

Polyimides 7: Synthesis, Characterization, and Properties of Novel Soluble Semifluorinated Poly(ether imide)s

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ABSTRACT: Three novel diamine monomers (VI, VII, and VIII) were synthesized. These diamine monomers lead to a number of semifluorinated poly(ether imide)s when reacted with different commercially available dianhydrides like pyromellitic dianhydride (PMDA), benzophenone tetracarboxylic acid dianhydride (BTDA), 2,2-bis (3,4-dicarboxyphenyl) hexafluoropropene (6FDA), and oxydiphthalic dianhydride (ODA) by thermal imidization route. Elemental analyses, IR and NMR techniques were used to characterize the monomers and polymers. The resulting polymers exhibited weight average molar masses up to 1.78×10^5 g mol⁻¹ in GPC with respect to polystyrene standard and have very good solubility in several organic solvents such as NMP, DMF, DMAc, DMSO, chloroform, and THF. Very good sol-

ubility of these polymers in CDCl₃ enables their complete characterization by proton as well as ¹³C-NMR techniques. The polymers showed very high thermal stability with decomposition temperature (5% weight loss) up to 511°C in air and high glass transition temperature up to 311°C depending upon the exact repeating unit structure. The polymer films showed high modulus (up to 2.9 GPa) as was evaluated by DMA. The polymers also showed very low water absorption (0.16%), low dielectric constant (2.35 at 1 MHz) and very good optical transmission. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3025–3044, 2007

Key words: polyimides; dielectric properties; glass transition

INTRODUCTION

Aromatic polyimides exhibit a number of outstanding properties, such as high thermal and mechanical properties as well as excellent chemical resistance.^{1–6} Since the commercialization of Kapton [pyromellitic dianhydride (PMDA)–ODA-based polyimide] by Du Pont, these materials have found widespread applications such as electrical insulating material and as interlayer/intermetal dielectrics (ILD/IMD). The PMDA–ODA-based polyimide exhibit very high glass transition temperature ($T_g \sim 390^\circ\text{C}$) and high mechanical strength (tensile strength, 158 MPa and tensile modulus, 3.2 GPa).⁷ For use as material for ILD/IMD, its dielectric constant (ϵ) should be rather high and unavoidable moisture absorption (ϵ , 3.1–3.5, water uptake %, 1.3–3.5). The major problem of rigid polyimides is insolubility and infusibility in their fully imidized form, leading to processing difficulties. They are generally processed from their poly(amide acid) precursors and then converted to polyimide via rigorous thermal treatment. This process has several limitations, such as poor shelf-life of the poly(amide acid) and emission of volatile byproducts (e.g., water) during imidization.

The search for new polyimides with improved processibility, higher glass transition temperature, and low dielectric constant has received significant attention since the commercialization of Ultem 1000 by General Electrical Company. Ultem 1000 is manufactured from the BPDA [bisphenol-A di(phthalic anhydride)] and MPD (meta phenylene diamine).⁷ This material possesses excellent flow characteristics and melt stability, because of flexible ether linkages in the main chain and serves as true high performance engineering thermoplastic. At the same time, high flexibility affects its glass transition temperature ($T_g \sim 217^\circ\text{C}$). Hence, it is of great interest to have a material that has the properties of Kapton with the processibility of Ultem 1000.

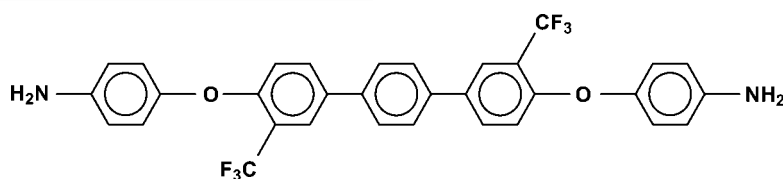
Solubilization of polyimides have been targeted by several means, such as introduction of flexible linkages,^{8,9} bulky substituents,^{10,11} or bulky units in the polymer backbone,^{12–14} incorporation noncoplanar^{15,16} or alicyclic units.¹⁷ Semifluorinated polyimides have got great attention in this regard from both academia and industry.^{18–22} Polyimides containing hexafluoroisopropylidene group (6F), trifluoromethyl or trifluoromethoxy groups serve to increase the free volume, thereby improving various properties, and also enhance solubilities of the fully cyclized polyimide, lower dielectric constant without forfeiture of thermal stability and concomitant decrease in crystallinity. The positive effect of fluorinated substituents

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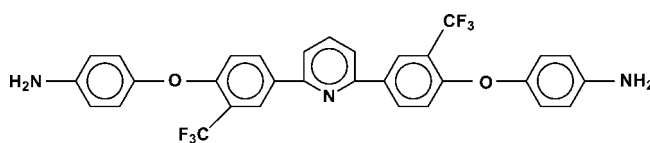
is reduced moisture absorption due to the nonpolar character of fluorocarbon groups, which *vis-à-vis* reduces the dielectric constant. NASA had reported one interesting fluorinated polyether imide, LARCTM-CPI, based on 2, 2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 2,2'-bis[4-(4-aminophenoxy) diphenylhexafluoropropane].²³ It was

commercialized through licensing. However, it is not available commercially at present.

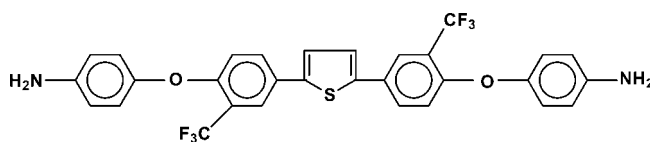
In the quest of novel new polymer structures with improved processability, high glass transition temperature, high thermal stability, and low dielectric constant we designed several poly(ether imide)s based on the following novel diamines.^{24–28}



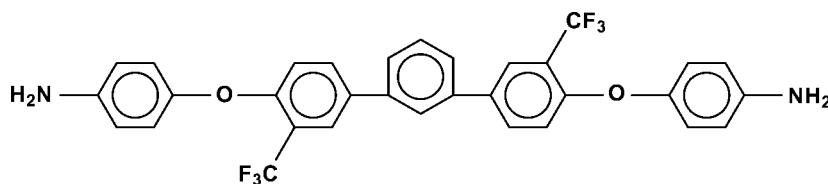
Monomer I



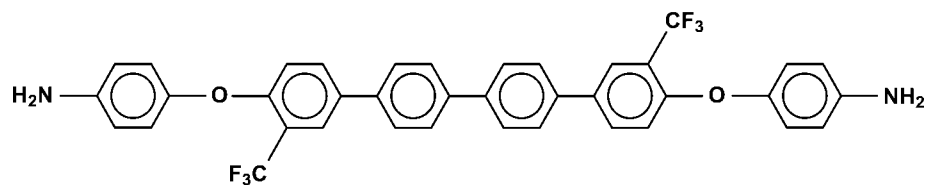
Monomer II



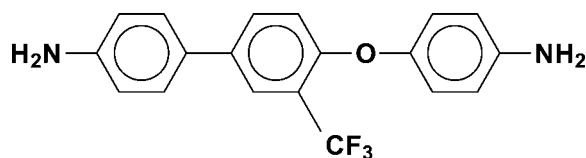
Monomer III



Monomer IV



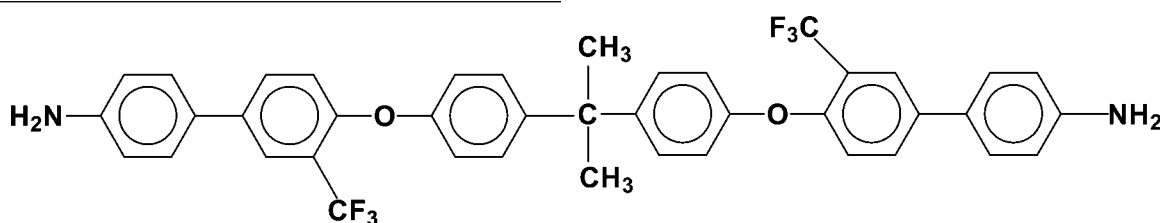
Monomer V



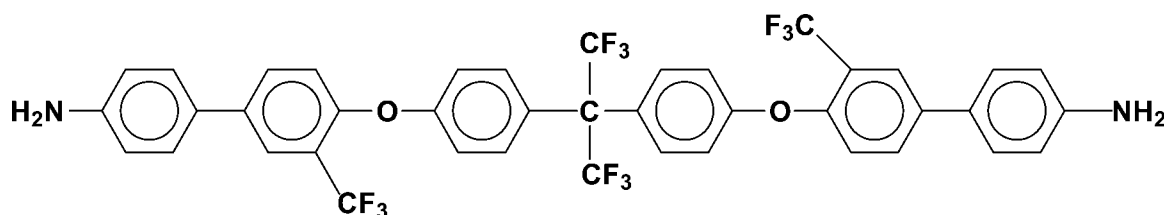
Monomer VI

The polyimides made out of these monomers (I–V) showed many interesting properties, e.g., high glass transition temperature (up to 316°C), high thermal stability in air, and reasonably low dielectric constant. However, our target to get organosoluble polymer was not very successful except for those that were made out of 6FDA as dianhydride. Kim's findings²⁹ insisted us to design the unsymmetrical monomer VI. However, the solubility of the poly(ether imide)s derived from this monomer³⁰ was not on par with Kim's findings. This provoked us to further manipulate the chemical structures of the diamine monomer through simple chemistry that can

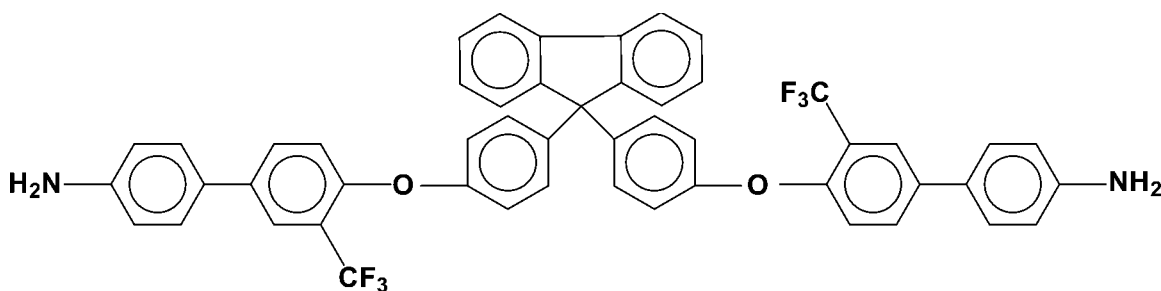
result in useful polymer structures having the define set of properties. We designed three novel diamine monomers (VII–IX) by adopting the concept of having both flexible and rigid units together; the flexible component will allow the free rotation and will lead to better solubility in organic solvents and the rigid biphenyl unit linked with the dianhydride moiety through imide linkages will help in getting higher glass transition temperature. In this paper we will discuss the properties of 12 novel poly(ether imide)s based on the three new diamines and a compare their properties with the previously reported poly(ether imide)s:



Monomer VII



Monomer VIII



Monomer IX

EXPERIMENTAL

General considerations

Carbon and hydrogen of the compounds were analyzed by Prejel method and nitrogen was analyzed by Kjeldhal method. ¹H-NMR (400 MHz), ¹³C-NMR (75

MHz), and ¹⁹F-NMR (100 MHz) spectra were recorded on a Bruker ARX 400 instrument [reference 0 ppm with TMS (¹H and ¹³C-NMR) or CFCl₃ (¹⁹F-NMR)]. IR spectra of the polymer films were recorded on a Nicolet-Impact-410 spectrophotometer using KBr pellets. Gel permeation chromatography was per-

formed with a Waters instrument. Tetrahydrofuran (THF) was used as eluant, and Styragel HR-4 columns were employed. The molecular weight and polydispersity are reported versus monodisperse polystyrene standard. DSC measurement was made on a TA Instruments DSC-2920 instrument, at a heating/cooling rate of 20°C/min under nitrogen. Glass transition temperature (T_g) was measured at the middle of the step transition in the second heating run. Thermogravimetry was performed on a TA Instruments thermogravimetric analyzer, Model TGA-2950. A heating rate of 10°C/min was used for determination of the decomposition temperature (T_d) at 5% weight loss under synthetic air. Dynamic mechanical analysis (DMA) was performed on a Netzsch, DMA-242 instruments in the tension mode on thin film (80–100 μ m) samples with a heating rate of 5°C/min (1 and 10 Hz). Mechanical properties of the thin polymer films were evaluated at room temperature on a Testometric Good Brand, Micro-350 instrument, under strain rate 5%/min. Dielectric constant of the polyimide films was measured with an YHP 4278 capacitance meter at 1 MHz at a temperature 35°C and relative humidity 45. Water absorption rates of the films were measured by a Mettler microbalance of sensitivity of 10^{-6} g after immersing the films in double distilled water for 72 h, at 30°C. UV-vis spectra were recorded on Specord 200 UV-Vis spectrophotometer.

