text{ cm}^{-1}$  in the FTIR spectrum of BPFBD confirmed the successful cross-coupling reaction between 4,4'-diamino-2,2'-diiodobiphenyl and PFDT (Supporting Information Fig. S7). The successful modification can also be realized from the appearance of

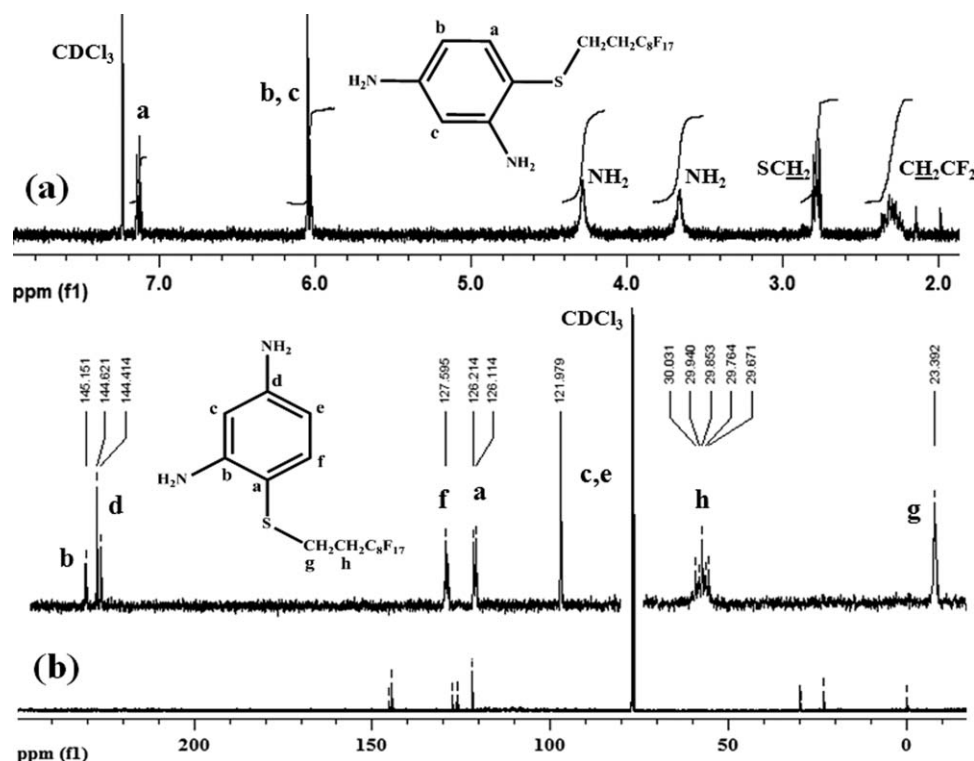


FIGURE 1 NMR spectra of DAPFB in CDCl<sub>3</sub> (a: <sup>1</sup>H NMR, b: <sup>13</sup>C NMR).

