Synthesis, Characterization and Comparison of Properties of Novel Fluorinated Polyimides Derived from Bisphenol-A-di(phthaleic anhydride)

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Four new poly(etherimide)s have been synthesized by reaction with commercially available bisphenol-A-(diphthaleic anhydride) (BPADA) with four different kinds of diamines, namely 4,4′-bis(p-aminophenoxy-3,3″-trifluoromethyl) terphenyl,4,4′-bis(3″-trifluoromethyl-p-aminobiphenyl ether)biphenyl,2,6-bis(3′-trifluoromethyl-p-aminobiphenyl ether)pyridine, 2,5-bis(3′-trifluoromethyl-p-aminobiphenylether)thiopene. The poly(etherimide)s are named as 1a, 1b, 1c and 1d, respectively. The synthesized polyimides show good solubility in various organic solvents. The polyimide films had low water absorption of 0.19–0.30% and low dielectric constant of 2.79–3.1 at 1 MHz. These polyimides showed very high thermal stability with decomposition temperature (5% wt loss) up to 522°C in nitrogen. Transparent thin films of these polyimides exhibited tensile strength up to 97 MPa, a modulus of elasticity up to 1.56 GPa and elongation at break up to 20%.

Keywords: dielectric properties; fluorinated poly(ether imide)s; mechanical properties; rheology; thermal properties

1 Introduction

Aromatic polyimides are well known for their outstanding thermal behavior, thermo-oxidative stability, solvent resistance, mechanical and electrical properties and are used in various applications such as electronics, gas separation membranes, coatings and composite materials in aerospace industries (1−6). Since the commercialization of Kapton (pyromellitic dianhydride (PMDA)−oxydianiline (ODA) based polyimide) by DuPont, these materials find widespread applications as electrical insulating material as interlayer dielectrics/inter metal dielectrics (ILD/IMD). The PMDA-ODA based polyimides exhibit very high glass transition temperature (Tg $\sim$ 390°C), high mechanical strength (158 MPa) and high tensile modulus (3.2 GPa) (7). For use as material for ILD/IMD, its dielectric constant (ε) is rather high and also has high moisture absorption (ε, 3.1−3.5, water uptake %, 1.3−3.5). The major problem of rigid polyimides is

their insolubility and infusibility in their fully imidized form, leading to processing difficulties.

The search of new polyimides with improved processability, higher glass transition temperature, and low dielectric constant than Ultem 1000 has received significant attention since its commercialization by General Electrical Company. Ultem 1000 is manufactured from BPADA [bisphenol-A-di(phthaleic anhydride)] and MPD (meta phenylene diamine). These materials possess excellent flow characteristics and melt stability, because of flexible linkages in the main chain and serve as true high performance engineering thermoplastics. Although Ultem 1000 has reasonably high glass transition temperature (Tg $\sim$ 217°C), the material has a rather high dielectric constant (ε, 3.15) (7).

Polyimides containing pendant trifluoromethyl (8–13) groups are of special interest. Incorporation of trifluoromethyl groups in the backbone tends to increase the free volume (14) and hence, helps in improving various properties such as solubilities, electrical insulation properties without affecting thermal stability. These groups also tend to reduce water uptake, crystallinity and color and on the other hand increases flame resistance, gas permeability and optical transparency. In this study we report successful synthesis of four new poly(etherimide)s and their characterization including spectroscopy, solubility, thermal, mechanical, dielectric and rheological properties.