Starting materials

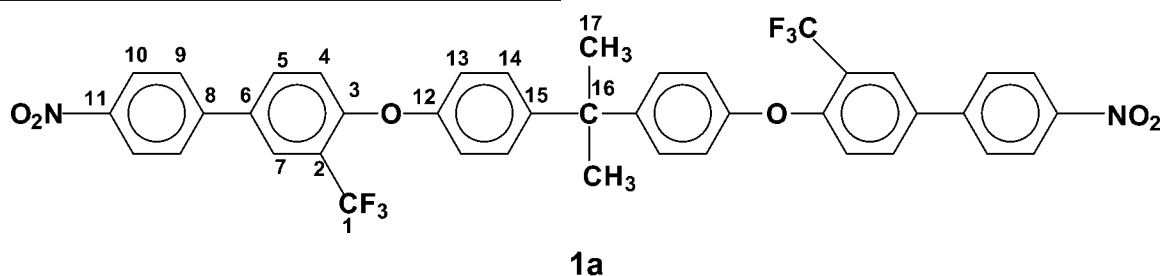
All reagents were purchased from Fluka (Switzerland), Lancaster (UK), and Arcos Chemical Company (UK) and used as received unless otherwise noted. PMDA and BTDA (Fluka, Switzerland) were purified by sublimation under reduced pressure. 6FDA (99%) (Lancaster), ODA (Aldrich, USA) were heated at 180°C prior to use. NMP (Fluka) and DMF (E Marck, India)

was purified by stirring with NaOH and distilled twice from P_2O_5 under reduced pressure. The synthesis of the compound 3-trifluoromethyl-4-fluoro-4'-nitro biphenyl was reported in our previous article.³⁰

Synthesis of diamine monomers VI, VII, and VIII

The diamine monomers were synthesized in two steps. In first step 3-trifluoromethyl-4-fluoro-4'-nitro biphenyl (5 g, 17.532 mmol), and a dihydroxy compound 4,4'-isopropylidene diphenol (2 g, 8.760 mmol), 4,4'-hexafluoroisopropylidene diphenol (2.95 g); 4,4'-9-fluorenylidene diphenol (2.996 g), anhydrous K_2CO_3 (8 g), DMF (50 mL) and toluene (50 mL) were weighed into a 250-mL three-necked round bottom flask equipped with nitrogen inlet, Dean-Stark apparatus, and reflux condenser. The mixture was heated with stirring to 135°C; the water due to deprotonation of phenol was removed via azeotropic distillation with toluene. After 4 h the toluene was removed from the reaction mixtures, the resulting solutions were heated at 160°C for 2 h. The reaction mixtures were cooled to room temperature and were precipitated in a large excess of distilled water. The precipitates were collected by filtration and dried overnight in vacuum oven at 80°C.

In the second step the dinitro compounds (6.5 g), Pd-C (Pd content 10%, 0.4 g) and 240 mL of ethanol were taken in a 500-mL three-necked round bottom flask equipped with a stirring bar, nitrogen inlet, and reflux condenser. To this mixture, hydrazine monohydrate 120 mL was added dropwise over a period of 1 h at 85°C. The reaction was maintained at reflux for another 12 h. The mixture was then filtered to remove Pd-C. The filtrate was concentrated under nitrogen atmosphere and allowed to crystallize. The solid crystals obtained on filtration were dried under vacuum at 80°C for several hours.

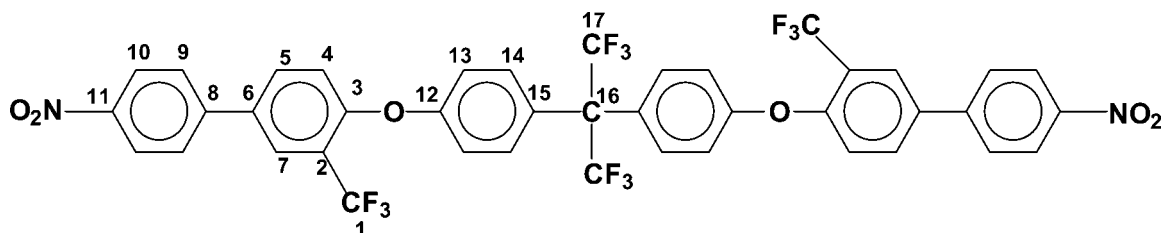


Yield: 5.9 g (89.39%). Melting point: 231°C (DSC, heating rate 5°C/min). Anal. Calcd for $(C_{41}H_{28}F_6O_6N_2)_n$ (758.661 g mol⁻¹): C, 64.91; H, 3.72; N, 3.69. Found: C, 63.64; H, 3.71; N, 3.71. IR (KBr) (cm⁻¹): 2972 (Aromatic C—H stretching), 1600 (C=C ring stretching band); 1347, 1254, 1135 (band due to C—F absorption); 1053

(symmetric C—O—C stretch); 830 (C—N stretch for Ar—NO₂); 754 (aromatic C—H band out of plane). ¹H-NMR (CDCl₃) δ (ppm): 8.26 (d, J = 8.2 Hz, 4H, H¹⁰); 7.86 (s, 2H, H⁷); 7.66 (d, J = 8.3 Hz, 4H, H⁹); 7.62 (d, J = 8 Hz, 4H, H⁵); 7.23 (d, J = 7.96 Hz, 4H, H⁴); 7.02 (d, J = 8.02 Hz, 4H, H¹⁴); 6.97 (d, J = 8.11 Hz, 4H, H¹³);

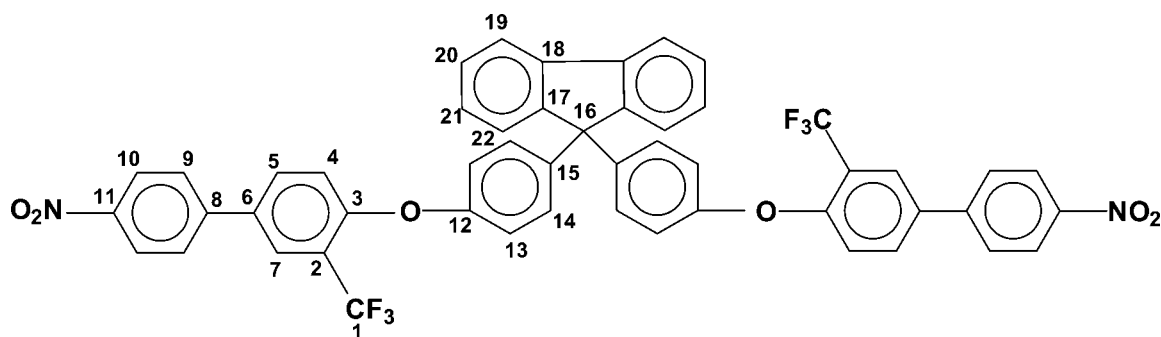
1.68 (s, 6H, H¹⁷). ¹³C-NMR (CDCl₃) δ (ppm): 156.51 (C¹²); 153.53 (C³); 147.1 (C¹¹); 147.03 (C⁸); 145.54 (C¹⁵); 132.95 (C⁵); 131.95 (C⁶); 128.44 (C⁹); 127.53 (C¹⁴);

126.16 (C⁷); 124.28 (C¹⁰); 123.03 (q, *J* = 271 Hz, C¹); 121.56 (q, *J* = 31 Hz, C²); 119.45 (C¹³); 119.1 (C⁴); 42.39 (C¹⁶); 30.94 (C¹⁷).

**2a**

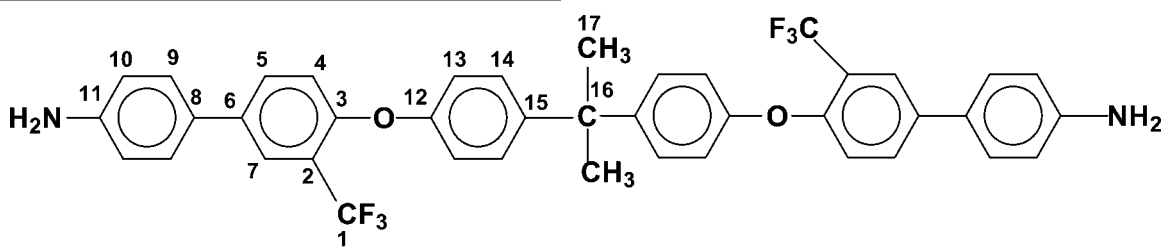
Yield: 6.07 g (96.11%). Melting point: 173°C (DSC, heating rate 5°C/min). Anal. Calcd for (C₄₁H₂₂F₁₂O₆N₂)_n (844.44 g mol⁻¹)_n: C, 58.32; H, 2.62; N, 3.32. Found: C, 58.28; H, 2.59; N, 3.38. ¹H-NMR (CDCl₃) δ (ppm): 8.28

(d, *J* = 8.59 Hz, 4H, H¹⁰); 7.8 (s, 2H, H⁷); 7.71 (d, *J* = 8.34 Hz, 2H, H⁵); 7.67 (d, *J* = 8.6 Hz, 4H, H¹⁴); 7.38 (d, *J* = 8.6 Hz, 4H, H⁹); 7.10 (d, *J* = 8.6 Hz, 4H, H⁹); 7.04 (d, *J* = 8.1 Hz, 2H, H⁴); 7.03 (d, *J* = 8.25 Hz, 4H, H¹³).

**3a**

Yield: 7.9 g (89%). Melting point: 221°C (DSC, heating rate 5°C/min). Anal. Calcd for (C₅₁H₃₀F₆O₆N₂)_n (880.7964 g mol⁻¹)_n: C, 69.54; H, 3.43; N, 3.18. Found: C, 67.28; H, 3.68; N, 3.3. ¹H-NMR (CDCl₃) δ (ppm): 8.24 (d, *J* = 8.7 Hz, 4H, H¹⁰); 7.8 (s, 2H, H⁷); 7.73 (d, *J* = 8.01

Hz, 2H, H¹⁹); 7.60 (d, *J* = 8.6 Hz, 4H, H⁹); 7.57 (d, *J* = 8.63 Hz 2H, H⁵); 7.36 (t, 2H, H²⁰); 7.34 (d, *J* = 8, 2H, H²²); 7.725 (t, 2H, H²¹); 7.17 (d, *J* = 8.42 Hz, 4H, H¹⁴); 6.95 (d, *J* = 8.6 Hz, 2H, H⁴); 6.88 (d, *J* = 8.26 Hz, 4H, H¹³).

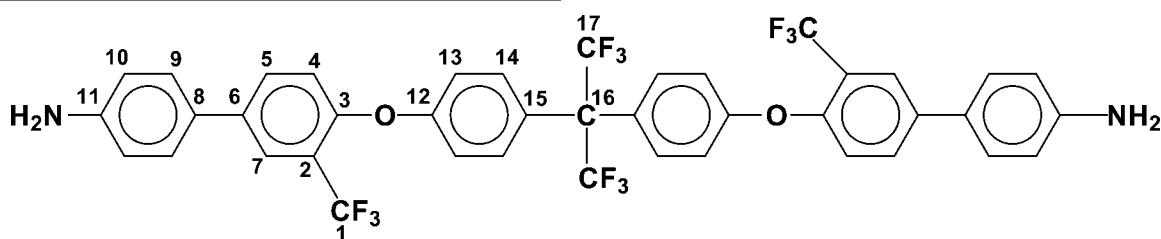
**VII**

Yield: 5.6 g (93.69%). Melting point: 163°C (DSC, heating rate 5°C/min). Anal. Calcd for (C₄₁H₃₂F₆O₂N₂)_n (698.693 g mol⁻¹)_n: C, 70.48; H, 4.62; N, 4.01. Found: C, 69.97; H,

4.69; N, 3.88. IR (KBr) (cm⁻¹): 3474, 3386 (N—H stretching); 3042, 2974, 2857 (aromatic C—H stretching), 1621 (C=C ring stretching band); 1409, 1333 (band due to

C—F absorption); 1249 (asymmetric C—O—C stretch); 1131, 1052, 1013 (symmetric C—O—C); 823 (C—H band out of plane). $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 7.72 (s, 2H, H^7); 7.5 (dd, $J = 8.8$ Hz, 2H, H^5); 7.29 (d, $J = 8.4$ Hz, 4H, H^{14}); 7.16 (d, $J = 8.8$ Hz, 4H, H^{13}); 6.9 (m, 6H, H^9 and H^4); 6.8 (d, $J = 8.4$ Hz, 4H, H^{10}); 3.69 (s, 4H, NH_2); 1.6 (s, 6H, H^{17}).

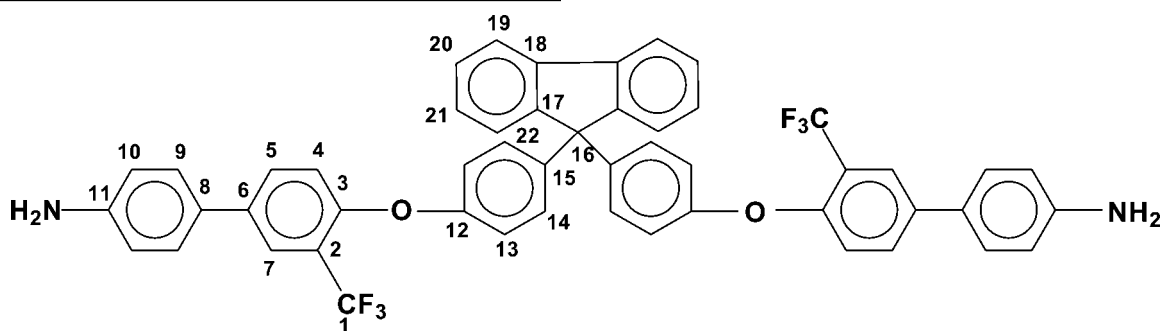
$^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 154.52 (C^{12}); 153.88 (C^3); 146.17 (C^{11}); 136.02 (C^{15}); 130.69 (C^5); 129.53 (C^6); 128.15 (C^9); 127.78 (C^{14}); 125.59 (C^8); 124.83 (C^7); 121.39 (q, $J = 30.7$ Hz, C^2); 120.69 (q, $J = 271$ Hz, C^1); 118.99 (C^4); 118.74 (C^{13}); 115.42 (C^{10}); 42.23 (C^{16}); 30.33 (C^{17}). $^{19}\text{F-NMR}$ (CDCl_3) δ (ppm): -61.94(F1).