C–H stretching vibration for –CH<sub>2</sub> group at 2927–2852 cm<sup>–1</sup>. Figure 1 shows the <sup>1</sup>H and <sup>13</sup>C NMR spectra of DAPFB in which all the peaks were clearly assigned. The <sup>1</sup>H NMR spectrum shows two singlets at 4.28 and 3.66 ppm corresponding to the two –NH<sub>2</sub> groups in DAPFB. Two multiplets appeared at the most up-field region: the multiplet at 2.29 ppm (higher multiplicity) can be assigned as –CH<sub>2</sub>CF<sub>2</sub> protons while the protons in –SCH<sub>2</sub> group resonate at 2.29 ppm (lower multiplicity). The down field protons can be assigned as aromatic protons. <sup>13</sup>C-NMR spectrum exhibits seven characteristic peaks; five coming for six aromatic carbons while the two methylene carbons constitute the remaining two signals. The clear multiplet centred at 29.8 ppm can be assigned as the methylene carbon of –CH<sub>2</sub>CF<sub>2</sub> group. The peaks of eight carbons of perfluorooctyl group disappeared due to the carbon-fluorine coupling effect.<sup>18</sup> <sup>19</sup>F NMR signals from the long perfluorinated alkyl chain were clearly observed as a triplet peak at –80.87 ppm corresponding to methyl fluorines (CF<sub>3</sub>–(CF<sub>2</sub>)<sub>7</sub>–) and multiple peaks from –113 to –126 ppm attributed to methylene fluorines (CF<sub>3</sub>–(CF<sub>2</sub>)<sub>7</sub>–) (Supporting Information Fig. S3). Similar trends were observed in the <sup>1</sup>H, <sup>13</sup>C NMR (Fig. 2) and <sup>19</sup>F NMR (Supporting Information Fig. S8) spectra of BPFBD. NH<sub>2</sub> protons resonate at 4.35 ppm while –SCH<sub>2</sub> and –CH<sub>2</sub>CF<sub>2</sub> protons appeared at 2.95 and 2.34 ppm, respectively. Eight peaks were obtained in the <sup>13</sup>C-NMR spectrum of BPFBD of which 6 for 12 aromatic carbons represented two carbons each. The peaks at 31.8 and 25.3 ppm can be assigned as the methylene carbon of –CH<sub>2</sub>CF<sub>2</sub> and –SCH<sub>2</sub> groups, respectively.

### Polyimides Synthesis and Characterization

Four fluorinated PIs were prepared by two-step polycondensation method involving ring-opening polyaddition of 6FDA with DAPFB, DAFB, DAIB, and BPFBD, leading to the appropriate poly(amic-acid) (PAA) intermediate and subsequent cyclodehydration (Scheme 3). In general, the cyclodehydration step (imidization step) can be achieved either by thermal treatment of PAA solution (thermal imidization) or by the addition of dehydrating agents, such as a mixture of acetic anhydride and pyridine to the PAA solution. Thermal imidization method often results low molecular weight PIs due to the possible chain breaking at very high imidization temperatures. Chemical imidization has an advantage over thermal imidization in this regard as it operates at relatively lower temperatures (more often at room temperature). On the other hand, chemical imidization is not suitable for insoluble PIs. Therefore, if a clear solution and not a suspension results during the polymerization reaction, chemical polyimidization using a dehydrating agent is better than the thermal imidization. Accordingly, in the present work, chemical imidization using acetic anhydride and pyridine as dehydrating agent has been utilized to prepare the soluble fluorinated PIs. The imidization proceeded homogeneously throughout the course of reaction and afforded clear, low-viscous polymer solutions. The obtained fluorinated PIs precipitated in off white (PI1 and PI3) and white (PI2 and PI4), powder-like form after the reaction mixture being poured into large excess of MeOH. The steric and electronic characteristics of the perfluorinated groups can reduce the nucleophilicity of the fluorinated diamines and thereby reducing their