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2 Experimental

2.1 General Considerations

Elemental carbon, hydrogen and nitrogen of the compounds were analyzed by the pyrolysis method using Vario EL (Elementar, Germany) elemental analyzer. ^{1}H-NMR and ^{13}C-NMR was recorded on a Bruker-500 MHz instrument; (reference zero ppm with TMS). IR spectra of the polymer films were recorded with a Netzsch 870 FTIR Spectrophotometer instrument. Gel permeation chromatography was performed with Agilent 1100 instrument. DMAc/2% H_2O/(3 g/l) LiCl were used as eluent (flow rate 0.5 ml/min) and RI detector was used to record the signal. The molecular weight of the polymers were recorded with respect to monodisperse poly(vinylpyridin). DSC measurements were made on a Netzsch DSC 200PC instrument at a heating/cooling rate of $20°C$/min under nitrogen. Glass transition temperature (T_g) was taken at the middle of the step transition in the second heating run. Thermal decomposition behavior of these polymers was measured on a Perkin-Elmer (Pyris Diamond) thermogravimetric analyzer at a heating rate of $10°C$/min under nitrogen. Dynamic mechanical thermal analysis was performed on a TA Instrument DMA-2980 (USA) under tension mode on thin film samples at a heating rate of $10°C$/min and were run at a frequency of 1 Hz. Mechanical properties such as tensile strength and elongation at break of the thin polymer films (30 × 0.1 mm) were measured at room temperature on a Hounsfield H10KS-0547 instrument under strain rate of 5%/min of the sample length. Water absorption of the films was measured by using a Sartorius balance of sensitivity of 10^{-6} g. The dry films were immersed into double distilled water for 24 h at $30°C$. Dielectric constant of the polyimide films was measured by the parallel plate capacitor method with a H1OKI 3535 LCR Hi Tester from 100 KHz to 1 MHz at a temperature of $30°C$. Rheology behavior of the films was studied by using a AR-1000 Rheometer.

2.2 Starting Materials

All reagents were purchased from Aldrich (USA), and used as received unless otherwise noted. Bisphenol−A-(diphthaleic anhydride), BPADA 97%, Aldrich, USA was heated at $120°C$ overnight prior to use. The diamine monomers used; 4,4′-bis(p-aminophenoxy-3,3″-trifluoromethyl) terphenyl, 4,4′-bis(3″-trifluoromethyl-p-aminobiphenyl ether)biphenyl, 2,6-bis(3′-trifluoromethyl-p-aminobiphenyl ether)pyridine, 2,5-bis(3′-trifluoromethyl-p-aminobiphenylether)thiopene in this investigation were prepared using the procedure reported in our previous articles (8, 9, 15). DMF (E.Merck, India) was purified by stirring with NaOH and distilled from P_2O_5.

2.3 Polymerization

All polymerization reactions were carried out in nitrogen atmosphere with constant flow. An equimolar amount of diamine and dianhydride monomers were used in all cases. A respective polymerization procedure is as follows. In a 50 mL round-bottomed flask equipped with nitrogen inlet and a magnetic stirrer was charged with 0.52 gm (0.908 mmol) of 4,4′-bis (p-aminophenoxy-3,3″-trifluoromethyl) terphenyl, 0.47 gm (0.908 mmol) of BPADA and 10 mL DMF was added in the flask. The resulting solution was stirred for 30 min at room temperature. The poly(amic acid) solution was cast onto clean and dry glass Petri dishes. The films were dried in vacuum oven at $80°C$ overnight followed by 100, 150, 200, $250°C$ for 1 h at each temperature and $300°C$ for 30 min and at $350°C$ for 15 min in each of the four cases for the preparation of polyimide films. Polyimide films were then removed by immersing the glass plates in boiling water.

Polyimide 1a
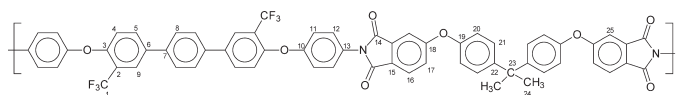
$(C_{63}H_{38}F_6O_8N_2)_n$ $(1065.01)_n$: Calcd. C 71.05, H 3.59, N 2.63; Found: C 69.85 H 3.72 N 2.59.

IR: 3053 (aromatic C-H), 2969 (-CH_3 group in BPADA), 1778 (C=O asymmetric stretching), 1720 (C=O symmetric stretching), 1618−1507, 1444 (aromatic C=C), 1378 (C-N stretching), 1333, 1247 (C-O-C), 1136 (C-F multiple stretch bending), 745 cm^{-1} (C-N bending).