VIII

Yield: 5.5 g (87%). Melting point: 93°C (DSC, heating rate 5°C/min). Anal. Calcd for $(\text{C}_{41}\text{H}_{26}\text{F}_{12}\text{O}_2\text{N}_2)_n$ (806.65 g mol $^{-1}$): C, 61.05; H, 3.25; N, 3.47. Found: C, 61.32; H, 3.22; N, 3.41. IR (KBr) (cm^{-1}): 3408.37 (N-H stretching); 2930 (aromatic C—H stretching); 1626 ($\text{C}=\text{C}$ ring stretching band); 1410, 1333, 1247, 1174 (band due to C—F absorption); 1053 (symmetric C—O—C); 825 (C—H band out of plane). $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 7.75 (s, 2H, H^7); 7.56 (dd, $J = 8.4$ Hz,

2H, H^5); 7.30 (d, $J = 8.4$ Hz, 8H, H^{13} and H^{14}); 6.99 (d, $J = 8.4$ Hz, 2H, H^4); 6.96 (d, $J = 9.2$ Hz, 4H, H^9); 6.67 (d, $J = 9.2$ Hz, 4H, H^{10}); 3.71 (s, 4H, NH_2). $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 157.68 (C^3); 152.37 (C^{11}); 146.41 (C^{15}); 137.35 (C^{12}); 131.82 (C^5); 130.90 (C^{13}); 128.25 (C^{14}); 127.89 (C^9); 127.37 (C^8); 125.06 (C^7); 120.96 (C^{10}); 118.19 (dq, $J = 32$ Hz, C^2); 117.93 (C^6); 115.47 (q, $J = 271$ Hz, C^1); 108.65 (C^{16}). $^{19}\text{F-NMR}$ (CDCl_3) δ (ppm): -69.4(F1)



IX

Yield: 6 g (91.9%). Melting point: 182°C (DSC, heating rate 5°C/min). Anal. Calcd for $(\text{C}_{51}\text{H}_{34}\text{F}_6\text{O}_2\text{N}_2)_n$ (820.83 g mol $^{-1}$): C, 73.63; H, 4.18; N, 3.41. Found: C, 74.79; H, 3.92; N, 3.86. IR (KBr) (cm^{-1}): 3479 (C—H stretching of substituted - CF_3 aromatic ring); 3428 (N-H stretching); 3146 (C—H stretching of condensed ring); 2895 (C—H stretching of fluorene moiety); 2823 (aromatic C—H stretching); 1673, 1605 ($\text{C}=\text{C}$ ring stretching skeleton band); 1382, 1243, 1084 (series of band due to C—F absorption); 1048 (aromatic C—O—C linkage); 897, 732 (aromatic C—H bend out of plane). $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 7.71 (d, $J = 7.92$ Hz, 2H, H^{19}); 7.69 (s,

2H, H^7); 7.469 (d, $J = 8.82$ Hz, 2H, H^5); 7.41 (d, $J = 8.52$ Hz, 2H, H^4); 7.34 (t, 2H, H^{20}); 7.278 (d, $J = 8.43$ Hz, 4H, H^{14}); 7.25 (t, 2H, H^{21}); 7.12 (d, $J = 8.82$ Hz, 4H, H^9); 6.88 (d, $J = 8.56$ Hz, 2H, H^{22}); 6.84 (d, $J = 8.76$ Hz, 4H, H^{13}); 6.68 (d, $J = 8.44$ Hz, 4H, H^{10}); 3.71 (s, 4H, NH_2). $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 155.497(C^{12}); 153.55 (C^3); 151.09 (C^{11}), 146.13 (C^{17}); 141.29 (C^{18}); 139.98 (C^{15}); 136.19 (C^5); 130.68 (C^6); 129.51 (C^{14}); 127.78 (C^9); 127.62 (C^{19} and C^{21}); 127.46 (C^{22}); 126.07 (C^8); 124.82 (C^7); 121.53 (dq $J = 30.2$ Hz, C^2); 120.68 (q, $J = 271$ Hz, C^1); 120.24 (C^{20}); 119.79 (C^4); 118.79 (C^{13}); 115.41 (C^{10}). $^{19}\text{F-NMR}$ (CDCl_3) δ (ppm): -64.9 (F1)

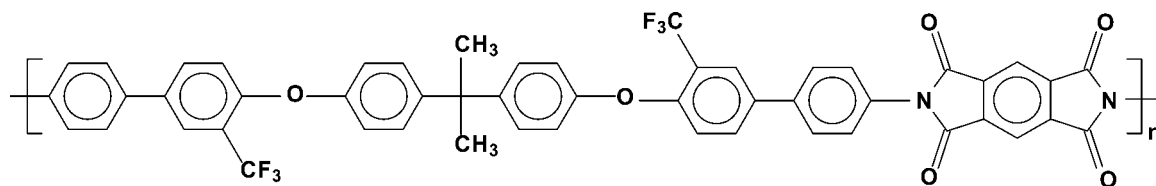
Polymerization

Equimolar amounts of diamine and dianhydride monomers were reacted in nitrogen atmosphere with constant flow. A representative polymerization procedure is as follows.

In a 50-mL round-bottomed flask equipped with a nitrogen inlet and outlet, a stir bar was charged with 1.0 g (1.431 mmol) of diamine monomer **VI** and 15 mL of purified and dry DMF. The solution was stirred until the diamine dissolved completely, then 0.3121 g

(1.431 mmol) PMDA was added to this solution slowly. The highly viscous solution resulted within 15 min was stirred continuously for 2 h at 15°C. The poly(amic acid) solution was cast onto clean and dry glass plates by a doctor blade, the films were dried in an oven at 80°C for 6 h, at 150, 200, 250, and 300°C for 1 h at each temperature, and 350°C for 30 min. Polyimide films were removed by immersing the glass plates in boiling water. The same procedure was adopted for other polymers.

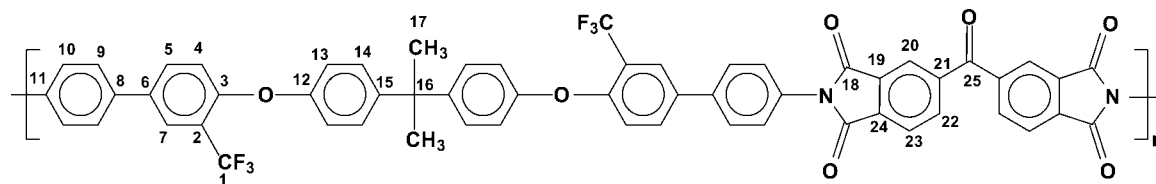
Polyimide 7a



Anal. Calcd for $(C_{51}H_{30}O_6F_6N_2)_n$ (880.796 g mol⁻¹): C, 69.55; H, 3.43; N, 3.2. Found: C, 69.49; H, 3.36; N, 3.1. IR (KBr) (cm⁻¹): 3042, 2969 (aromatic C—H stretching); 1778 (C=O asym. stretching); 1731 (C=O sym. stretching); 1618 (C=C ring stretching band); 1492 (C—F

absorption); 1375 (asymmetric C—O—C stretching); 1132, 1053 (symmetric C—O—C stretching); 815 (C—N bending); 728 (aromatic C—H band out of plane); 686 (C=O bending). No NMR data is available due to insufficient solubility in CDCl₃ of this polymer.

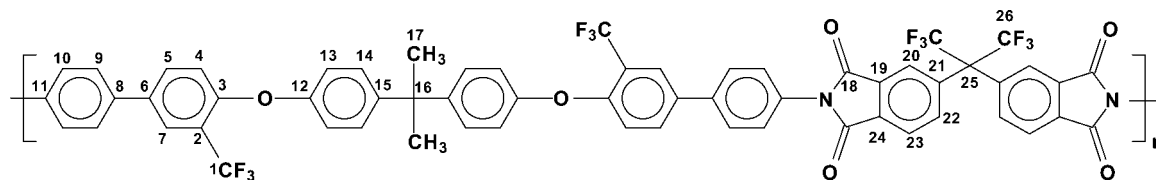
Polyimide 7b



Anal. Calcd for $(C_{58}H_{34}O_7F_6N_2)_n$ (984.904 g mol⁻¹): C, 69.55; H, 3.43; N, 3.2. Found: C, 69.49; H, 3.36; N, 3.1. IR (KBr) (cm⁻¹): 3049, 2968 (aromatic C—H stretching); 1781 (C=O asym. stretching); 1727 (C=O sym. stretching); 1618 (C=C ring stretching band); 1490 (C—F absorption); 1373 (asymmetric C—O—C stretching); 1134, 1053 (symmetric C—O—C stretching); 826 (C—N bending), 719 (aromatic C—H band out of plane). ¹H-NMR (CDCl₃) δ (ppm): 8.24 (m, 4H, H²⁰ and H²²); 7.94 (d, *J* = 7.2 Hz, 2H, H²³); 7.8 (s, 2H, H⁷); 7.64

(m, 6H, H⁵ and H¹⁴); 7.51 (d, *J* = 8.09 Hz, 4H, H⁹); 7.21 (d, 4H, *J* = 9.6 Hz, H¹⁰); 6.97 (m, 6H, H⁴ and H¹³); 1.66 (s, 6H, H¹⁷). ¹³C-NMR (CDCl₃) δ (ppm): 192.77 (C²⁵); 166.00 (C¹⁸); 155.51 (C³); 153.93 (C¹²); 146.69 (C²¹); 141.99 (C¹¹); 139.54 (C¹⁵); 135.89 (C²⁴); 135.04 (C²²); 134.55 (C⁸); 132.17 (C¹⁹); 131.67 (C⁵); 130.74 (C⁶); 128.33 (C²⁰); 127.75 (C¹⁴); 126.87 (C⁹); 125.92 (C⁷); 124.5 (q, *J* = 271 Hz, C¹); 124.66 (C²³); 124.22 (C⁴); 121.43 (q, *J* = 31.2 Hz, C²); 119.25 (C¹⁰); 119.17 (C¹³); 42.34 (C¹⁶); 31.00 (C¹⁷). ¹⁹F NMR (CDCl₃) δ (ppm): -62.28 (F1)

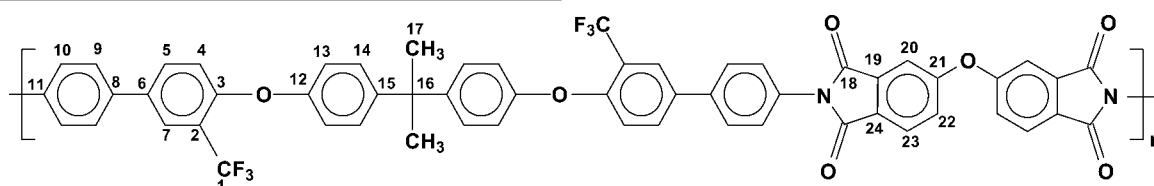
Polyimide 7c



Anal. Calcd for $(C_{60}H_{34}O_6F_{12}N_2)_n$ (1106.91 g mol⁻¹)_n: C, 65.10; H, 3.09; N, 2.53. Found: C, 65.08; H, 3.12; N, 2.48. IR (KBr) (cm⁻¹): 3042, 2969, 2968 (aromatic C—H stretching); 1785 (C=O asym. stretching); 1727 (C=O sym. stretching); 1619 (C=C ring stretching band); 1491 (C—F absorption); 1374 (asymmetric C—O—C stretching); 1141, 1053 (symmetric C—O—C stretching); 826.7 (C—N bending); 721 (aromatic C—H band out of plane). ¹H-NMR (CDCl₃) δ (ppm): 7.99 (d, *J* = 8 Hz, 2H, H²³); 7.879 (s, 2H, H²⁰); 7.835 (d, *J* = 8 Hz, 2H, H²²); 7.8 (s, 2H, H⁷); 7.596 (m, 6H, H⁵ and H¹⁴); 7.45

(d, *J* = 8.4 Hz, 4H, H⁹); 7.19 (d, *J* = 8.8 Hz, H¹⁰); 6.94 (m, 6H, H⁴ and H¹³); 1.637 (s, 6H, H¹⁷). ¹³C-NMR (CDCl₃) δ (ppm): 165.93 (C¹⁸); 155.46 (C¹²); 153.91 (C³); 146.65 (C²¹); 139.50 (C¹¹); 139.21 (C¹⁵); 135.96 (C¹⁹); 134.54 (C⁸); 132.63 (C²²); 132.34 (C⁵); 131.62 (C⁶); 130.71 (C²⁴); 128.29 (C¹⁴); 127.73 (C²³); 126.90 (C⁹); 125.87 (C²⁰); 125.41 (C¹⁰); 124.63 (C⁷); 124.20 (C⁴); 123.35 (q, *J* = 271 Hz, C¹); 121.39 (q, *J* = 31.2 Hz, C²); 119.21 (C¹³); 119.13 (C²⁶); 65.2 (C²⁵); 42.30 (C¹⁶); 30.96 (C¹⁷). ¹⁹F NMR (CDCl₃) δ (ppm): -62.29 (F1); -63.53 (F25).