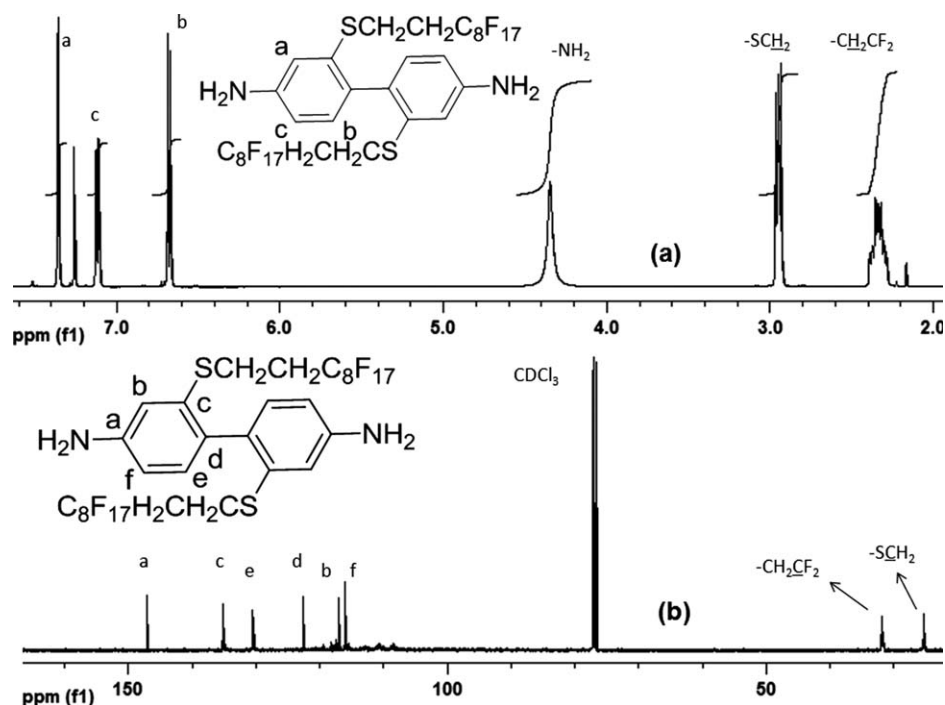


FIGURE 2 NMR spectra of BPFBD in  $\text{CDCl}_3$  (a:  $^1\text{H}$  NMR, b:  $^{13}\text{C}$  NMR).

reactivity towards electrophilic dianhydrides. The presence of large number of highly electronegative fluorine atoms in the perfluorodecylthio side group reduced the reactivity of DAPFB and BPFBD towards 6FDA and that necessitates the longer reaction time and higher imidization temperature for DAPFB and BPFBD based PIs (PI2 and PI4).

The chemical structures of PIs were confirmed by means of elemental analysis, ATR FTIR,  $^1\text{H}$  NMR, and  $^{19}\text{F}$  NMR spectroscopy. All the PIs exhibited characteristic imide group absorptions bands in the region of  $1788\text{--}1785\text{ cm}^{-1}$  (asymmetrical carbonyl stretching vibrations),  $1732\text{--}1719\text{ cm}^{-1}$

(symmetrical carbonyl stretching vibrations),  $1367\text{--}1358\text{ cm}^{-1}$  (C–N stretch), and  $1101\text{--}1091$  and  $723\text{--}716\text{ cm}^{-1}$  (imide ring deformation), together with some strong absorption bands in the region of  $1256\text{--}1137\text{ cm}^{-1}$  due to the C–F stretching (Fig. 3). The absence of amide and carboxyl bands indicates a virtually complete conversion of the PAAs precursor into PIs.

The repeat unit structures of PI2 and PI4 were also well-supported by the  $^1\text{H}$  NMR spectra, as shown in Figure 4.  $^1\text{H}$

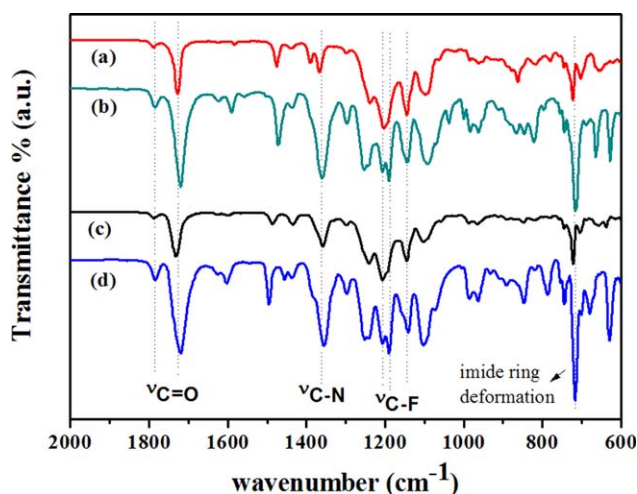


FIGURE 3 ATR FTIR spectra of (a) PI4 (b) PI3 (c) PI2 (d) PI1. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