^{1}H-NMR (CDCl$_3$): δ = 7.94 (s, 2H, H[9]), 7.89 (d, 2H, H[16], J = 8 Hz), 7.74(d, 2H, H[5], J = 8 Hz), 7.67 (s, 4H, H[8]), 7.43(m, 6H, H[12] and H[25]), 7.34 (m, 6H, H[4] and H[11]), 7.19 (d, 4H, H[20], J = 8 Hz), 7.14 (d, 2H, H[17], J = 8 Hz), 7.04 (d, 4H, H[21], J = 8 Hz), 1.76 (s, 6H, H[24]).

^{13}C-NMR (CDCl$_3$): δ = 166.8, 163.9, 156.1, 154.3, 153.9, 152.7, 147.6, 138.6, 135.9, 134.2, 131.7, 128.8, 128.1, 127.5, 125.8, 125.0, 124.3, 122.1, 122.0, 121.7(q, C[1], J = 272 Hz), 119.9, 119.5, 111.9, 42.6 (C[23]), 31.0 (C[24]).

Polyimide 1b
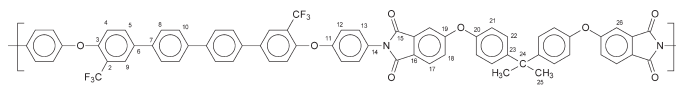
$(C_{69}H_{42}F_6O_8N_2)_n$ $(1141.10)_n$: Calcd.C 72.62, H 3.71, N 2.45; Found: C 72.49 H 3.82 N 2.33.

IR: 2969 (-CH_3 group in BPADA), 1778 (C=O asymmetric stretching), 1724 (C=O symmetric stretching), 1600−1505, 1444 (aromatic C=C), 1376 (C-N stretching), 1331, 1247 (C-O-C), 1134 (C-F multiple stretch bending), 745 cm^{-1}(C-N bending).

^{1}H-NMR (CDCl$_3$): δ = 7.95 (s, 2H, H[9]), 7.90 (d, 2H, H[17], J = 8 Hz), 7.73(m, 6H, H[5] and H[10]), 7.67 (d, 4H, H[8], J = 8 Hz), 7.43(m, 6H, H[13] and H[26]), 7.35 (m, 6H, H[12] and H[4]), 7.19 (d, 4H, H[21], J = 8 Hz), 7.14 (d, 2H, H[18], J = 8 Hz), 7.04 (d, 4H, H[22], J = 8 Hz), 1.76 (s, 6H, H[25]).

^{13}C-NMR (CDCl$_3$): δ = 166.8, 166.7, 163.9, 156.1, 153.9, 152.7, 147.6, 139.9, 138.3, 136.1, 134.2, 131.7, 128.8, 128.1, 127.6, 125.8, 125.0, 122.3, 121.7(q, C^1, J = 272 Hz), 120.0, 119.9, 119.6, 111.9, 42.5(C^{24}), 31.0(C^{25}).

Polyimide 1c
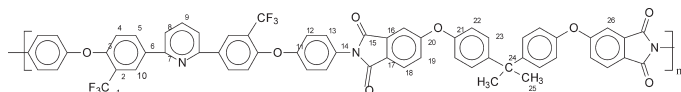
(C$_{62}$H$_{37}$F$_6$O$_8$N$_3$)$_n$ (1065.99)$_n$: Calcd.C 69.85, H 3.49 N 3.94; Found: C 69.77 H 3.61 N. 3.88.

IR: 3068 (aromatic C-H), 2969 (-CH$_3$ group in BPADA), 1777 (C=O asymmetric stretching), 1724 (C=O symmetric stretching), 1618–1500, 1444 (aromatic C=C), 1378 (C-N stretching), 1326, 1251 (C-O-C), 1133 (C-F multiple stretch bending), 744 cm^{-1} (C-N bending).

^{1}H-NMR (CDCl$_3$): δ = 8.45 (s, 2H, H^{10}), 8.25 (d, 2H, H^{17}, J = 8 Hz), 7.88(m, 3H, H^8 and H^9), 7.70 (d, 2H, H^{21}, J = 8 Hz), 7.43(m, 6H, H^{13} and H^{26}), 7.34 (m, 6H, H^4 and H^{12}), 7.19 (m, 6H, H^5 and H^{18}), 7.03 (d, 4H, H^{22}, J = 8 Hz), 1.75 (s, 6H, H^{25}).

