Synthesis and Characterization of Highly Soluble Poly(ether imide)s Containing Indane Moieties in the Main Chain

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ABSTRACT: A new indane containing unsymmetrical diamine monomer (**3**) was synthesized. This diamine monomer leads to a number of novel semifluorinated poly (ether imide)s when reacted with different commercially available dianhydrides like benzene-1,2,4,5-tetracarboxylic dianhydride (PMDA), benzophenone-3,3′,4,4′-tetracarboxylic dianhydride (BTDA), 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), 4,4′-oxydiphthalic anhydride (ODPA), and 4,4′-(4,4′-Isopropylidenediphenoxy)bis(phthalic anhydride) (BPADA) by thermal imidization route. All the poly(ether imide)s showed excellent solubility in several organic solvents such as *N*-methylpyrrolidone (NMP), *N*, *N*-dimethylformamide (DMF), *N*, *N*-dimethylacetamide (DMAc), tetrahydrofuran (THF), chloroform (CHCl₃) and dichloromethane (DCM) at room temperature. These light yellow poly (ether imide)s showed very low water absorption (0.19–0.30%) and very good optical transparency. Wide angle X-ray diffraction measurements revealed that these polymers were amorphous in nature. The polymers exhibited high thermal stability up to 526°C in nitrogen with 5% weight loss, and high glass transition temperature up to 265°C. The polymers exhibited high tensile strength up to 85 MPa, modulus up to 2.5 GPa and elongation at break up to 38%, depending on the exact polymer structure. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3640–3651, 2009

Key words: poly (ether imide)s; solubility; thermal stability; optical transparency

INTRODUCTION

Aromatic polyimides are one of the most outstanding class of high-performance polymers that exhibit a number of outstanding properties, such as excellent thermal and thermo-oxidative stability, solvent resistance, mechanical, and electrical properties.[1] They are finding wide range of applications in the field of electronic, aerospace, as well as membranes for gas separation and elsewhere.[1–4] Aromatic polyimides such as Kapton and Novax are the representatives of high performance polymer because of their excellent thermal stabilities, mechanical, electrical properties, and chemical resistance.[5] However, the main drawbacks of these classes of polymers are their insolubility and intractability, which causes difficulties in both synthesis and processing. Therefore, the processing of the polyimides is generally carried out via soluble poly(amic acid) precursors, which are cast onto a glass plate and then converted into thin polyimide films by a rigorous thermal treatment.[6,7] However, this process has several limitations, which include emission of volatile by-products during curing, such as water that create strength-weakening voids in thick parts and a storage instability of poly(amic acid) intermediates.[1,8] Solubilization of polyimides have been targeted by several means, such as introduction of flexible linkages,[9,10] bulky substituents,[11,12] or bulky units in the polymer backbone,[13,14] incorporation of alicyclic[15] or noncoplanar[16,17] units.

Poly(ether imide)s have attracted great attention as they provide better processability owing to the presence of flexible ether linkages, which lead to decrease in glass transition temperatures without forfeiture of their thermal stabilities.[18–23] An important example is Ultem 1000 resin developed and commercialized by General Electric Co., made from 4,4′-(4,4′-isopropylidenediphenoxy)bis(phthalic anhydride) and *m*-phenylene diamine,[24,25] which exhibits reasonable thermal stability and good mechanical properties together with good moldability.

Semifluorinated polyimides have got great attention in this regard from both academia and industry.[26–31] It is found that polyimides containing trifluoromethyl groups serves to increase the free volume, thereby improving various properties like solubility, electrical insulating properties, gas

permeability, flame resistance, environmental stability, and optical transparency without affecting thermal stability to that of nonfluorinated one.[32–34] Fluorinated substituent reduces moisture absorption due to the nonpolar character of fluorocarbon groups, which vis-à-vis reduces the dielectric constant. Because of all these interesting properties of the fluorinated polymers, considerable attention has been devoted to the preparation of new classes of fluorinated aromatic polyimides, especially trifluoromethyl ($-CF_3$) containing polyimides.[32–40] Furthermore, introduction of unsymmetrical structure into the main chain of the polyimide can lead to the improvement in solubility, melt processability, and other desirable properties.[41–47] Most of the above approaches for soluble polyimides are aimed at reduction of several types of chain–chain interaction, such as chain packing (e.g., crystallinity) and charge transfer and electronic polarization interactions.[6,38]

In light of these observations, we were interested to synthesize organosoluble polyimides. For this a new fluorinated unsymmetrical diamine monomers (**3**) have been synthesized. This investigation deals with the synthesis and characterization of several poly(ether imide)s by using this new diamine monomer.