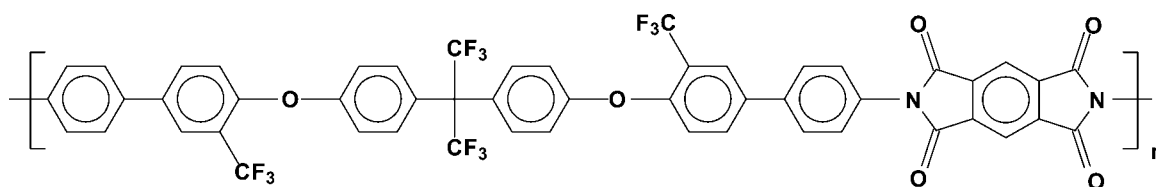
Polyimide 7d



Anal. Calcd for $(C_{57}H_{34}O_7F_6N_2)_n$ (972.893 g mol⁻¹)_n: C, 70.37; H, 3.52; N, 2.88. Found: C, 70.28; H, 3.54; N, 2.79. IR (KBr) (cm⁻¹): 3040, 2967, (aromatic C—H stretching); 1779 (C=O asym. stretching); 1727 (C=O sym. stretching); 1607 (C=C ring stretching band); 1401 (C—F absorption); 1371 (asymmetric C—O—C stretching); 1134, 1053 (symmetric C—O—C stretching); 815 (aromatic C—H band out of plane). ¹H-NMR (CDCl₃) δ (ppm): 7.96 (d, *J* = 8.4 Hz, 2H, H²³); 7.81 (s, 2H, H⁷); 7.6 (m, 6H, H⁴ and H²²); 7.5 (s, 2H, H²⁰); 7.47

(d, *J* = 8.4 Hz, 4H, H⁹); 7.42 (d, *J* = 8 Hz, 2H, H⁵); 7.19 (d, *J* = 8.8 Hz, 4H, H¹⁰); 6.952 (m, 6H, H⁴ and H¹³); 1.642 (s, 6H, H¹⁷). ¹³C-NMR (CDCl₃) δ (ppm): 166.13 (C¹⁸); 161.22 (C²¹); 155.41 (C¹²); 153.95 (C³); 146.64 (C¹¹); 139.26 (C¹⁵); 134.66 (C⁸); 134.61 (C¹⁹); 131.63 (C⁵); 131.00 (C⁶); 128.30 (C¹⁴); 127.66 (C⁹); 127.29 (C²³); 126.87 (C¹⁰); 126.31 (C²²); 125.876 (C⁷); 124.91 (C⁴); 123.30 (q, *J* = 271 Hz, C¹); 121.4 (q, *J* = 31 Hz, C²); 119.18 (C¹³); 114.02 (C²⁰); 43.32 (C¹⁶); 30.98 (C¹⁷). ¹⁹F NMR (CDCl₃) δ (ppm): -62.29 (F1)

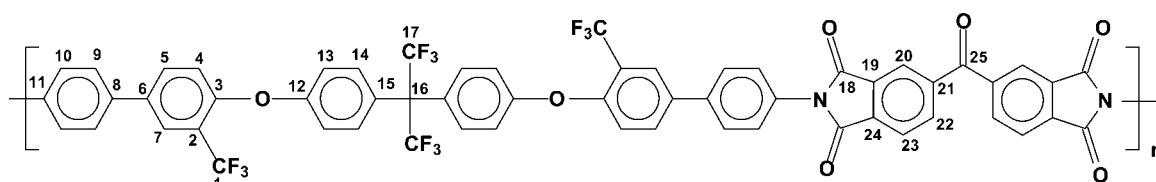
Polyimide 8a



Anal. Calcd for $(C_{51}H_{24}O_6F_{12}N_2)_n$ (988.74 g mol⁻¹)_n: C, 61.95; H, 2.45; N, 2.83. Found: C, 61.73; H, 2.32; N, 2.89. IR (KBr) (cm⁻¹): 2932, 2856 (aromatic C—H stretching), 1778 (C=O asym. Stretching), 1735 (C=O sym. stretching), 1608 (C=C ring stretching band), 1513 (C—F

absorption), 1384 (asymmetric C—O—C stretching), 1098, 1053 (symmetric C—O—C stretching), 823 (C—N bending), 728 (aromatic C—H band out of plane), 686 (C=O bending). No NMR data is available due to insufficient solubility in CDCl₃ of this polymer.

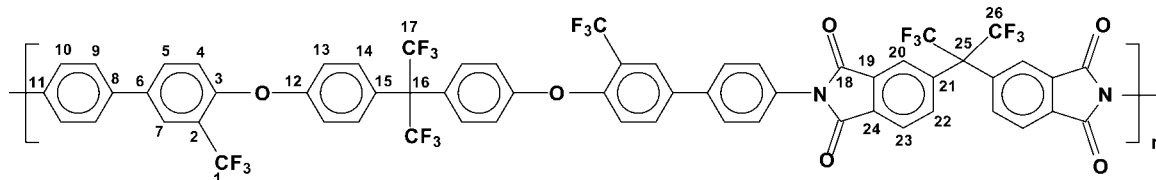
Polyimide 8b



Anal. Calcd for $(C_{58}H_{28}O_7F_{12}N_2)_n$ (1092.85 g mol⁻¹)_n: C, 63.75; H, 2.5843; N, 2.56. Found: C, 63.71; H, 2.63; N, 2.48. IR (KBr) (cm⁻¹): 3073 (aromatic C—H stretching); 1781 (C=O asym. stretching); 1727 (C=O sym. stretching); 1607 (C=C ring stretching band); 1491 (C—F absorption); 1374 (asymmetric C—O—C stretching); 1135, 1054 (symmetric C—O—C stretching); 826 (C—N bending); 720 (aromatic CH band out of plane). ¹H-NMR (CDCl₃) δ (ppm): 8.25 (m, 4H, H²⁰ and H²²); 8.11 (d, *J* = 8.2 Hz, 2H, H²³); 7.87 (s, 2H, H⁷); 7.66 (m, 6H,

H⁵ and H¹⁴); 7.53 (d, *J* = 8 Hz, 4H, H⁹); 7.36 (d, 4H, *J* = 8.6 Hz, H¹⁰); 7.08 (d, 2H, *J* = 8 Hz, H⁴); 7.02 (d, 4H, 8 Hz, H¹³). ¹³C-NMR (CDCl₃) δ (ppm): 192.72 (C²⁵); 165.96 (C¹⁸); 157.07 (C³); 153.92 (C²¹); 141.90 (C¹⁵); 139.23 (C¹¹); 135.88 (C²⁴); 134.98 (C¹²); 132.11 (C⁸); 131.90 (C⁵ and C¹⁹); 130.92 (C²²); 128.39 (C⁶); 127.80 (C¹⁰ and C¹³); 126.88 (C²⁰); 125.53 (C¹⁴); 124.80 (C⁹); 124.44 (C²³); 124.11 (q, *J* = 271 Hz, C¹); 122.42 (q, *J* = 32.2 Hz, C²); 120.59 (C⁷); 118.39 (C⁴). ¹⁹F-NMR (CDCl₃) δ (ppm): -62.19 (F1); -64.29 (F17).

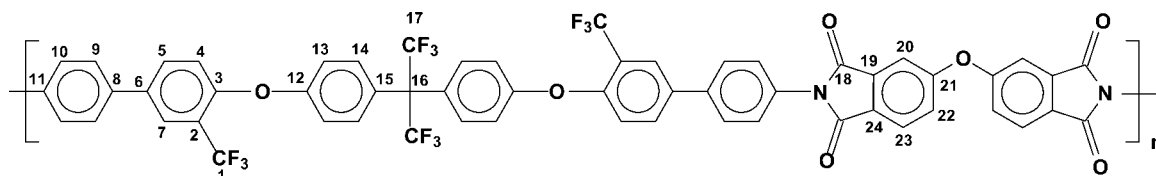
Polyimide 8c



Anal. Calcd for $(C_{60}H_{28}O_6F_{18}N_2)_n$ (1214.7758 g mol⁻¹)_n: C, 59.32; H, 2.32; N, 2.32. Found: C, 60.39; H, 2.56; N, 2.28. IR (KBr) (cm⁻¹): 3049 (aromatic C—H stretching); 1786 (C=O asym. stretching); 1728 (C=O sym. stretching); 1608 (C=C ring stretching band); 1492 (C—F absorption); 1374 (asymmetric C—O—C stretching); 1140, 1054 (symmetric C—O—C stretching); 827 (C—N bending); 721 (aromatic C—H band out of plane). ¹H-NMR (CDCl₃) δ (ppm): 8.01 (d, *J* = 8.2 Hz, 2H, H²³); 7.9 (m, 6H, H¹⁴ and H²⁰); 7.65 (m, 6H, H⁷, H⁵

and H²²); 7.49 (d, *J* = 8.1 Hz, 4H, H⁹); 7.36 (d, *J* = 8 Hz, 4H, H¹⁰); 7.08 (d, *J* = 8.6 Hz, 2H, H⁴); 7.02 (d, *J* = 8.4 Hz, 4H, H¹³). ¹³C-NMR (CDCl₃) δ (ppm): 165.94 (C¹⁸); 157.11 (C³); 153.94 (C²¹); 139.27 (C¹⁵); 136.01 (C¹¹); 135.87 (C¹²); 132.64 (C⁸); 132.35 (C¹⁹); 131.94 (C⁵); 130.86 (C²⁴); 128.56 (C¹³); 127.84 (C¹⁰); 127.16 (C⁶); 126.97 (C¹⁴); 126.10 (C²³); 125.46 (C⁹); 124.24 (C²⁰); 122.66 (C⁷); 122.14 (q, *J* = 32.9 Hz, C²); 120.61 (C⁴); 120.51 (q, *J* = 271 Hz, C¹); 118.42 (C¹⁷ and C²⁶). ¹⁹F NMR (CDCl₃) δ (ppm): -62.18 (F1); -63.54 (F17); -64.29 (F25).

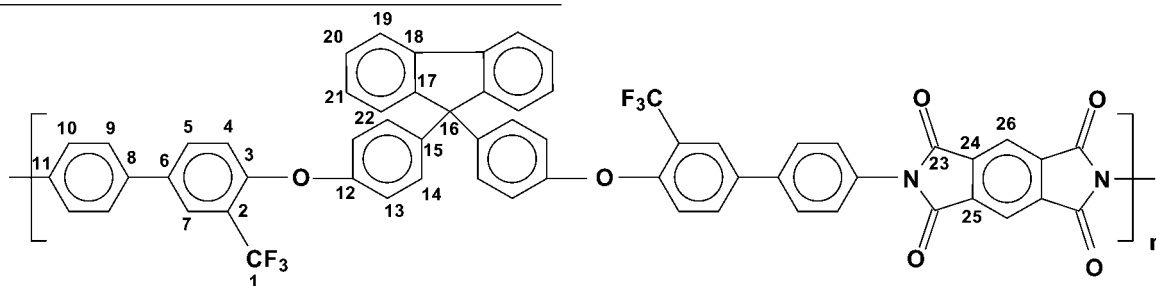
Polyimide 8d



Anal. Calcd for $(C_{57}H_{28}O_7F_{12}N_2)_n$ (1080.83 g mol⁻¹)_n: C, 63.34; H, 2.61; N, 2.59. Found: C, 63.14; H, 2.73; N, 2.48. IR (KBr) (cm⁻¹): 3049, 2920 (aromatic C—H stretching); 1780 (C=O asym. stretching); 1727 (C=O sym. stretching); 1608 (C=C ring stretching band); 1491 (C—F absorption); 1372 (asymmetric C—O—C stretching); 1135, 1054 (symmetric C—O—C stretching); 814 (C—N bending); 744 (aromatic C—H band out of plane). ¹H-NMR (CDCl₃) δ (ppm): 7.98 (d, *J* = 8.4 Hz, 2H, H²³); 7.86 (s, 2H, H⁷); 7.6 (m, 6H, H⁴ and

H²²); 7.51 (m, 6H, H⁹ and H²⁰); 7.45 (d, *J* = 8.07, 2H, H⁵); 7.36 (d, *J* = 8.58 Hz, 4H, H¹⁰); 7.07 (d, *J* = 8.57 Hz, 2H, H⁴); 7.02 (d, *J* = 8.89 Hz, 4H, H¹³). ¹³C-NMR (CDCl₃) δ (ppm): 166.14 (C¹⁸); 161.24 (C²¹); 157.13 (C³); 153.87 (C¹⁵); 139.02 (C¹¹); 135.96 (C¹²); 134.60 (C⁸); 131.93 (C¹⁹ and C⁵); 131.22 (C¹³); 128.66 (C⁶); 127.77 (C¹⁰); 126.93 (C¹⁴); 126.37 (C⁹); 126.10 (C²³); 124.97 (C²⁴); 123.10 (q, *J* = 271 Hz, C¹); 122.59 (C⁷); 122.44 (q, *J* = 31.7 Hz, C²); 120.62 (C²²); 118.40 (C²⁰); 114.05 (C⁴). ¹⁹F NMR (CDCl₃) δ (ppm): -62.18 (F1); -64.301 (F17).