^{13}C-NMR (CDCl$_3$): δ = 166.8, 166.7, 155.7, 155.0, 152.7, 147.6, 138.1, 134.4, 134.2, 131.7, 128.8, 127.8, 125.9, 125.0, 124.4(q, C^1, J = 272 Hz), 124.3, 122.2, 122.1, 119.7, 118.7, 111.9, 42.5 (C^{24}), 31.0 (C^{25}).

Polyimide 1d
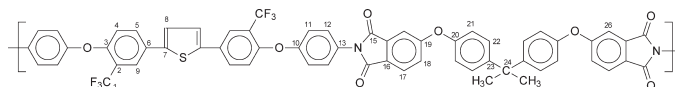
(C$_{61}$H$_{36}$F$_6$O$_8$N$_2$S)$_n$ (1071.03)$_n$: Calcd. C 68.40, H 3.38 N 2.61; Found: C 68.35, H 3.52 N 2.55.

IR: 2969 (-CH$_3$ group in BPADA), 1778 (C=O asymmetric stretching), 1724 (C=O symmetric stretching), 1600–1506, 1445 (aromatic C=C), 1377 (C-N stretching), 1328, 1247 (C-O-C), 1136 (C-F multiple stretch bending), 745 cm^{-1} (C-N bending).

^{1}H-NMR (CDCl$_3$): δ = 7.89 (d, 2H, H^{16}, J = 10 Hz), 7.86 (s, 2H, H^9), 7.69 (m, 2H, H^5), 7.43(m, 6H, H^{12} and H^{17}), 7.35 (m, 6H, H^{11} and H^{25}), 7.29 (s, 2H, H^8), 7.17 (m, 4H, H^{21}), 7.08 (d, 2H, H^4, J = 9 Hz,),7.04 (d, 4H, H^{20}, J = 8 Hz,), 1.76 (s, 6H, H^{24}).

^{13}C-NMR (CDCl$_3$): δ = 166.8, 166.7, 163.9, 155.9, 154.2, 152.7, 147.6, 142.0, 134.2, 131.7, 130.3, 129.7, 128.8, 127.7, 125.8, 124.9.0, 124.5, 124.1, 121.7 (q, C^1, J = 272 Hz), 120.0, 119.6, 112.0, 42.6 (C^{23}), 31.0 (C^{24}).

3   Results and Discussion

The diamino monomers were reacted with bisphenol-A diphthaleic anhydride (BPADA) to give the corresponding polyimide, shown in Figure 1. The synthesis of polyimides
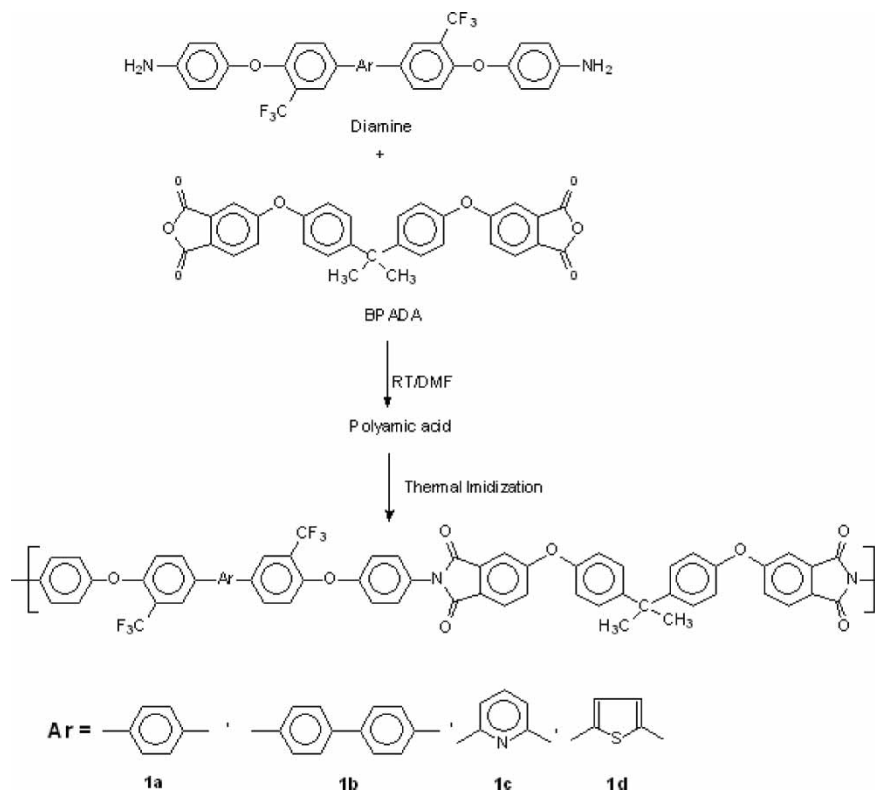
Fig. 1.   Reaction scheme and structures of novel poly(etherimide)s.