EXPERIMENTAL SECTION

General considerations

The elements, carbon, hydrogen, and nitrogen were analyzed by pyrolysis method using vario EL (Elementar, Germany) elemental analyzer. ^1H and ^{13}C NMR were recorded on a Bruker 500 MHz instrument (Switzerland) using $CDCl_3$ as solvent (reference zero ppm with respect to TMS). IR spectra of the polymer films were recorded with a Bruker IFS 55 spectrophotometer. DSC measurements were made on a NETZSCH DSC 200PC instrument at a heating/cooling rate of 20°C min^{-1} in nitrogen. Glass transition temperature (T_g) was taken at the middle of the step transition in the second heating run. Thermogravimetry was measured on NETZSCH TG 209 F1 thermal analyzer instrument. A heating rate of 10°C min^{-1} was used for determination of the decomposition temperature under nitrogen. Viscosity was measured by Ubbelohde viscometer at 34°C in DMF as solvent. Mechanical properties such as tensile strength and elongation at break of the thin polymer films (30 × 10 × 0.1 mm^3) were measured at room temperature on a Hounsfield (UK) H10KS–0547 instrument under strain rate of 5% min^{-1} of the sample length. Water absorption of the films was calculated from the weight gain by a balance of sensitivity of 10^{-6} g after immersing the films into distilled water for 72 h at 30°C. Room

temperature ultraviolet spectrophotometer (UV) measurement was done using Detector SD–2000 (Ocean Optics Inc.) and source lamp DH–2000. X-ray diffaction study was conducted by Rigaku, Ultema III X-ray diffractometer with a Cu K$_\alpha$ ($\lambda = 0.154$ nm) source, operated at 40 kV and 40 mA. GPC was performed in Waters instrument 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.

Starting materials

Benzene-1,2,4,5-tetracarboxylic dianhydride (PMDA), benzophenone-3,3′,4,4′-tetracarboxylic dianhydride (BTDA), 4,4′-(hexafluoro-isopropylidene)diphthalic anhydride (6FDA), 4,4′-oxydiphthalic anhydride (ODPA), and 4,4′-(4,4′-Isopropylidenediphenoxy)-bis(phthalic anhydride) (BPADA) were purchased from Aldrich, USA. The dianhydrides were heated to 120°C overnight under vacuum prior to use. 4, 4′-Isopropylidenephenol (BPA) (Loba Chemie, India) was used after recrystallization from toluene. N, N-Dimethylformamide (DMF, Merck, India) were purified by stirring with NaOH and distilled from P_2O_5 under reduced pressure. Sulfuric acid and formic acid were purchased from Merck, India. The synthesis of 3-trifluoromethyl-4-fluoro-4′-nitro biphenyl has already been reported in an article.[41]

Synthesis of diamino monomer

The new diamine monomer (**3**) was synthesized starting from commercially available BPA in three steps:

3-(4-Hydroxy-phenyl)-1,1,3-trimethyl-indan-5-ol (1)