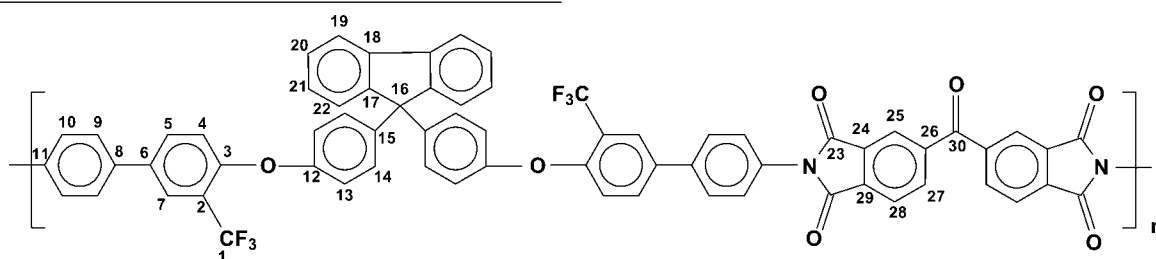
Polyimide 9a



Anal. Calcd for $(C_{61}H_{32}O_6F_6N_2)_n$ (1002.89 g mol⁻¹)_n: C, 73.05; H, 3.22; N, 2.79. Found: C, 72.09; H, 3.32; N, 2.85. IR (KBr) (cm⁻¹): 3040 (aromatic C—H stretching); 1780 (C=O asym. stretching); 1728 (C=O sym. stretching); 1618 (C=C ring stretching band); 1492, 1435 (C—F absorption); 1374 (asymmetric C—O—C stretching); 1053 (symmetric C—O—C stretching); 820 (C—N bending); 729 (aromatic C—H band out of plane); 669 (C=O bending). ¹H-NMR (CDCl₃) δ (ppm): 8.44 (s, 2H, H²⁶); 7.81 (s, 2H, H⁷); 7.73 (d, *J* = 7.6 Hz, 2H, H¹⁹); 7.63 (d, *J* = 8.15 Hz, 4H, H⁹); 7.58 (d, *J* = 8.62 Hz, 2H,

H⁵); 7.51 (d, *J* = 8.4 Hz, 4H, H¹⁴), 7.37 (t, 2H, H²⁰); 7.32 (d, 7.26 Hz, 2H, H²²); 7.25 (t, 2H, H²¹); 7.16 (d, *J* = 8.68 Hz, 4H, H¹⁰); 6.9 (d, *J* = 8.64 Hz, 2H, H⁴); 6.83 (d, *J* = 8.57 Hz, 4H, H¹³). ¹³C-NMR (CDCl₃) δ (ppm): 164.98 (C²³); 160.46 (C¹²); 155.08 (C³); 150.97 (C¹⁷); 141.86 (C¹¹); 140.04 (C¹⁸); 139.72 (C¹⁵); 137.16 (C²⁴); 134.65 (C⁸); 131.67 (C⁵); 130.18 (C⁶); 129.69 (C¹⁰); 127.87 (C²²); 127.79 (C¹⁴); 126.71 (C²⁰ and C¹⁹); 126.08 (C⁹); 124.58 (C²⁵); 121.87 (C⁷); 121.3 (q, *J* = 32.7 Hz, C²); 120.35 (C⁴); 120.123 (q, *J* = 271 Hz, C¹); 119.32 (C¹³); 29.69 (C¹⁶).

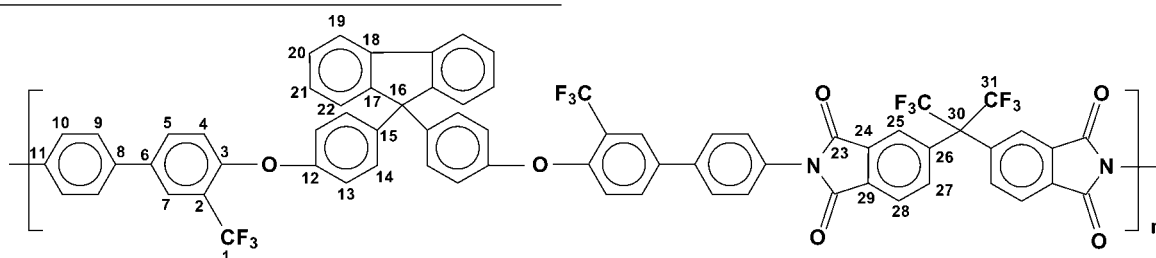
Polyimide 9b



Anal. Calcd for $(C_{68}H_{36}O_7F_6N_2)_n$ (1107.002 g mol⁻¹)_n: C, 73.78; H, 3.2779; N, 2.531. Found: C, 72.93; H, 3.17; N, 2.59. IR (KBr) (cm⁻¹): 3062 (aromatic C—H stretching); 1781 (C=O asym. stretching); 1727 (C=O sym. stretching); 1618 (C=C ring stretching band); 1489, 1447 (C—F absorption); 1372 (asymmetric C—O—C stretching); 1134, 1053 (symmetric C—O—C stretching); 823 (C—N bending); 735 (aromatic C—H band out of plane). ¹H-NMR (CDCl₃) δ (ppm): 8.23 (s, 2H, H²⁵); 8.21 (d, *J* = 7.5 Hz, 2H, H²⁸); 8.09 (d, *J* = 7.28 Hz, 2H, H²⁷); 7.79 (s, 2H, H⁷); 7.71 (d, *J* = 7.38 Hz, 2H, H¹⁰); 7.61 (d, *J* = 7.88 Hz, 4H, H⁹); 7.56 (d, *J* = 8.59 Hz,

2H, H⁵); 7.48 (d, *J* = 7.99 Hz, 4H, H¹⁴); 7.36 (t, 2H, H²⁰); 7.34 (d, *J* = 7.18 Hz, 2H, H²²); 7.24 (t, 2H, H²¹); 7.16 (d, *J* = 8.51 Hz, 4H, H¹⁰); 6.94 (d, *J* = 8.5, 2H, H⁴); 6.88 (d, *J* = 8.25 Hz, 4H, H¹³). ¹³C-NMR (CDCl₃) δ (ppm): 192.72 (C³⁰); 165.95 (C²³); 154.94 (C¹²); 150.95 (C³); 141.91 (C¹⁷); 141.80 (C²⁶); 140.01 (C¹⁸); 139.45 (C¹⁵); 136.89 (C²⁹); 135.00 (C²⁷); 134.75 (C⁸); 132.14 (C²⁴); 131.62 (C⁵); 130.74 (C⁶); 129.65 (C¹⁰); 127.84 (C²⁵); 127.71 (C²²); 126.83 (C¹⁴); 126.06 (C¹⁹ and C²¹); 125.86 (C⁹); 125.24 (C²⁸); 124.77 (C²⁰); 121.85 (C⁷); 121.775 (q, *J* = 271 Hz, C¹); 121.57 (q, *J* = 31.3 Hz, C²); 119.43 (C⁴); 119.27 (C¹³); 64.44 (C¹⁶).

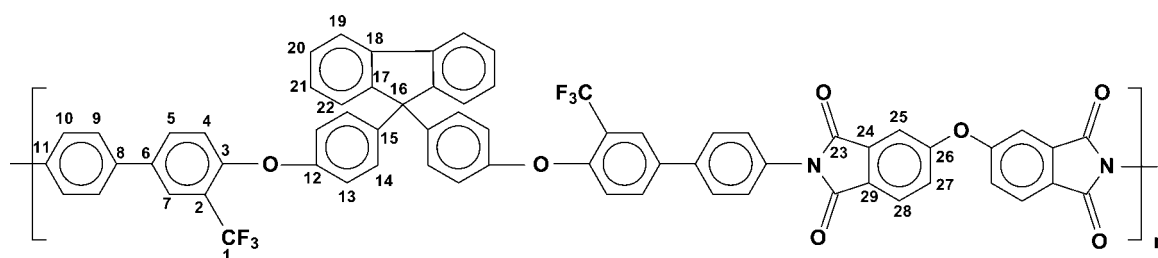
Polyimide 9c



Anal. Calcd for $(C_{70}H_{36}O_6F_{12}N_2)_n$ (1228.98 g mol⁻¹): C, 68.41; H, 2.952; N, 2.28. Found: C, 69.02; H, 2.89; N, 2.34. IR (KBr) (cm⁻¹): 3042 (aromatic C—H stretching); 1785 (C=O asym. stretching) 1727 (C=O sym. stretching); 1618 (C=C ring stretching band); 1490, 1434 (C—F absorption); 1373 (asymmetric C—O—C stretching); 1141, 1054 (symmetric C—O—C stretching); 823 (C—N bending); 693 (aromatic C—H band out of plane). ¹H-NMR (CDCl₃) δ (ppm): 7.99 (d, *J* = 7.98 Hz, 2H, H²⁸); 7.87 (s, 2H, H²⁵); 7.83 (d, *J* = 7.87 Hz, 2H, H²⁷); 7.79 (s, 2H, H⁷); 7.71 (d, *J* = 7.25 Hz, 2H, H¹⁹); 7.60 (d, *J* = 8.36 Hz, 4H, H⁹); 7.55 (d, *J* = 8.70

Hz, 2H, H⁵); 7.44 (d, *J* = 8.38 Hz, 4H, H¹⁴); 7.35 (t, 2H, H²⁰); 7.31 (d, *J* = 7.26 Hz, 2H, H²²); 7.24 (t, 2H, H²¹); 7.16 (d, *J* = 8.71 Hz, 4H, H¹⁰); 6.93 (d, *J* = 8.81 Hz, 2H, H⁴); 6.87 (d, *J* = 8.64 Hz, 4H, H¹³). ¹³C-NMR (CDCl₃) δ (ppm): 165.84 (C²³); 154.02 (C¹²); 150.96 (C³); 141.80 (C²⁶); 140.01 (C¹⁷); 139.46 (C¹¹); 139.22 (C¹⁸); 135.96 (C¹⁵); 134.75 (C⁸); 132.62 (C²⁴); 132.33 (C²⁷); 131.62 (C⁵); 130.72 (C⁶); 129.65 (C²⁹); 127.84 (C²²); 127.74 (C¹⁰); 126.90 (C¹⁴); 126.06 (C²⁸); 125.89 (C²⁵); 125.41 (C¹⁹); 124.77 (C⁷); 124.57 (C²¹); 124.21 (C⁹); 123.3 (q, *J* = 271 Hz, C¹); 121.24 (q, *J* = 31.1 Hz, C²); 120.31 (C²⁰); 119.42 (C⁴); 119.28 (C¹³); 64.44 (C¹⁶).

Polyimide 9d



Anal. Calcd for $(C_{67}H_{36}O_7F_6N_2)_n$ (1094.99 g mol⁻¹): C, 73.49; H, 3.314; N, 2.56. Found: C, 73.34; H, 3.43; N, 2.61. IR(KBr) (cm⁻¹): 3065, 3054 (aromatic C—H stretching); 1779 (C=O asym. stretching); 1726 (C=O sym. stretching); 1606 (C=C ring stretching band); 1489 (C—F absorption); 1370 (asymmetric C—O—C stretching); 1131, 1053 (symmetric C—O—C stretching); 813 (C—N bending), 742 (aromatic C—H band out of plane). ¹H-NMR (CDCl₃) δ (ppm): 7.97 (d, *J* = 7.92 Hz, 2H, H²⁸); 7.81 (s, 2H, H⁷); 7.74 (d, *J* = 7.49 Hz, 2H, H¹⁹); 7.6 (d, *J* = 8.4 Hz, 4H, H⁹); 7.579 (d, *J* = 9.2 Hz, 2H, H⁵); 7.523 (s, 2H, H²⁵); 7.46 (d, *J* = 8.4 Hz, 4H, H¹⁴); 7.44 (d, *J* = 8.36 Hz, 2H, H²⁷); 7.38 (d, *J* = 7.54 Hz, 2H, H²²); 7.34 (t, 2H, H²⁰); 7.261 (t, 2H, H²¹); 7.18 (d, *J* = 8.7 Hz, 4H, H¹⁰); 6.95 (d, *J* = 8.76 Hz, 2H, H⁴); 6.90 (d, *J* = 8.7 Hz, 4H, H¹³). ¹³C-NMR (CDCl₃) δ (ppm): 166.13 (C²³); 162.58 (C²⁶); 161.22 (C¹²); 155.02 (C³); 150.98 (C¹⁷); 141.78 (C¹¹); 140.02 (C¹⁸); 139.21 (C¹⁵); 134.87 (C⁵); 134.61 (C²⁴); 131.63 (C⁶); 131.02 (C¹⁰); 129.66 (C¹⁴); 127.85 (C⁹); 127.67 (C²²); 127.29 (C²¹); 126.86 (C¹⁹); 126.08 (C²⁸); 125.89 (C²⁰); 125.52 (C⁸); 124.91 (C²⁹); 124.59 (C⁷); 122.02 (q, *J* = 271 Hz, C¹); 121.25 (q, *J* = 31 Hz, C²); 120.32 (C²⁷); 119.45 (C⁴); 119.27 (C¹³); 114.03 (C²⁵); 64.45 (C¹⁶).

RESULTS AND DISCUSSION

Synthesis of diamine monomers (VII, VIII, and IX)

The key compound to the monomers is 3-trifluoromethyl-4-fluoro-4'-nitrobiphenyl. The 3-trifluoro-

methyl-4-fluoro-4'-nitrobiphenyl was synthesized via Suzuki coupling of 4-nitro-bromobenzene and 4-fluoro-3-trifluoromethyl phenyl boronic acid. This compound was reacted through the nucleophilic displacement reaction with various bis hydroxy compound like 4,4'-Isopropylidenediphenol, 4,4'-(Hexafluoro-isopropylidene) diphenol, 4,4'-(9-fluorenylidene) diphenol to form dinitro derivatives. After reduction of these dinitro derivatives three new diamine monomers were obtained. The detail reaction scheme of the synthesis of the diamine monomers is shown in Figure 1. Although, 5-bromo-2-fluoro-benzotrifluoride is used as starting material in the present synthesis, the same final structures can be arrived with 5-bromo-2-chloro-benzotrifluoride. However, the chloro displacement is not that facile like fluoro; it needs higher reaction temperature (NMP as solvent in place of DMF) and results in lower yield. The reaction conditions need to be optimized. All the final diamines and intermediate dinitro compounds have been well characterized and analytical details are reported in experimental section.