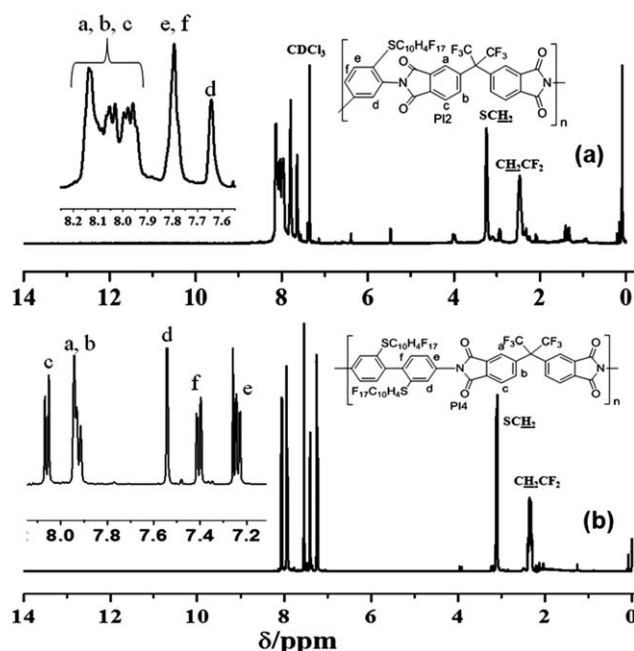


FIGURE 4  $^1\text{H}$  NMR spectra of (a) PI2 and (b) PI4 in  $\text{CDCl}_3$ .

**TABLE 1** Elemental Analysis and GPC Molar Mass of PIs

Polyimide Code	Formula (Molecular Weight)		Elemental Analysis (%)			GPC Molar Mass	
			C	H	N	$M_w \times 10^{-4}$	PDI
PI1	(C <sub>25</sub> H <sub>9</sub> F <sub>7</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub>	Calcd.	56.19	1.70	5.24	5.38	1.8
	(534.34) <sub>n</sub>	Found	56.78	1.54	5.18		
PI2	(C <sub>35</sub> H <sub>13</sub> F <sub>23</sub> N <sub>2</sub> O <sub>4</sub> S) <sub>n</sub>	Calcd.	42.27	1.32	2.82	3.01	2.1
	(994.52) <sub>n</sub>	Found	41.39	1.57	3.04		
PI3	(C <sub>31</sub> H <sub>12</sub> F <sub>6</sub> I <sub>2</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub>	Calcd.	44.05	1.55	3.31	4.19	1.6
	(844.24) <sub>n</sub>	Found	43.47	1.31	3.45		
PI4	(C <sub>51</sub> H <sub>20</sub> F <sub>40</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub> ) <sub>n</sub>	Calcd.	39.55	1.30	1.81	1.89	2.3
	(1548.78) <sub>n</sub>	Found	42.15	1.23	1.64		

NMR chemical shifts of PI2 and PI4 were assigned according to the labeling presented in Figure 4. The assignments of all the protons are in complete agreement with the proposed PI structures. The most down field protons are of 6FDA (8.2–7.9 ppm) while the remaining aromatic protons are of diamines (7.8–7.6 for DAPFB and 7.6–7.2 ppm for BPFBD). The aliphatic protons resonate at 3.24 and 2.46 ppm in PI2 while at 3.11 and 2.33 ppm in PI4. The spectra confirm the fully imidized structure, as indicated by the absence of PAA proton peaks (between 10 and 14 ppm) and clear proton assignment in accordance with the repeat unit structure. The <sup>1</sup>H NMR spectra of PI1 and PI3 (Supporting Information Figs. S9 and S10, respectively) were similar to that of PI2 and PI4. The incorporation of hexafluoroisopropylidene group [C(CF<sub>3</sub>)<sub>2</sub>] and perfluorodecylthio group [S(CH<sub>2</sub>)<sub>2</sub>(CF<sub>2</sub>)<sub>7</sub>CF<sub>3</sub>] in PI2 and PI4 can be realized by the <sup>19</sup>F NMR spectra of PI2 and PI4 (Supporting Information Figs. S11 and S12, respectively). The integration ratio of peaks a (assigned as –CF<sub>3</sub> of C(CF<sub>3</sub>)<sub>2</sub> group) and b (assigned as –CF<sub>3</sub> of S(CH<sub>2</sub>)<sub>2</sub>(CF<sub>2</sub>)<sub>7</sub>CF<sub>3</sub> group) in Supporting Information Figures S11 and S12 confirmed the presence of one and two perfluorodecylthio group(s) per unit repeat structure of PI2 and PI4, respectively. The elemental analysis values of the polymers generally agreed well with the calculated values for the proposed structures. The observed values were in good agreement with the calculated ones. The results of the elemental analyses and GPC analyses of the polyimides are listed in Table 1. The molecular weight values,  $M_w$ , are in the range of 53,800–18,900 Da, and polydispersity index ( $M_w/M_n$ ) in the domain of 2.3–1.6, a range expected for condensation polymers. The  $M_w$  values of PI2 and PI4 were lower than PI1 and PI3. The presence of large number of highly electronegative fluorine atoms in the perfluorodecylthio side group reduced the reactivity of DAPFB and BPFBD towards 6FDA and thereby results polyimides with lower molecular weights.