Table 1. Molecular weight, PDI and solubilities of the polymers

Polymer	M_n(g/mol)	PDI	NMP	DMF	DMAc	DMSO	THF	CHCl$_3$	CH$_2$Cl$_2$	Acetone
1a	32000	2.38	+	+	+	−	+	+	+	−
1b	34000	3.12	+	+	+	−	−	+	+	−
1c	28000	2.68	+	+	+	−	+	+	+	−
1d	27000	2.67	+	+	+	−	+	+	+	−

M_n, number average molecular weight; PDI, Polydispersity index; +, soluble at room temperature; − , insoluble at reflux.

was carried out via poly(amic acid) intermediate. The diamines were reacted with an equimolar amount of BPADA in a measured amount of dry DMF at room temperature. In all the cases the reaction became highly viscous within 10−15 min, the reaction was continued for 30 min. The poly(amic acid) was cast on dry Petri dishes and heated the film through various stages up to 350°C to remove the solvent and water formed by the imidization. The transparent, pale−yellowish films were obtained in all cases. Polyimide films were also observed to be clear, tough and flexible. Gel permeation chromatography was run in [DMAc/2% H$_2$O/ (3 g/l) LiCl] solvent and values presented in Table 1 indicate formation of high molar masses.

3.1 Polymer Solubility

The solubilities of the resulting polyimides were investigated in different organic solvents as presented in Table 1. The polymers are observed to have good solubility in various organic solvents such as chloroform, dicholoromethane, N-methyl-2-pyrollidinone, dimethylformamide and in N, N-dimethylacetamide while insolubility is observed in the case of dimethylsulfoxide as solvent. The polymers are found to be soluble in tetrahydrofuran except polymer 1b due to the presence of rigid quadriphenyl unit in the polymer backbone. Compared to the previous reported articles (14, 16) these polymers showed dramatic improvement in solubility due to the two ether linkages in the dianhydride moiety.