Synthesis of the poly(ether imide)s

Several poly(ether imide)s were prepared from the synthesized diamine monomers and various aromatic dianhydrides in DMF under nitrogen atmosphere adapting the standard protocol of polyamic acid synthesis. Typically, the poly(amic acid)s were prepared by dissolving the diamines in measured amount of purified and dry DMF and adding a molar equivalent

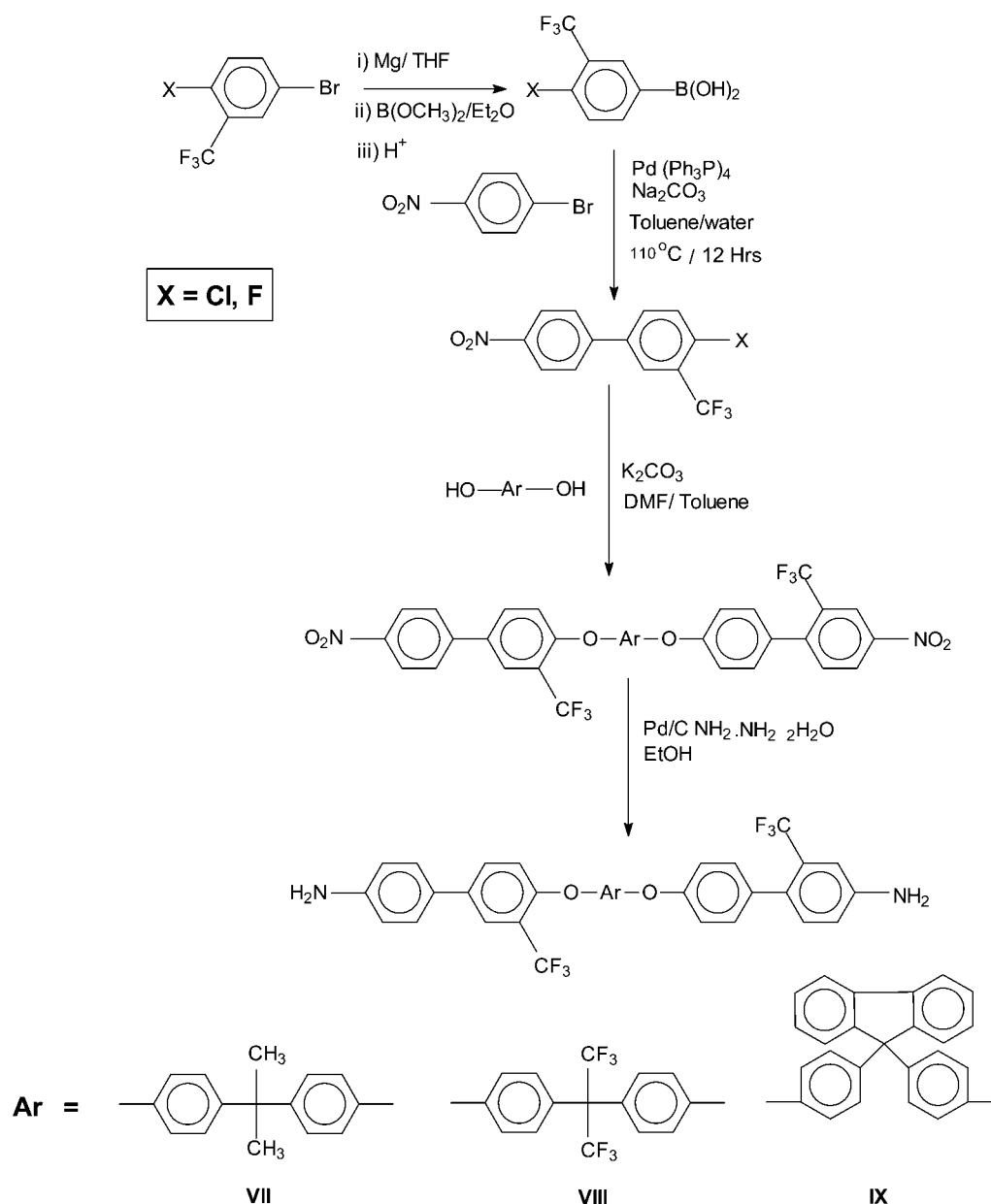


Figure 1 Reaction scheme and structures of the diamine monomers.

of dianhydride monomers to it. In all cases the reaction mixture become highly viscous within 10–15 min; the reactions were continued for 2 h. The reaction temperature was maintained at 15°C. The poly(amic acid) solutions were spread on glass plate and heated overnight at 80°C to evaporate the maximum amount of solvent. The imidization and removal of solvent and water (formed during imidization) was carried out by sequential heating a leveled temperature controlled ($\pm 1^\circ\text{C}$) vacuum oven at 100°C, 150°C, 200°C, 300°C for 1 h, and at 350°C for 30 min under slow stream of nitrogen. The glass plates containing the polyimide films were allowed to cool down to 150°C and were kept overnight under vacuum to ensure the complete removal of any residual solvent in the polyimide film.

The oven temperature was slowly brought down to room temperature. The resulting polyimide films were removed from the glass plate by soaking in boiling water. The transparent, fingernail cressable films were obtained in all cases. In total 12 poly(ether imide)s were prepared from three diamine monomers (**VI**, **VII**, and **VIII**) and four commercial dianhydrides like PMDA, BTDA, 6FDA, and ODA. The reaction scheme of synthesis and structures of the poly(ether imide)s are shown in Figure 2.

Polymer solubility and molecular weight

The solubilities of the poly(ether imide)s were tested in various solvents. Table I summarizes these results.

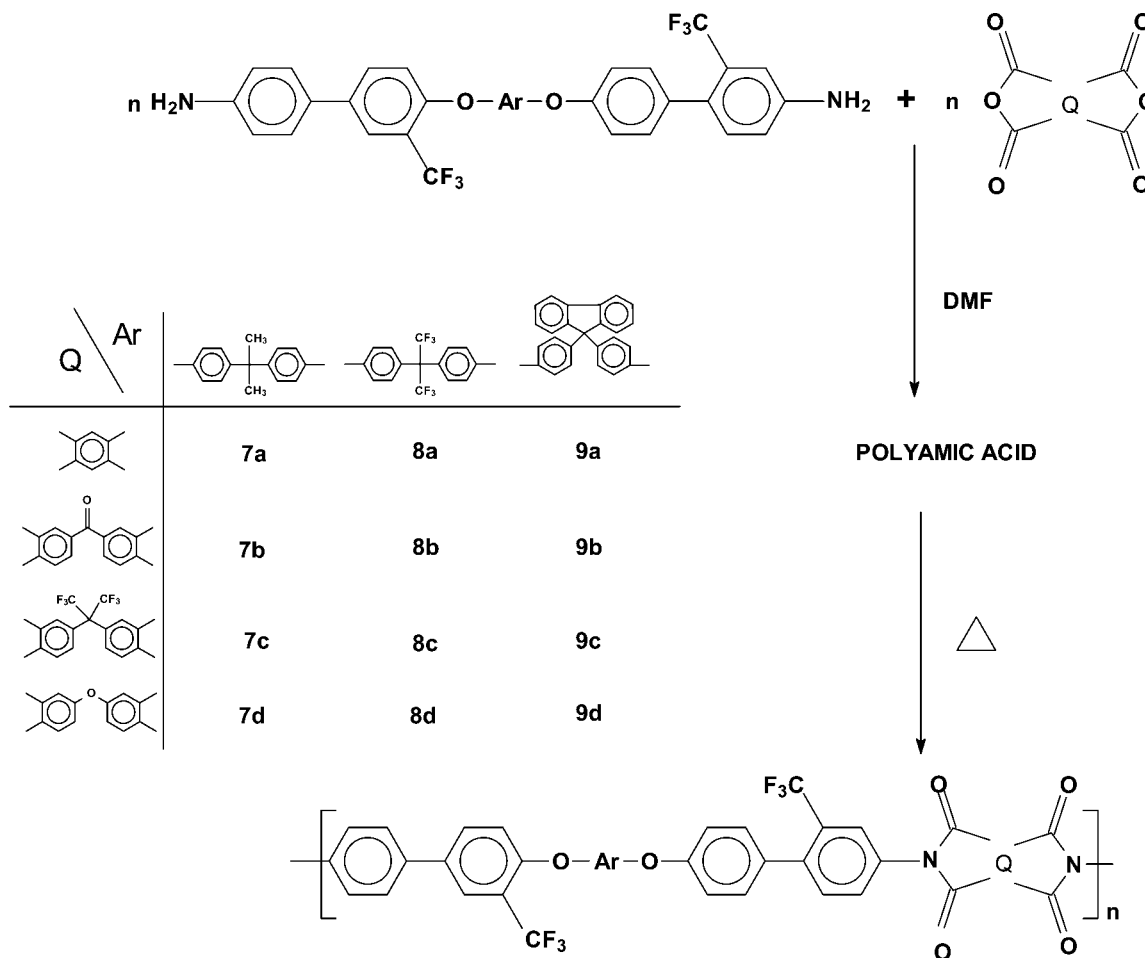


Figure 2 Reaction scheme and structures of the poly(ether imide)s.

It was attempted to obtain 10% (W/V) solution of all polymers in many organic solvents. In general the poly(ether imide)s showed very good solubility in many organic solvents and better than the analogous polymers derived previously from the diamine monomers I–V.^{24–28} The polymers, which are derived from 6FDA

and ODA, are soluble even in chloroform and toluene at room temperature and comparable to many poly(arylene ether)s reported by us previously.^{31–33} This observation ruled out the previous observation that unsymmetrical monomers are required to get better solubility.²⁹ It can be argued that flexible units are

TABLE I
Properties of Poly(ether imide)s

Polymers	η_{inh}	$\lambda_{cut-off}$ value	t_r	M_n	M_w	PDI	Film quality
7a	1.22	521	71	–	–	–	Clear
7b	1.18	527	71	23,689	91,879	3.87	Clear, flexible
7c	1.25	449	75	60,842	15,4213	2.69	Clear, flexible
7d	1.27	445	74	30,712	76,648	2.49	Clear, flexible
8a	1.11	507	75	–	–	–	Clear
8b	0.82	537	73	17,083	42,826	2.50	Clear, flexible
8c	1.28	455	89	64,156	17,8832	2.65	Clear, flexible
8d	1.21	430	69	35,622	97,200	2.73	Clear, flexible
9a	0.88	521	71	17,248	39,592	2.29	Clear, flexible
9b	0.91	521	70	17,589	59,232	3.36	Clear, flexible
9c	0.81	455	74	20,155	49,464	2.45	Clear, flexible
9d	1.21	455	72	30,685	87,783	2.86	Clear, flexible

η_{inh} , inherent viscosity of the cured polyimide in NMP at 30°C; λ , Wavelength in nm; t_r , Optical transmission (%); M_n , Number average molecular weight; M_w , Weight average molecular weight; PDI, Poly dispersity index.

TABLE II
Solubility of Semifluorinated Polyimides

Polymer	NMP	DMF	DMAc	DMSO	THF	CHCl ₃	Acetone
7a	+	r+	r+	r+	—	—	—
7b	+	+	0	0	+	+	—
7c	+	+	+	+	+	+	0
7d	+	+	+	+	+	+	—
8a	+	r+	0	0	—	—	—
8b	+	+	r+	r+	+	+	—
8c	+	+	+	+	+	+	0
8d	+	+	+	+	+	+	—
9a	+	+	0	0	+	+	—
9b	+	+	+	+	+	+	—
9c	+	+	+	+	+	+	+
9d	+	+	+	+	+	+	—

+, Soluble at room temperature; 0, Soluble at heating; r+, Soluble at reflux temperature; —, Insoluble.

more important to get polymer solubility than the asymmetry of the structure.

The poly(ether imide)s showed inherent viscosities ranging from 0.82–1.27 dL/g, indicating medium to high molecular weight polymer formation. The polymers derived from 6FDA, showed relatively low inherent viscosities in comparison to their respective molar masses. This is due to the decreasing of inherent viscosity with an increasing number of trifluoromethyl groups in the dianhydride. This point is also illustrated with hydrodynamic volume, which depends on molecular weight and structure of the polymer. The trifluoromethyl group decreases the inter-

chain interaction with increasing fluorine atoms.^{34,35} This in turn affect the hydrodynamic volume of the polymer in solvent and show lower inherent viscosities. Because of very good solubility in THF of all the polymers except **6a** and **7a**, it was possible to estimate the molar masses of the polymers by GPC. The weight and number average molar mass values of the polymers are given in Table II. The molar mass values and polydispersity index are in the range expected in a condensation polymerization reaction. A representative GPC plot of the polymer **9a** that is derived from PMDA-based dianhydride is shown in Figure 3.