### Solubility

In order to examine the solubility of the PIs, both polar (*N*-methyl-2-pyrrolidinone (NMP), dimethylacetamide (DMAc), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ace-

tone), and nonpolar (toluene, xylene, chloroform (CHCl<sub>3</sub>), tetrahydrofuran (THF)) solvents were used to dissolve these PIs at room temperature (25 °C) or at 60 °C. The PIs were considered to be soluble in a solvent if a solution of 5% (w/w) concentration could be prepared. All the four PIs studied are soluble in all of these common organic solvents except in toluene and in xylene (Table 2). The excellent solubility of these PIs certainly due to the presence of bulky, asymmetric, fluorinated hexafluoroisopropylidene group on the 6FDA moieties that disrupts the conjugation of the aromatic rings and thereby hinder the charge transfer interactions between neighboring molecules. PI2 and PI4 were even soluble in highly nonpolar toluene and xylene. The higher solubility of PI2 and PI4 is considered due mainly to the differences in chain packing caused by the aliphatic perfluorodecylthio side group. The presence of hydrophobic, bulky long alkyl chain perfluorodecylthio side group resulted in reduction of the interchain interaction which leads to less efficient chain packing. The resulting relatively loose packing of these PIs allows solvent molecules to penetrate through the polymeric chains better and thereby improve the solubility.

### Crystallinity

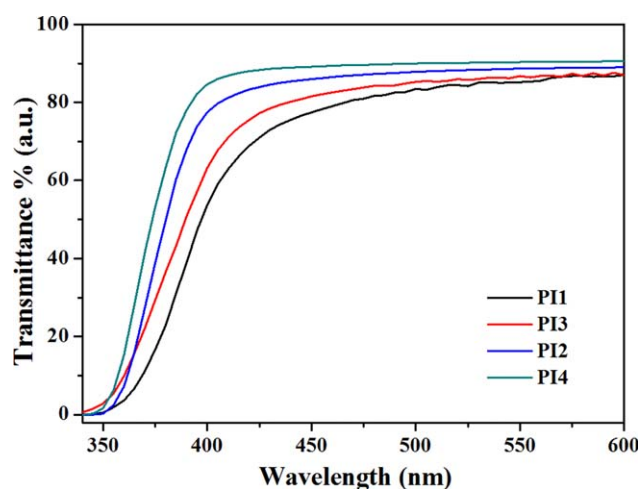
Supporting Information Figure S13 shows WAXD patterns of the fluorinated PIs. For all these PIs, the reflection patterns are featureless and very broad that appeared in the region  $2\theta = 8^\circ$ – $23^\circ$  (centred at  $2\theta = 16^\circ$ ), indicating that they are

**TABLE 2** Solubility Data of the Polyimides Synthesized in this Work

PI	Solvents <sup>a</sup>							
	NMP	DMAc	DMF	DMSO	Toluene	Xylene	CHCl <sub>3</sub>	THF
PI1	++	++	++	++	±	+	++	++
PI2	++	++	++	++	++	++	++	±
PI3	++	++	++	++	±	++	++	++
PI4	++	++	+	+	++	++	++	±

<sup>a</sup> Solubility: (++) soluble at room temperature; (+) soluble upon heating at 60 °C; (±) partially soluble or swells.