BPA (50 g) was dissolved and stirred in conc. sulfuric acid (300 g) at 25°C. After dissolving completely (about 20 min) the solution was poured slowly into an ice-water ($\sim$ 1.5 L), under vigorously stirring. Sticky solid of pale orange color was formed instantaneously. After the completion of addition, the temperature of the mixture was allowed to rise to room temperature during the next 1 h by stirring. The solid precipitate was filtered, washed several times with water, and dried. The precipitate was then dissolved in 150 mL formic acid and the solution was stirred for a period of 1 h, the insoluble portion was removed by filtration. After that, the formic acid was removed by distillation from the filtrate and a crude product was obtained. The crude product was purified by column chromatography (silica gel) using ethyl acetate-hexane (20 : 80) as eluent.
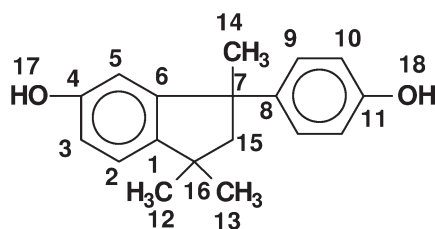
Yield: 28.5 g (49%). Melting point: 197.9°C. Anal. Calcd. for ($C_{18}H_{20}O_2$) (268.1463 g mol^{-1}): C, 80.56%; H, 7.51%. Found C, 80.21%; H, 7.24%. IR (KBr) (cm^{-1}): 3496, 3413 (O—H stretching); 2954, 2922 (Aromatic C—H stretching), 2858 (Aliphatic C—H stretching), 1608 (C=C ring stretching band), 815 (aromatic C—H band out of plane). ^{1}H NMR (DMSO-d_6): δ (ppm) 9.13 (s, 1H, H17); 9.09 (s, 1H, H18); 6.99 (d, J = 8.2 Hz, 1H, H2); 6.95 (d, J = 8.5 Hz, 2H, H9), 6.64 (d, J = 8.1 Hz, 1H, H3); 6.63 (d, J = 8.4 Hz, 2H, H10); 6.41 (d, J = 8 Hz, 1H, H5); 2.17 (dd, J = 102 Hz, J' = 12.9 Hz, 2H, H15); 1.53 (s, 3H, H14); 1.25 (s, 3H, H12); 0.96 (s, 3H, H13). ^{13}C NMR

(DMSO-d6): δ (ppm) 157.29, 155.92, 151.22, 142.99, 141.89, 128.29, 123.95, 115.64, 115.41, 111.83, 60.24, 50.45, 42.64, 31.89, 31.81, 31.44.
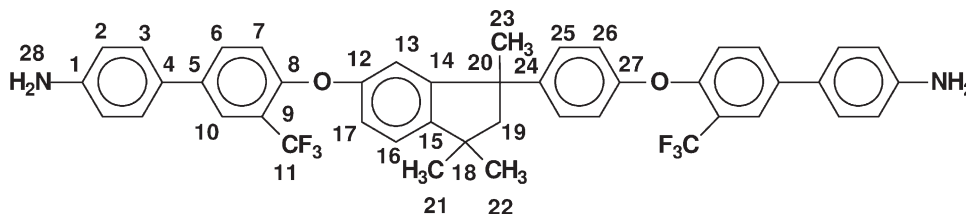
Synthesis of the dinitro compound (2)

3-Trifluoromethyl-4-fluoro-4′-nitrobiphenyl (11 g, 38.57 mmol), 3-(4-Hydroxy-phenyl)-1,1,3-trimethyl-indan-5-ol (1)(5.171 g, 19.28 mmol), K_2CO_3 (13.29 g, 96.43 mmol), dry DMF (90 mL), and dry toluene (90 mL), were intensively stirred under a constant flow of nitrogen and heated at 110°C for 3 h. The temperature of the reaction mixture was then raised to 150°C. During this period the water formed from the deprotonation was removed azeotropically by toluene. The reaction mixture was maintained at this temperature for another 4 h. The temperature was brought down to room temperature and the reaction mixture was precipitated in a large excess of distilled water.
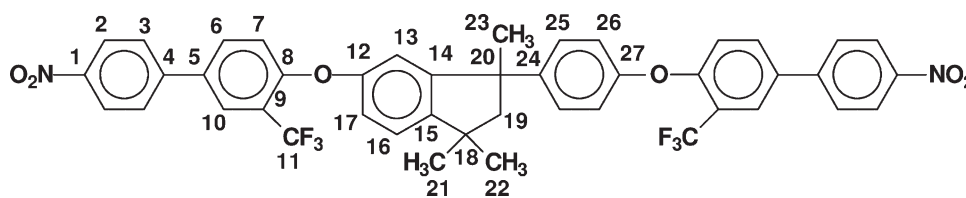
Yield: 14.83 g (97%). Melting point: 161°C. Anal. Calcd. for ($C_{44}H_{32}F_6N_2O_6$) (798.7251 g mol^{-1}): C, 66.16%; H, 4.04%; N, 3.51%; Found: C, 65.93%; H, 3.89%; N, 3.42%. IR (KBr) (cm^{-1}): 2958 (Aromatic C—H stretching), 2862 (Aliphatic C—H stretching), 1619 (C=C ring stretching band), 1348 (band due to C—F absorption), 1251 (asymmetric C—O—C stretch), 1130 (symmetric C—O—C stretch), 855 (C—N stretch for aromatic—NO_2), 825 (aromatic C—H bend out of plane). ^{1}H NMR (CDCl$_3$): δ (ppm) 8.31 (d, J = 8.4 Hz, 4H, H2); 7.9 (s, 2H, H10); 7.69 (d, J = 8.4 Hz, 4H, H3), 7.66 (d, J = 8.8 Hz, 2H, H6); 7.24 (d, J = 8 Hz, 1H, H16); 7.22 (d, J = 8.4 Hz, 2H, H25); 7.05-6.98 (m, 5H, H7, H17, H26); 6.87 (s, 1H, H13); 2.37 (dd, J = 71.2 Hz, J' = 12.8 Hz, 2H, H19); 1.70 (s, 3H, H23); 1.38 (s, 3H, H21); 1.11 (s, 3H, H22).