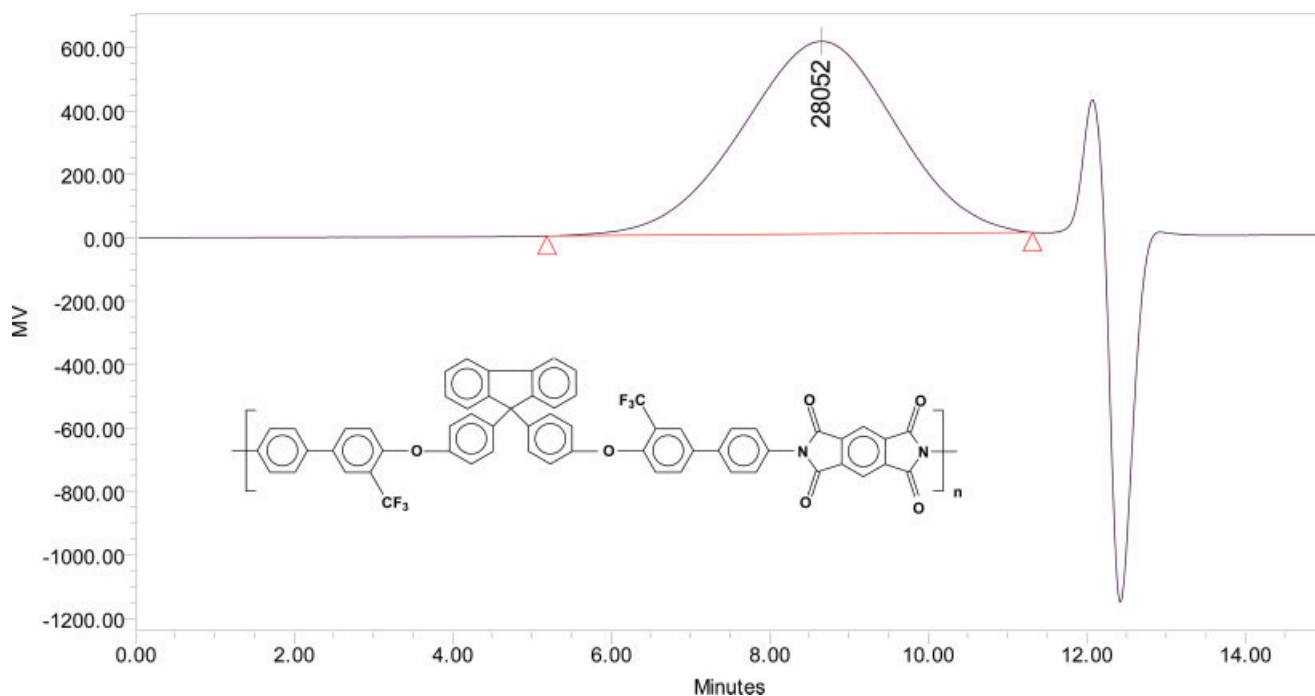


Figure 3 GPC chromatogram of poly(ether imide), **9a**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Polymer characterization

The structures of the poly(ether imide)s were confirmed from elemental analyses as well as IR and NMR spectroscopy. These polymers displayed IR spectra with similar pattern; absorption band at about $1760\text{--}1785\text{ cm}^{-1}$ (C=O asymmetric stretching) $1735\text{--}1745\text{ cm}^{-1}$ (C=O symmetric stretching) $1360\text{--}1385\text{ cm}^{-1}$ (C—N stretching band) $1060\text{--}1065$; $740\text{--}745\text{ cm}^{-1}$ (ring deformation), $680\text{--}720\text{ cm}^{-1}$ (C=O bending) corresponding to the characteristic of imide band. No absorption bands were found at $3400\text{--}3600\text{ cm}^{-1}$ corresponding to —OH stretching, at 1720 cm^{-1} corresponding to C=O stretching of carboxylic acid and also at 1660 cm^{-1} corresponding to C=O amide stretching; indicating complete conversion of poly(amic acid) to poly(ether imide)s during imidization.^{24–26} The ^1H , ^{13}C , and ^{19}F NMR spectra of polyimides were taken in CDCl_3 solvent. All these spectra support the polymer structures and analytical details are given in experimental section. The aromatic proton in polymer backbone lies between 8.5 and 6.8 ppm. The carbonyl carbon in ^{13}C spectra of the polymers showed maximum down field among all the carbons. This is due to the deshielding effect of oxygen atom. The carbon attached with — CF_3 group showed quartet with coupling constant $\sim 272\text{ Hz}$ indicating $J_{\text{C-F}}$ coupling.^{31,32} Representative ^1H and ^{13}C -NMR spectra of poly(ether imide) **9a** is shown in Figure 4 and Figure 5 respectively.

Optical properties

Thin optical transparencies of the thin polymer films ($30\text{--}40\text{ }\mu\text{m}$) were measured using UV-vis spectrophotometer. The percentage of transmission values at $430\text{--}580\text{ nm}$ is reported in Table II. These polymers exhibited high optical transmission in the UV-vis region of the electromagnetic spectrum. The poly(ether imide)s **7c**, **8c**, and **9c** exhibited optical transparencies as high as 75, 89, and 74% respectively. The presence of large number of — CF_3 groups in polymer backbone disturbed conjugation, which was interrupting the extended Π -system, and exhibited very high optical transparencies.

Thermal properties

The thermal stabilities of the poly(ether imide)s were evaluated by TGA. The polymers showed excellent thermal stability in air as expected in case of aromatic polyimides.^{24–29} The 5% weight loss and 10% weight loss temperature in air of the poly(ether imide)s are summarized in Table III. Relatively low thermal stability of the polymers **7a**, **7b**, **7c**, and **7d** in air is due to the presence oxidizable isopropylidene linkages in the polymer backbone. These polymers showed comparable thermal stability with other poly(ether imide)s in the series when the thermal stability was investigated in nitrogen atmosphere. However, these values are simply for the data sake or may have aca-

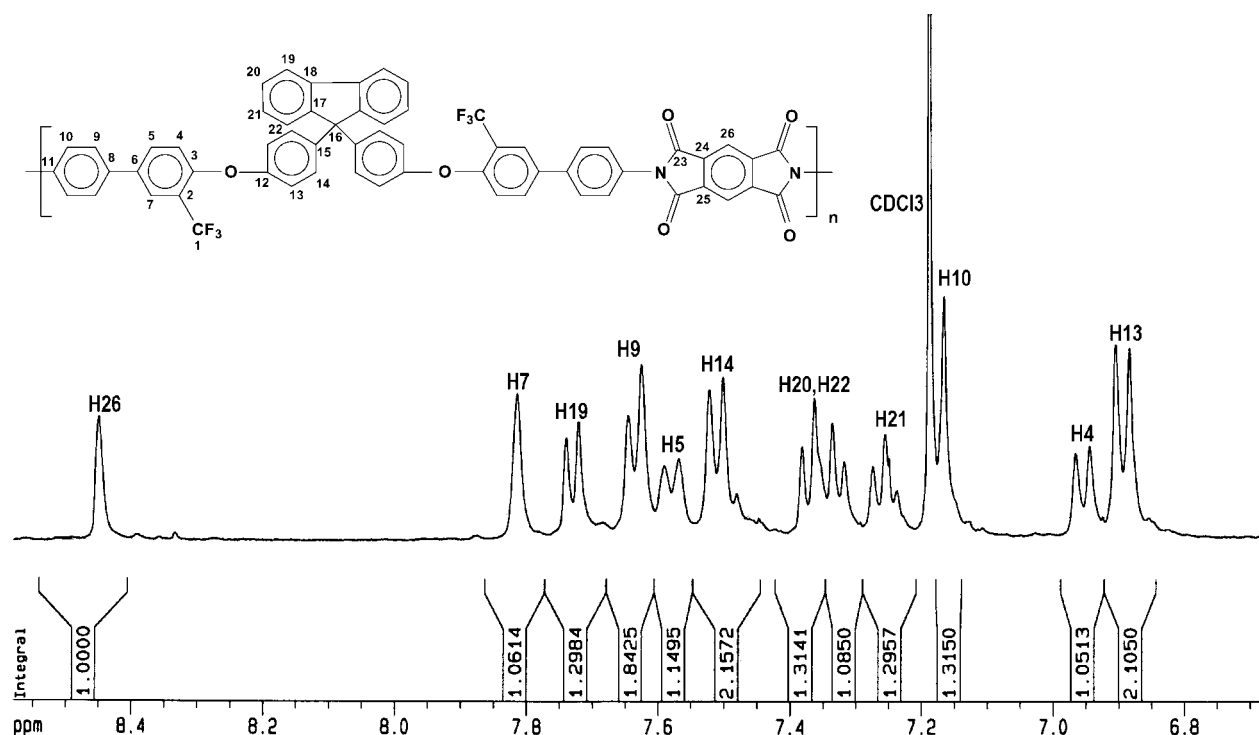


Figure 4 ^1H NMR spectrum of poly(ether imide), **9a**.

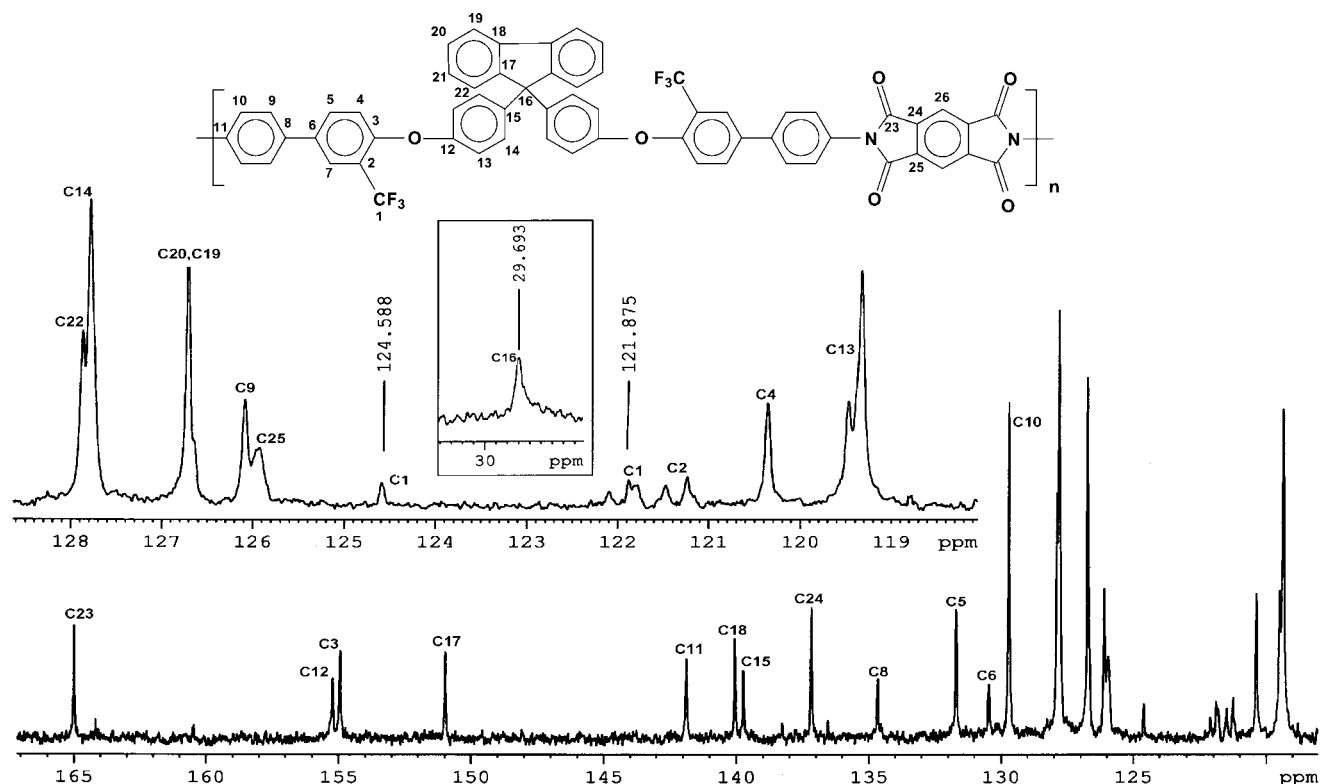


Figure 5 ^{13}C NMR spectrum of poly(ether imide), 9a.

demic interest but do not have any practical implication. All these poly(ether imide)s showed comparative thermal stability in air to the analogous polymer structure derived from the diamine monomers I–V.^{24–29} The higher thermal stability of fluorine-containing polyimides is due to their rigid structure and may be due to their higher degree of aromaticity. The TGA thermograms of the series 9 polymers are shown in Figure 6.

The glass transition temperatures (T_g) of the poly(ether imide)s were evaluated by DSC and DMA.

Both DSC and DMA detected no melting or crystallization transition of the polyimides. All the polymers showed amorphous or glassy morphology. The glass transition temperature values are summarized in Table III. The T_g s of all polymers followed the same trend in both DSC and DMA plots. Glass transition temperatures of the polymers depend on many factors such as polymer symmetry, intermolecular force, and rigidity of polymer backbone.^{24–26} The PMDA-based polyimides showed higher T_g values than other dianhydride-based polymers, which can be explained on

TABLE III
Thermal Properties of Poly(ether imide)s

Polymers	T_g (°C)		T_d (°C)	
	DSC	DMA	5% weight loss temp. in air	10% weight loss temp. in air
7a	255	262	468	506
7b	235	240	492	528
7c	242	253	475	514
7d	228	230	493	529
8a	259	269	506	527
8b	242	246	508	535
8c	246	260	501	525
8d	235	235	495	532
9a	309	313	516	546
9b	284	283	511	558
9c	297	285	501	528
9d	254	272	509	552

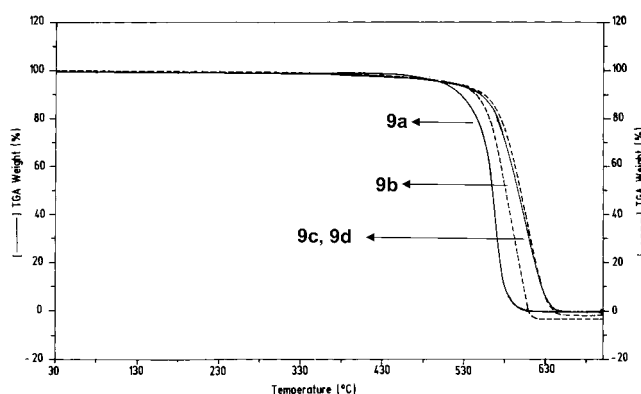


Figure 6 TGA thermograms of the poly(ether imide)s, 9a–9d.

the basis of rigid PMDA moieties in the polyimides backbone.²⁴ The higher T_g values of 6FDA-based polymers in comparison with BTDA-based polymers were expected because of the presence of bulky 6F unit in the polymer backbone and the same trend was observed. The polyimides, which were derived from ODA, showed lowest T_g in the series. This is because of the presence of additional flexible ether linkage coming from the dianhydride unit.²⁹ The T_g s of poly(ether imide)s were in the range of 235–313°C.