**FIGURE 5** Optical transmission spectra of the PI films. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

all amorphous. This is due to the diffraction of a poor intermolecular packing combined with amorphous halo.<sup>32</sup> The maxima of the broad peaks shifted toward lower  $2\theta$  values (higher d-spacing) with the introduction of perfluorodecylthio side group in the polyimide network (PI1,  $2\theta = 16.7^\circ$ , d-space = 5.3 Å; PI2,  $2\theta = 15.8^\circ$ , d-space = 5.7 Å; PI3,  $2\theta = 16.6^\circ$ , d-space = 5.4 Å, PI4,  $2\theta = 15.1^\circ$ , d-space = 5.9 Å). Introduction of the hydrophobic, bulky, long alkyl chain aliphatic perfluorodecylthio side groups in the polymer backbone increase the disorder of the polymer chains, resulting in decreasing of the interchain interactions and thereby reducing the chain packaging efficiency to hinder the polymer crystallization. The d-spacing is usually considered to represent the distance between segments of different chains and related to the free volume of a polymer. Normally, as the d-spacing value increases, the free volume also increases and so as the solubility of polymer. PI2 and PI4 with higher d-spacing value showed higher solubility even in highly nonpolar solvents such as toluene and xylene.

### Optical Properties

Optical transparency of the PI films is considered to be a crucial factor for various optical applications. Generally, aromatic PI films exhibit intense colors ranging from light

yellow to deep brown, depending on their structures, due to the formation of intra- or intermolecular CTC. Figure 5 exhibits the UV-vis absorption spectra of PI films ( $\approx 20 \mu\text{m}$  thick). The data are summarized in Table 3. All of these PIs are actually based on 6FDA which usually show better optical transparency than most of the other commercially available dianhydrides due to the presence of bulky  $-\text{CF}_3$  group in 6FDA that is quite effective in hindering the CTC formation between polymer chains through steric hindrance.<sup>33</sup> The spectral shapes of the four PIs vary considerably depending on the nature of diamines. The cutoff wavelengths ( $\lambda_0$ ) of the films are in the range of 382–408 nm. Transmittances of the PI films measured at 450 nm are 74% for PI1, 85% for PI2, 80% for PI3, and 89% for PI4. The polyimide film prepared from BPFBD and 6FDA (PI4) was completely colorless. The much improved optical transmittance of PI2 and PI4 compare to PI1 and PI3 may be due to the presence of bulky, electron withdrawing perfluorodecylthio side group in DAPFB and BPFBD which effectively decreases the CTC formation between polymer chains through steric hindrance and the inductive effect (by decreasing the electron-donating property of diamine moieties). The interchain cohesive force becomes weaker due to lower polarizability of the C–F bond of the perfluorinated side groups in DAPFB and BPFBD and this also may have contributed towards higher film transparency of PI2 and PI4. The decrease in intermolecular CTC formation in PI2 and PI4 is also evidenced from their much higher solubility in toluene and xylene.

### Thermal Properties

The thermal deformation and decomposition behavior of the PIs were evaluated by DSC and TGA measurements under nitrogen. The results are presented in Table 3. Supporting Information Figure S14 compares the DSC curves of the synthesized fluorinated PIs. The  $T_g$  values of the polymers taken from the second heating curves obtained in DSC plots were found to be in the range of 209–294 °C. The  $T_g$ s of PI2 and PI4 from DAPFB and BPFBD (220 and 209 °C, respectively) were much lower than PI1 and PI3 (273 and 294 °C, respectively). All the four PIs reported in this work were synthesized from the same dianhydride (6FDA) and, therefore, we can assume that the differences between  $T_g$  values are originating from the diamine component. It appears that the fluorinated side groups in DAPFB and BPFBD have some influence on the