Synthesis of diamine monomer (3)

The dinitro compound (2) (13 g), Pd-C (Pd content 1%, 0.4 g) and 440 mL of ethanol were taken in a three-necked round-bottom flask equipped with a stirring bar, nitrogen inlet, and a reflux condenser. To this mixture, hydrazine mono hydrate (220 mL) was added dropwise for more than 1 h at 85°C. The reaction was maintained at reflux for another 20 h. The mixture was then filtered to remove Pd-C. The filtrate was concentrated under nitrogen; the solid product obtained was isolated on filtration. The product was further crystallized from ethanol/water to give light yellow crystals.

Yield: 10.8 g (90%). Melting point: 138°C. Anal. Calcd. for $(C_{44}H_{36}F_6N_2O_2)$ (738.7593 g mol^{-1}): C, 71.53%; H, 4.91%; N, 3.79%; Found: C, 71.13%; H, 4.77%; N, 3.68%. IR (KBr) (cm^{-1}): 3483 (N—H stretching); 3034, 2957 (aromatic C—H stretching), 2862 (Aliphatic C—H stretching); 1622 (C=C ring stretching band), 1442 (band due to C—F absorption), 1245 (asymmetric C—O—C stretch), 1129 (symmetric C—O—C stretch), 819 (C—N stretch for aromatic - NH_2). ^1H NMR $(CDCl_3)$: δ (ppm) 7.78 (s, 2H, H10); 7.54 (m, 2H, H6); 7.35 (d, $J = 7.6$ Hz, 4H, H3); 7.17 (d, $J = 8.4$ Hz, 1H, H16), 7.16 (d, $J = 8.8$ Hz, 2H, H25); 6.99-6.91(m, 5H, H7, H17, H26); 6.83 (s, 1H, H13); 6.73 (d, $J = 8.8$ Hz, 4H, H2); 3.8 (broad, H28); 2.33 (dd, $J = 76.0$ Hz, $J' = 13.2$ Hz, 2H, H19); 1.67 (s, 3H, H23); 1.36 (s, 3H, H21); 1.08 (s, 3H, H22). ^{13}C-NMR $(CDCl_3)$: δ(ppm) 155.57, 154.45, 154.05, 150.77, 148.08, 146.33, 146.19, 136.00, 135.73, 130.74, 128.04, 127.85, 127.81, 126.7 (q, $J = 291.5$ Hz, C11), 124.92, 127.83, 120.77 (q, $J = 36$ Hz, C9), 119.45, 118.92, 116.05, 115.48, 59.59, 50.42, 42.56, 30.87, 30.81, 30.53.