3.2 Spectroscopy

The formation of poly(ether imides)s was confirmed by FTIR spectroscopy. FTIR spectra of the polyimide films prepared by thermal imidization method show the absorption bands at 1780 cm^{-1}(C=O asymmetric stretching), 1720 cm^{-1} (C=O symmetric stretching), 1378 cm^{-1} (C-N stretching), 745 cm^{-1} (C=O bending), corresponding to the characteristic imide bands (14, 17). FTIR spectra of the polymers
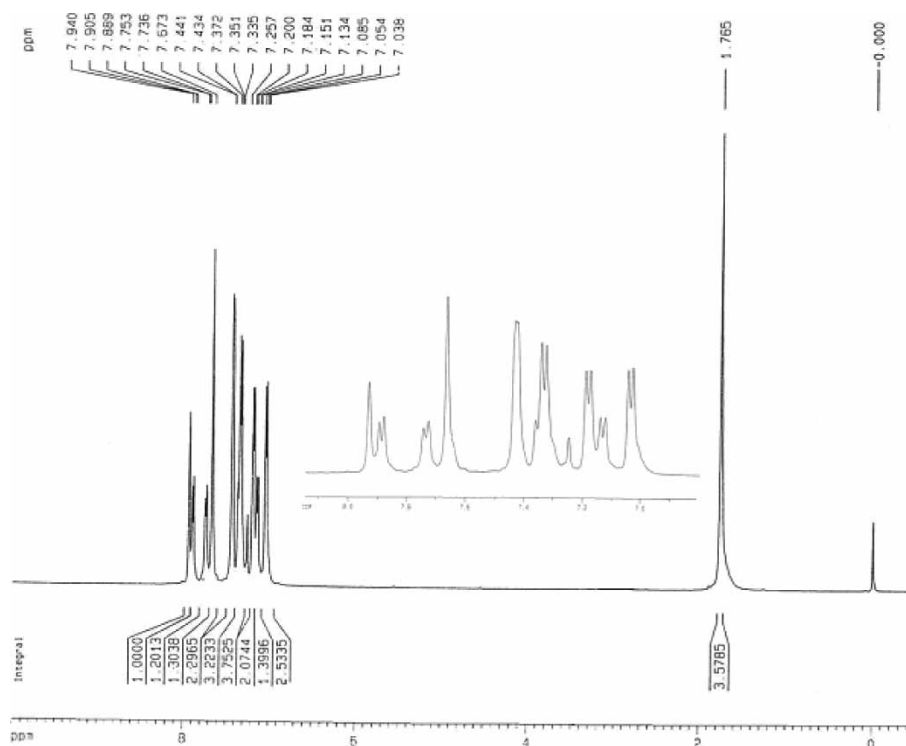
Fig. 2. ^{1}H-NMR spectra of poly(etherimide), **1a**.
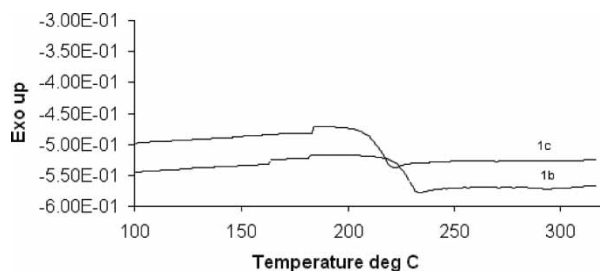
Fig. 3. DSC plots of poly(etherimide)s.

Fig. 4. Catenation angles of the different substituted arylene groups.

showed no absorption band at 1720 cm^{-1} corresponding to C=O stretching of carboxylic acid and 1660 cm^{-1} corresponding to C=O amide stretching indicating full imidization. ^{1}H-NMR spectrum of poly(ether imide) 1a is shown in Figure 2 and it reveals good matching of integrated peaks for chemically different protons in all polymers.
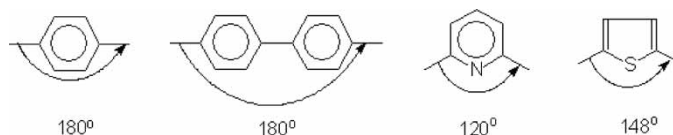
3.3 DSC Measurements

The poly(ether imide)s exhibited no crystallization or melting transition in DSC measurements. These polymers show glass transition temperature, which indicate amorphous morphology. DSC curves of 1b and 1c are shown in Figure 3. The glass transition values are summarized in Table 2.

3.4 DSC Curves of Polymer 1b and 1c

The polymers 1b have been observed to exhibit highest T$_g$ values than other polymers, which is due to the presence of rigid quadriphenyl unit in the backbone. The next higher glass transition is observed containing terphenyl unit namely 1a due to rigid unit in the polymer backbone. The following order of glass transition is obtained: quadriphenyl >1, 4 diphenyl benzene >2, 6-diphenyl pyridine >2,5-diphenyl thiophene. This order could be explained on considering three factors: rigidity, catenation angle (Figure 4) of different groups as shown in the following scheme and polarity.