**TABLE 3** Thermal, Mechanical Properties, and Dielectric Constants of API Films

PIs	TS (MPa)	EB (%)	TM (GPa)	$\epsilon$	$W_A$ (%)	$\theta_W$ (°)	$\lambda_0$ (nm)	$T_d^5$ (°C)	$T_d^{10}$ (°C)	$T_g$ (°C)	$R_{w700}$ (%)
PI1	120 ± 6	6 ± 1	2.6 ± 0.4	3.10	1.31	91.97 ± 2.5	408	467	494	273	51
PI2	101 ± 5	8 ± 1	1.7 ± 0.3	2.86	0.40	97.37 ± 1.5	388	413	420	220	34
PI3	101 ± 8	5 ± 1	2.1 ± 0.5	2.98	1.14	93.73 ± 1.5	396	438	459	294	44
PI4	76 ± 9	10 ± 1	1.5 ± 0.4	2.71	0.32	107.03 ± 3.0	382	404	409	209	36

TS: tensile strength, EB: elongation at break, TM: tensile modulus,  $\epsilon$ : dielectric constant,  $W_A$ : water absorption,  $\theta_W$ : water contact angle,  $\lambda_0$ : cutoff wavelength,  $T_g$ : glass transition temperature;  $T_d^5$ ,  $T_d^{10}$ : temperatures at 5 and 10% weight loss, respectively;  $R_{w700}$ : residual weight ratio at 700 °C in nitrogen.



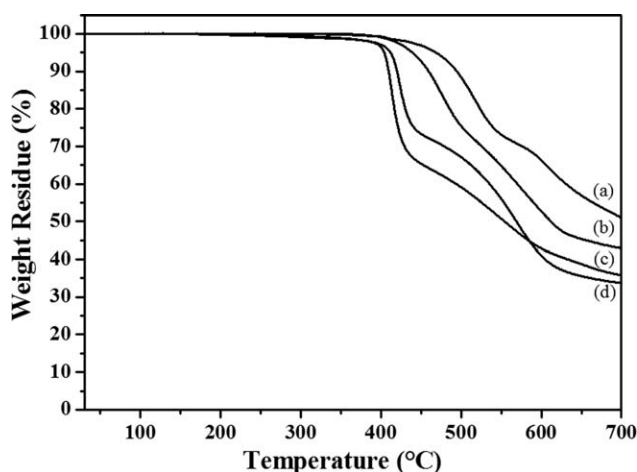


FIGURE 6 TGA curves of the (a) PI1 (b) PI3 (c) PI4 and (d) PI2.

lower  $T_g$ s of PI2 and PI4. The incorporation of bulky, electron withdrawing, hydrophobic perfluorodecylthio side group lowers cohesive energy and reduces the formation of inter-chain CTC and thereby the interchain packing density also weakens considerably that shifts the glass transitions to lower temperatures. An additional decrease in interchain packing density might also have occurred in PI4 due to the noncoplanar structure of the two ortho-substituted phenyl rings of BPFBD (2,2'-disubstituted biphenyl structure) and this explains the lowest glass transition temperature of PI4.

As shown in Figure 6 (TGA), all PIs showed good thermal stability, such as 5% weight loss temperatures ( $T_d^5$ ) in the range of 404–467 °C and 10% weight-loss temperatures ( $T_d^{10}$ ) in the range of 409–494 °C. Weight residues at 700 °C ranging from 34 to 51% are observed in nitrogen. PI2 and PI4 with perfluorodecylthio side group diamines (DAPFB and BPFBD) exhibited lower  $T_d^5$  and  $T_d^{10}$  compared to PI1 and PI3. This result is basically consistent with the glass transition results. Unlike the single step decomposition of PI1 and PI3, thermal decomposition in PI2 and PI4 occurred in two steps.

The first decomposition in perfluorinated PI2 and PI4 can be due to the loss of perfluorodecylthio side groups.