Polymerization

The poly (ether imide)s were prepared from the synthesized diamine monomer and various aromatic dianhydrides in DMF under nitrogen atmosphere adopting the standard procedure of polyamic acid synthesis. An equimolar amount of diamine and dianhydride monomers were used in all cases. A typical polymerization procedure is as follows. A 25-mL round-bottomed flask equipped with nitrogen inlet and a magnetic stirrer was charged with 0.41066 g (0.555886 mmol) of the di-amine monomer (3), 0.28933 g (0.555886 mmol) of BPADA, and 5 mL DMF. The mixture was stirred at room temperature. The reaction mixture become highly viscous within 10–15 min and the reaction was continued for 1 h. The poly(amic acid) solution was cast onto clean and dry glass petridish. The film were dried in vacuum oven at 80°C overnight followed by 100, 150, 200, for 1 h at each temperature and at 250°C for 30 min. Finally, the temperature was brought down to 150°C, and the films were kept under vacuum overnight. Polyimide films were then removed from the glass plates and were used for further characterization.

Polyimide a

Anal. Calcd for $(C_{54}H_{34}O_6F_6N_2)_n$ (920.8480 g $mol^{-1})_n$: C, 70.43%; H, 3.72%; N, 3.04%; Found: C, 69.74%; H, 3.62%; N, 2.96%. IR (KBr) (cm^{-1}): 3490 (—N< stretching), 3045 (aromatic C—H stretching), 2959, 2868 (aliphatic C—H stretching), 1778 (C=O asym. stretching), 1719 (C=O sym. stretching), 1613 (aromatic C=C ring stretching band), 1496 (C—F absorption), 1351 (asymmetric C—O—C stretching), 1170, 1052 (symmetric C—O—C stretching), 824 (C—N bending). ^1H NMR $(CDCl_3)$: δ (ppm) 8.55 (s, 2H); 7.89 (s, 2H); 7.79–7.76 (m, 6H); 7.56 (d, $J = 7.4$ Hz, 4H); 7.23 (d, $J = 7.8$ Hz, 2H); 7.21 (d, $J = 7.8$ Hz, 1H); 7.20-6.98 (m, 5H); 6.86 (s, 1H); 2.37 (dd, $J = 91.7$ Hz, $J' = 12.8$ Hz, 2H); 1.71 (s, 3H); 1.39 (s, 3H); 1.13 (s, 3H). ^{13}C NMR $(CDCl_3)$: δ(ppm) 167.1, 155.8, 155.6, 154.8, 150.87, 147.18, 146.42, 141.15, 139.26, 135.25, 134.3, 132.4, 131.8, 128.6, 127.92, 126.61, 124.83, 123.98, 123.29 (q, $J = 268.6$ Hz, C11), 121.17 (q, $J = 31.5$ Hz, C9), 119.34, 119.09, 118.50, 116.44, 59.46, 50.38, 42.57, 30.84, 30.76, 30.51.

Polyimide b

Anal. Calcd for $(C_{61}H_{38}O_7F_6N_2)_n$ (1024.9540 g $mol^{-1})_n$: C, 71.48%; H, 3.74%; N, 2.73%; Found: C, 71.11%; H, 3.59%; N, 2.62%. IR (KBr) (cm^{-1}): 3490 (—N< stretching), 3045 (aromatic C—H stretching), 2960, 2868 (aliphatic C—H stretching), 1780 (C=O asym. stretching), 1726 (C=O sym. stretching), 1619 (aromatic C=C ring stretching band), 1489 (C—F absorption), 1374 (asymmetric C—O—C stretching), 1170, 1054 (symmetric C—O—C

stretching), 825 (C—N bending). ^{1}H NMR (CDCl$_3$): δ (ppm) 8.28 (s, 2H); 8.25 (d, J = 7.5 Hz, 2H); 8.12 (d, J = 7 Hz, 2H); 7.88 (s, 2H); 7.67-7.63 (m, 6H); 7.54 (d, J = 7.1 Hz, 4H); 7.22 (d, J = 7.2 Hz, 2H); 7.20 (d, J = 8 Hz, 1H); 7.02-6.98 (m, 5H); 6.88 (s, 1H); 2.36 (dd, J = 94.4 Hz, J' = 13.2 Hz, 2H); 1.71 (s, 3H); 1.38 (s, 3H); 1.11 (s, 3H). ^{13}C-NMR