A macromolecule exhibits more extended geometry (i.e., higher catenation angle provided by the different building blocks) is expected to have higher glass transition temperature. Similarly, if the polymer molecule is built up of rigid units, it is expected to have higher glass transition temperature. The catenation angle between 1,4′-diphenyl benzene and 4,4′-diphenyl biphenyl units is the same, that show,
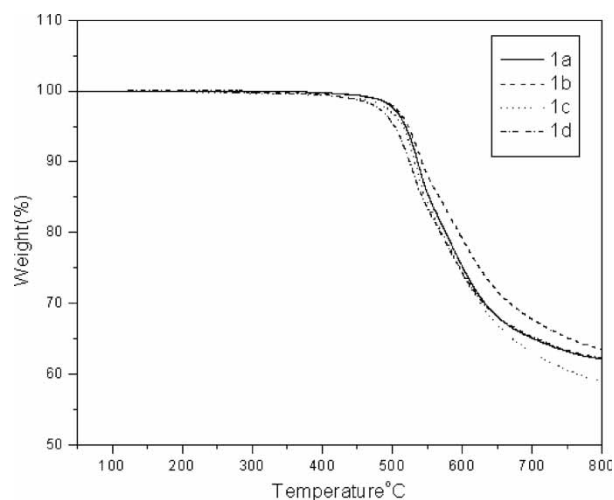
Fig. 5. TGA plots of poly(etherimide)s.
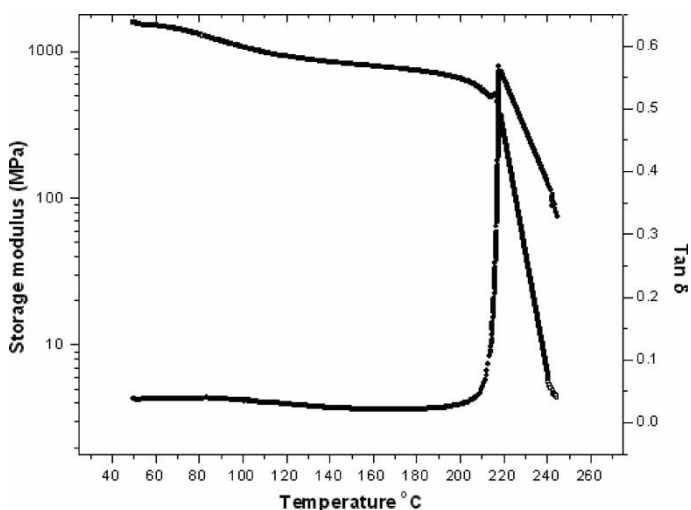
Fig. 6. DMA plot of the poly(etherimide) 1b.

Table 2. Thermal properties of the poly(etherimide)s.

Polymer	DSC T$_g$(°C)	DMA (tan ∂) T$_g$(°C)	T$_d$(°C) 5% Wt loss	T$_d$(°C) 10% Wt loss	Residual mass at 800°C
1a	216	210	519	536	62.13
1b	228	218	522	541	63.48
1c	214	204	514	532	59.05
1d	212	202	504	525	62.29

Table 3. Mechanical, dielectric and water absorption behavior of poly(etherimide)s

| Polymer	Tensile break (MPa)	Modulus (GPa)	Elongation at break (%)	Dielectric constant 1 MHz	Water absorption (%) after 24 h
1a	73	1.15	9.80	2.79	0.24
1b	93	1.44	20.17	2.8	0.19
1c	97	1.43	9.26	3.07	0.22
1d	69	1.56	5.10	3.14	0.30

180°; however, the polymer containing 4,4′diphenyl biphenyl units exhibiting higher T_g is due to rigidity of this unit. The glass transition temperature of the polyimides containing pyridine and thiophene units in the polymer backbone shows a different behavior. A lowering in glass transition is observed for the thiophene containing polymers than the pyridine containing polymers although the catenation angle for thiophene moiety is 148° (18) which is higher than the pyridine moiety, 120°. This may be due to the polarity of the pyridine ring. Pyridine has more extended geometry than thiophene; at the same time pyridine has four times more polarity than thiophene ($\mu_{pyridine} = 7.4 \times 10^{-30}$ Cm; $\mu_{thiophene} = 1.83 \times 10^{-30}$ Cm), (19) which is the probable reason for higher Tg for pyridine ring containing polymers. It is also to be noted that the T_g of polymer 1b is higher than commercially available Ultem 1000 (Tg, 217°C) based on Bisphenol-A (diphthaleic anhydride) (BPADA) and m-phenylene diamine (MPD) (20).