### Mechanical and Dielectric Properties

All of the PIs afforded transparent, free standing and tough films. The mechanical properties of the fully aromatic fluorinated PIs were investigated using the stress-strain curves (Supporting Information Fig. S15) obtained from UTM and the average values of five different measurements for each PI are listed in Table 3. All of these four PIs exhibited appreciable mechanical stiffness, tensile strength varying from 76 to 120 MPa, elongation at break from 5 to 10%, and tensile modulus in the range 1.5–2.6 GPa indicating that they are strong and tough polymeric materials. Apart from lower inter-chain packing density, the relatively lower molecular weight ( $M_w$ ) of PI4 may have contributed towards its lower mechanical stiffness.

The dielectric constants of PI films, reported in Table 3 were in the range of 2.71–3.10 measured at 1 MHz. PI2 and PI4 exhibited lower dielectric constants than PI1 and PI3. The lowest dielectric constant was obtained for PI4 (2.71). The lower dielectric constants of the PI2 and PI4 are mainly attributed to the higher fluorine content in these two polyimides. The strong electronegativity of fluorine atoms would result in very low C–F polarizability while the high free volumes originated from the bulky perfluorodecylthio side groups ensured less efficient chain packing and thereby decreasing the dielectric constants.

### Water Absorption

Table 3 shows the water absorption of the PIs. All the four PIs exhibited very low water absorptions ( $W_A\%$ ) which ranges from 0.32 to 1.31%. All these PIs are actually based on 6FDA which is known to produce PIs with low moisture absorption due to the hydrophobic nature of the  $-\text{CF}_3$  group. PI2 and PI4 exhibited lower moisture absorption of 0.40 and 0.32%, respectively. The lower water absorption of the PI2 and PI4 might be due to the higher hydrophobicity derived from the presence of perfluorodecylthio side groups in their polymer backbones.


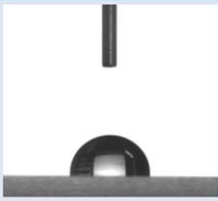


PI1	PI2	PI3	PI4
			
$91.97^\circ \pm 2.5^\circ$	$97.37^\circ \pm 1.5^\circ$	$93.73^\circ \pm 1.5^\circ$	$107.03^\circ \pm 3.0^\circ$

FIGURE 7 Water contact angle on the polymer films PI1–PI4. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

## Static Contact Angles

Static contact angles of water dripped onto the surface of the polyimide films were tested to investigate the hydrophobic character of PIs film surfaces and the measured contact angle values were in the range of 91.97°–107.03°. The water contact angles ( $\theta_w$ ) of the PI films are listed in Table 3. Figure 7 depicts the profiles of a droplet on the PI surface. PI2 and PI4 displayed higher  $\theta_w$  values, 97.37° and 107.03°, respectively, therefore better hydrophobic characteristics, compared to PI1 and PI3 (91.97° and 93.73°, respectively). The results indicate that the presence of hydrophobic trifluoromethyl group of 6FDA and perfluorodecylthio group of DAPFB/BPFBD in the polyimide backbone of PI2 and PI4 could efficiently lead to the migration of the fluorocarbon chain segments to the film surface and thereby fluorine enrichment at the surface, thus reducing the surface tension and making the surface more hydrophobic.<sup>34</sup>

## CONCLUSIONS

The efficient synthesis of two new perfluorodecylthio substituted aromatic diamines DAPFB and BPFBD was reported in this work. Both DAPFB and BPFBD were reactive enough to yield two new perfluorinated aromatic polyimides (PI2 and PI4) by the polycondensation with 6FDA. A comparative investigation between the perfluorinated PIs (PI2 and PI4) and nonperfluorinated PIs (PI1 and PI3) revealed that PI2 and PI4 exhibited higher solubility and optical transparency, but lower thermal and mechanical properties due to the presence of bulky, electron withdrawing perfluorodecylthio side group which lowers cohesive energy and reduces CTC formation and interchain packing density. The much higher concentration of hydrophobic fluorinated substituents in PI2 and PI4 increases their hydrophobicity and decreases moisture absorption and dielectric constant. The eminent combination of several properties guaranteed PI2 and PI4 as potential candidates for high-performance microelectronic applications.

## ACKNOWLEDGMENTS

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