(CDCl$_3$): δ(ppm) 192.76, 165.99 (C28, C31), 156.02, 155.56, 154.94, 153.86, 150.91, 148.57, 146.78, 141.90, 139.47, 135.87, 134.21, 132.16, 131.63, 130.74, 128.17, 127.69, 126.84, 125.90, 124.78, 124.39, 123.98, 123.33 (q, J = 265.4 Hz, C11), 121.19 (q, J = 31.8 Hz, C9), 119.34, 119.08, 118.51, 116.45, 59.55, 50.46, 42.61, 30.86, 30.78, 30.52.
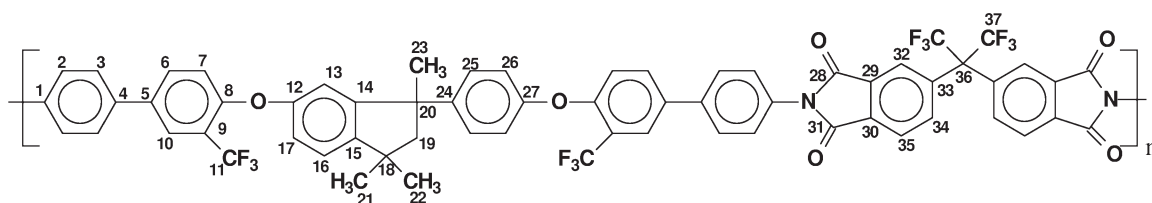
Polyimide c

Anal. Calcd for (C$_{63}$H$_{38}$O$_6$F$_{12}$N$_2$)$_n$ (1146.9665 g mol^{-1})$_n$: C, 65.97%; H, 3.34%; N, 2.44%; Found: C, 65.63%; H, 3.26%; N, 2.29%. IR (KBr) (cm^{-1}): 3495 (—N< stretching), 3045 (aromatic C—H stretching), 2960, 2866 (aliphatic C—H stretching), 1785 (C=O asym. stretching), 1729 (C=O sym. stretching), 1606 (aromatic C=C ring stretching band), 1490 (C—F absorption), 1374 (asymmetric C—O—C stretching), 1170, 1054 (symmetric C—O—C stretching), 825 (C—N bending). ^{1}H NMR (CDCl$_3$):δ (ppm) 8.06 (d, J = 7.9 Hz, 2H); 7.96 (s, 2H); 7.9 (d, J = 7 Hz, 2H); 7.88 (s, 2H); 7.68-7.63 (m, 6H); 7.52 (d, J = 8 Hz, 4H); 7.22 (d, J = 7.6 Hz, 2H); 7.20 (d, J = 8.1 Hz, 1H); 7.04-6.98 (m, 5H); 6.88 (s, 1H); 2.36 (dd, J = 94.3 Hz, J' = 13.1 Hz, 2H); 1.71 (s, 3H); 1.38 (s, 3H); 1.11 (s, 3H). ^{13}C NMR (CDCl$_3$): δ(ppm) 166.07, 165.90, 156.03, 155.57, 154.98, 153.90, 150.90, 148.58, 146.78, 139.57, 139.26, 136.02 (C29, C30), 134.56, 134.29, 132.70, 132.40, 131.67, 130.75, 128.18, 127.77, 126.94, 125.94, 125.45, 123.98, 123.36 (q, J = 275.3 Hz, C11), 121.26 (q, J = 30.6 Hz, C9), 119.36, 119.10, 118.54, 116.48, 59.58, 50.48, 42.62, 31.04, 30.87, 30.54.
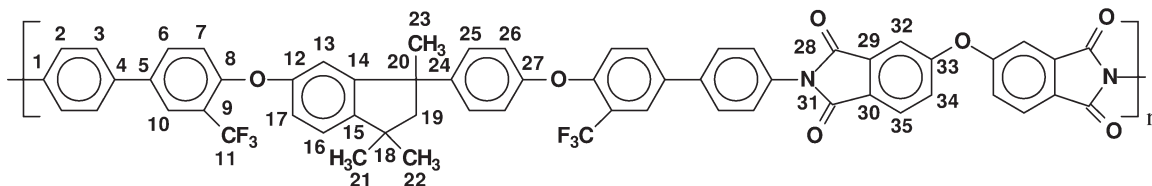
Polyimide d