3.5 Thermal Stability

The thermal properties of the poly(ether imide)s are evaluated by TGA. The TGA curves for the polymers are shown in Figure 5. The thermal properties are summarized in Table 2. The 5% wt loss temperature of these polymers in nitrogen is in the range of 504–522°C. All the polymers showed high thermal stability as expected in the case of polyimides. The polymers showed very high char residue in nitrogen within 59 to 63.

3.6 DMA Measurements

The representative dynamic mechanical behaviors of the polymer film 1b are shown in Figure 6. The T_g's taken
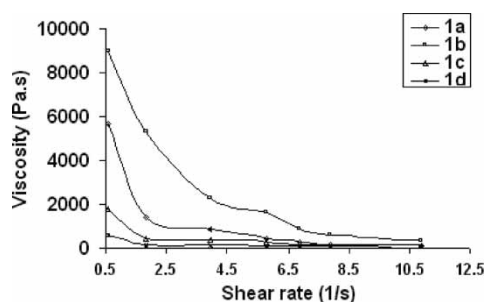
Fig. 7. Rheological behavior of the poly(ether imide)s.

from the tan ∂ peaks at 1 Hz are given in Table 2. These values are in good agreement with the calorimetric T_g values. The polymers retained very good mechanical properties up to the T_g's as observed from the storage modulus plots of the polymers.

3.7 Mechanical Properties

The mechanical properties of thin polyimide films cast from DMF are shown in Table 3. The poly(etherimide)s exhibited the expected ductile mechanical behavior characteristics with elongation behavior up to 20%. The polymer exhibited high tensile strength up to 97 MPa and Young's modulus up to 1.56 GPa. It is observed from Table 3 that the polymers, having more extended geometry, results in more elongation at break than the polymers having less extended geometry. Polymers 1c and 1d containing pyridine and thiophene moiety in the backbone showed less elongation at break than polymers 1a and 1b.

3.8 Dielectric Properties and Water Absorption Behavior

The dielectric constant of the polymer films was determined from capacitance values by using a capacitance meter from 100 KHz to 1 MHz at 30°C. The dielectric constant of the polymers is reported in Table 3. A water absorption study of the poly(ether imide)s was done by immersing rectangular pieces of samples (30 × 10 mm) in double distilled water after taking the initial weight at room temperature. Final weight was taken after 24 h and water absorption was calculated; % Water absorbed = [(Weight of the wet film − weight of the dry film)/Weight of the dry film] × 100. Water absorption values of these polymers are as low as 0.19 wt% in the case of polymer 1b characteristics of semi-fluorinated poly(ether imide)s. These values are observed to be less than Ultem 1000 which have water absorption of 1.52% (7) and Kapton (3%).

3.9 Rheology

It is interesting to know how apparent viscosity changes when shear rates change in a very wide range. The flow curve of the polymers (Figure 7) showed very pronounced non-Newtonian flow as a gradual decrease of apparent viscosity. At low shear rates, Newtonian behavior is observed and apparent viscosity

corresponding to this region of the flow curve is called zero-shear or initial or maximum Newtonian viscosity. Then the decrease of apparent viscosity is observed - typical of non-Newtonian behavior.

4   Conclusions

Four new fluorinated poly(etherimide)s have been synthesized on reaction with bisphenol-A (diphthaleic anhydride) with different trifluoromethyl-substituted diamines. The polymers were well characterized by thermal, mechanical and dielectric properties. The synthesized polymers exhibited good solubility in different organic solvents. The resulting poly(etherimide)s are amorphous and exhibited very good thermal stability. These polymers have good mechanical strength and modulus. These poly(etherimide)s have been observed to have low moisture uptake and low dielectric constant and hence, are promising materials for electronic applications and as gas separation membranes.

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