Glass transition temperature of the polymers depends on the diamine structure also. Polymers derived from the diamine (VII) containing 6F-bisphenol exhibited higher T_g s with respect to the analogous poly(ether imide)s derived from the diamine (VI) containing bisphenol-A. The higher T_g of the poly(ether imide)s 8a–8d in comparison with the analogous polymer structure 7a–7d is due to the bulky nature of 6F-isopropylidene in comparison to isopropylidene group that restrict the flexibilizing effect.^{31,32} The polymers 9a–9d showed highest T_g among the series in comparison to their analogous structure. This is because of presence of bulky fluorene unit in the polymer backbone.³² It is well known that with the increase in rigidity, T_g also increases. The DSC curves of the series 7 polymers are shown in Figure 7. The T_g values of these series of polymers are higher than that of many commercial poly(ether imide)s; e.g., Ultem 1000 ($T_g = 217^\circ\text{C}$), based on BPADA [bisphenol-A di(phthalic anhydride)] and MPD (*m*-phenylene diamine)⁷ and comparable to BTDA–ODA-based polyimide ($T_g = 279^\circ\text{C}$).²² The T_g values of this series of polymers are lower than that of kapton films derived from PMDA–ODA ($T_g = 390^\circ\text{C}$).⁷

Mechanical properties

The DMA plot of the polymers predicts the properties of a polymer in real application and this helps in designing a polymer for a particular application. Not

only it talks about the T_g s of a polymer but it also gives the storage modulus values of the polymers and its change with temperature. Figure 8 shows the DMA plots of the series 9 polymers. The dynamic mechanical analysis of all the poly(ether imide)s reported in this investigation showed very good retention of storage modulus of the polymer up to the glass transition temperature. This finding helps in designing these polymers for high temperature application. The $\tan \delta$ peak at 10 Hz of these polymers was used to calculate the T_g . The values are shown in Table III. These values are in good agreement with the values obtained from the DSC measurements. Young's modulus values of polymers obtained from the storage modulus plot at 30°C are shown in Table IV. The Young's modulus of the polymers was as high as 2.9 GPa.

The mechanical properties of all the poly(ether imide)s films are shown in Table IV. Representative stress–strain plots for 7a and 7d are shown in Figure 9. These poly(ether imide)s showed very high tensile strength (75–129 MPa) and elongation at break up to 72%. The polyimides derived from bis-2,2[4(2'-trifluoromethyl-4'(4''aminophenyl) phenoxy)-phenyl] isopropylidene and oxydiphthalic anhydrides exhibited a very high elongation at break 72%. The nature of the plot indicates the ductile behavior of the material. This polymer also exhibited good tensile strength up to 125 MPa and Young's modulus up to 2.9 GPa. The poly(ether imide)s derived from VII, i.e., from the diamine containing fluorene unit showed least elongation at break (7%) in the series. This could be due to the rigid nature of fluorene group.³¹ However; to get a realistic picture on the mechanical properties of these polymers, it is essential to evaluate the mechanical properties of the molded specimens. There are chances of formation of defective structures during preparation of dense solution cast film, which may affect the final mechanical properties of the polymers. It is anticipated that the reported values will improve further if molded specimen is used.

These values are comparable to those many other commercially available polyimides (Ultem 1000: ten-

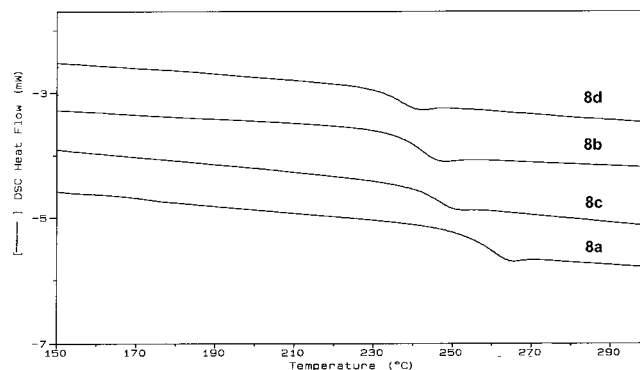


Figure 7 DSC curves of the poly(ether imide)s, 8a–8d.

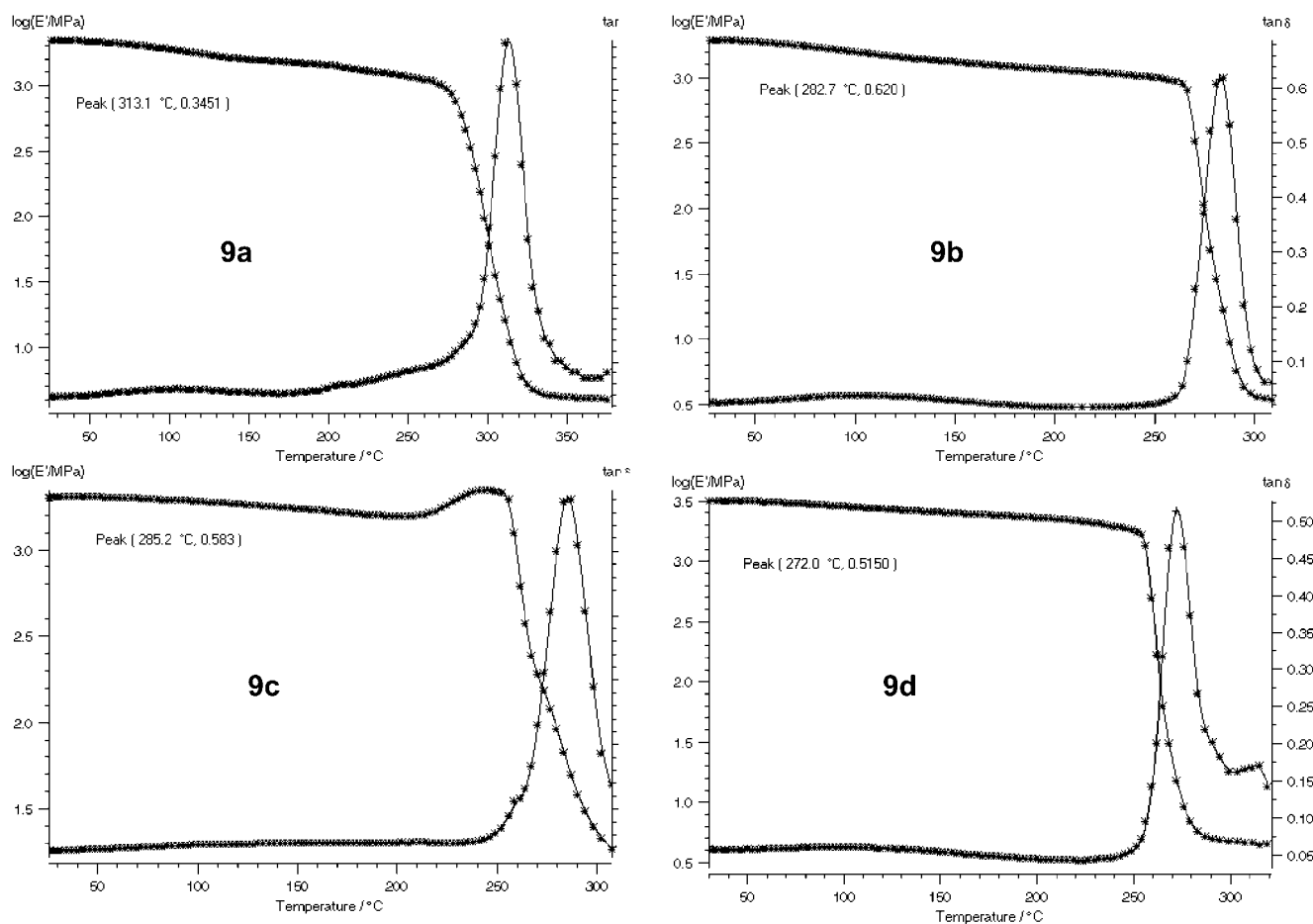


Figure 8 DMA plots of the poly(ether imide)s, 9a–9d.

sile strength 105 MPa; tensile modulus, 3.0 GPa; elongation at break, 60%; Ultem 6000: tensile strength 103 MPa; elongation at break, 30%; Avimid N; tensile strength, 110 MPa; tensile modulus, 4.13 GPa; elongation at break, 6%).⁷

Water absorption and dielectric properties

Water absorption is a great concern when the polymers are used in electronic packaging as dielectric insulation.^{6,7} The absorbed water in the polymer structure affects their dielectric performance. Hence, for materials designed for such type of applications the water absorption data is an essential parameter. The water absorption of the poly(ether imide)s films was measured at 30°C. The water absorption value for these polyimides lies between 0.16 and 0.32%. The exact values for different polymers are given in the Table V. The 6FDA-containing polyimides showed the lowest water absorption that is due to the presence of more number of hydrophobic $-\text{CF}_3$ group; in other sense more amount of fluorine content in the polymer structure.³⁵ A trend (with some deviation) in water absorption versus polymer structure is found that

depends on the percentage fluorine content in the polymer. In general the water absorption values of these polymers were lower than that of nonfluorinated polyether imides, such as ULTEM 1000 (1.52%) and Kapton H (3%).⁷ The dielectric constant of polyimides films was measured by using a capacitance meter (1 MHz at 30°C, RH 45%).

TABLE IV
Mechanical Properties of Poly(ether imide)s

Polymer	Modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
7a	2.5	115	56
7b	2.8	121	17
7c	2.5	97	15
7d	2.5	125	72
8a	2.9	112	28
8b	2.5	128	10
8c	2.4	75	13
8d	2.5	108	27
9a	2.0	102	7
9b	2.8	122	12
9c	2.0	119	9
9d	2.4	112	9

The dielectric constant and the dissipation factor are the important properties to determine the use of a material in interlayer dielectrics. Typically, low dielectric constant with low dielectric loss is desirable when material is used in high speed, high frequency circuit. It would be better to measure these properties at high frequency; however, due to nonavailability of such instrument we have measured these properties at 1 MHz by using one YHP 4278 capacitance meter. The capacitance values of polymer thin films were evaluated by keeping the film in between two copper electrodes. The capacitance values were finally converted to the dielectric constant values from the thickness of the films. The dielectric constant values of the poly(ether imide)s films are presented in Table V. In general these polymers exhibited low dielectric constant. The lowest dielectric constant value was obtained 2.35 for polymer **8c** that contains 30.56% (w/w) fluorine. The percentage of fluorine content effect the dielectric properties, as the fluorine content increase dielectric constant decrease, 6FDA-containing polymers (**7c**, **8c**, and **9c**) showed lowest dielectric constant in their series.

The dielectric constant values of the synthesized polyimides were also compared with some of the commercially available polyimides. The dielectric constant values of these films are lower than that of Kapton H ($\epsilon = 3.5$ at 1 kHz), Upilex R ($\epsilon = 3.5$ at 1 kHz), Upilex S ($\epsilon = 3.5$ at 1 kHz), and Ultem 1000 ($\epsilon = 3.15$ at 1 kHz) types of polyimide materials and comparable to those of many semifluorinated poly(ether imide)s

TABLE V
Dielectric Constant and Other Physical Properties of the Poly(ether imide)s

Polymers	Fluorine content (%)	Water absorption (%)	$\epsilon_{\text{wet}}/1$ MHz
7a	12.94	0.32	3.18
7b	11.57	0.28	3.09
7c	20.59	0.21	2.79
7d	11.72	0.25	3.05
8a	23.05	0.19	2.87
8b	20.86	0.21	2.78
8c	30.56	0.16	2.35
8d	21.09	0.24	2.62
9a	11.36	0.22	2.81
9b	10.29	0.24	2.85
9c	18.55	0.21	2.51
9d	10.41	0.27	2.78

(6FDA-MPD: $\epsilon = 3.0$; 6FDA-7FMDA: $\epsilon = 2.9$; 6FDA-13FMDA: $\epsilon = 2.7$).⁷

CONCLUSIONS

Three novel diamine monomers have been prepared that lead to several organosoluble poly(ether imide)s. The monomers and the polymers have been well characterized by different analytical techniques. The synthesized polymers showed unique set of thermal, mechanical, and dielectric properties. Initial results indicated that these polymers are superior to many other commercially available poly(ether imide)s and can be used in microelectronic packaging.

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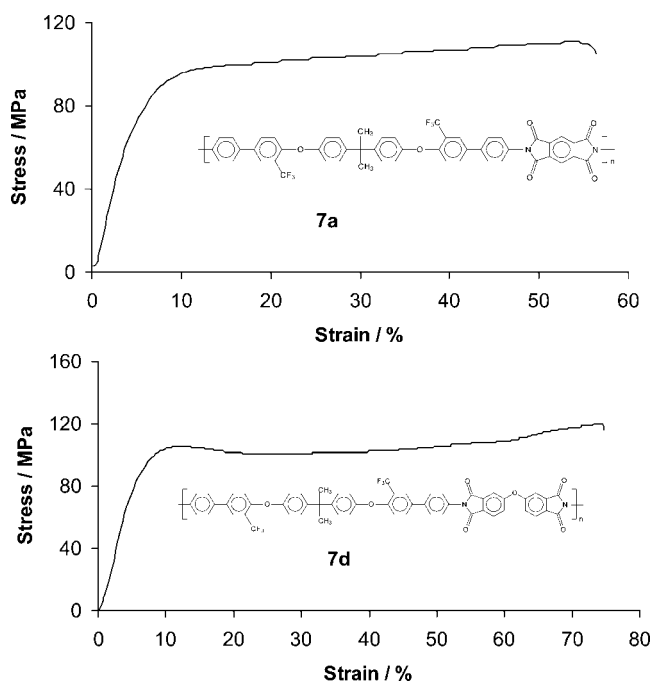


Figure 9 Representative stress-strain plot of the poly(ether imide)s, **7a** and **7d**.

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