Anal. Calcd for (C$_{60}$H$_{38}$O$_7$F$_6$N$_2$)$_n$ (1012.9433 g mol^{-1})$_n$: C, 71.14%; H, 3.78%; N, 2.77%; Found: C, 70.87%; H, 3.68%; N, 2.65%. IR (KBr) (cm^{-1}): 3488 (—N< stretching), 3046 (aromatic C—H stretching), 2959, 2865 (aliphatic C—H stretching), 1780 (C=O asym. stretching), 1725 (C=O sym. stretching), 1610 (aromatic C=C ring stretching band), 1486 (C—F absorption), 1372 (asymmetric C—O—C stretching), 1134, 1053 (symmetric C—O—C stretching), 821 (C—N bending). ^{1}H NMR (CDCl$_3$): δ (ppm) 7.90 (s, 2H); 7.88 (d, J = 7 Hz, 2H); 7.65 (d, J = 7.5 Hz, 2H); 7.64 (d, J = 8.5 Hz, 4H); 7.51 (d, J = 8.2 Hz, 4H); 7.44 (s,2H); 7.33 (d, J = 8.5 Hz, 2H); 7.22 (d, J = 7.5 Hz, 2H); 7.20 (d, J = 8 Hz, 1H); 7.05-6.98 (m, 5H); 6.88 (s, 1H); 2.36 (dd, J = 94.8 Hz, J' = 13.1 Hz, 2H); 1.70 (s, 3H); 1.38 (s, 3H); 1.10 (s, 3H). ^{13}C NMR (CDCl$_3$): δ(ppm) 166.16, 161.27, 155.98, 155.52, 155.03, 153.95, 150.91, 148.57, 146.76, 139.30, 134.68, 134.41, 131.67, 131.06, 128.18, 127.68, 127.36, 126.90, 126.34, 125.93, 123.99, 123.36 (q, J = 271.3 Hz, C11), 121.40 (q, J = 31.1 Hz, C9), 119.34, 119.13, 118.57, 116.47, 114.40, 114.07, 59.60, 50.50, 42.63, 41.5, 30.87, 30.54.
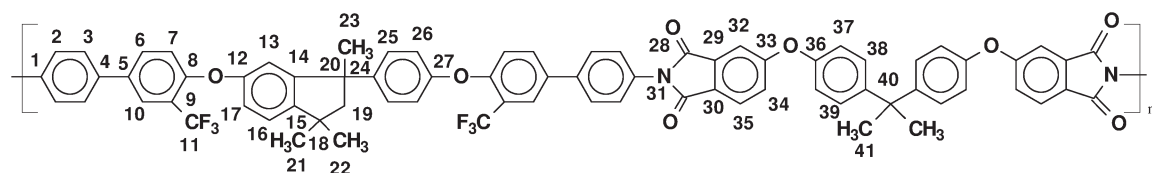
Polyimide e

Anal. Calcd for $(C_{75}H_{52}O_8F_6N_2)_n$ (1223.2144 g $mol^{-1})_n$: C, 73.64%; H, 4.28%; N, 2.29%; Found: C, 73.21%; H, 4.12%; N, 2.11%. IR (KBr) (cm^{-1}): 3489 (—N< stretching), 3046 (aromatic C—H stretching), 2959, 2865 (aliphatic C—H stretching), 1780 (C=O asym. stretching), 1725 (C=O sym. stretching), 1610 (aromatic C=C ring stretching band), 1489 (C—F absorption), 1372 (asymmetric C—O—C stretching), 1135, 1054 (symmetric C—O—C stretching), 821 (C—N bending). ^1H NMR (CDCl$_3$): δ (ppm) 8.02 (d, J = 8 Hz, 2H); 7.88 (s, 2H); 7.68-7.64 (m, 9H); 7.58 (s, 2H); 7.54 (d, J = 8.2 Hz, 4H); 7.49 (d, J = 7.8 Hz, 2H); 7.22 (d, J = 8.3 Hz, 4H); 7.04-6.99 (m, 9H); 6.89 (s, 1H); 2.37 (dd, J = 95.0 Hz, J' = 13.0 Hz, 2H); 1.79 (s, 6H); 1.34 (s, 6H); 1.11 (s, 3H). ^{13}C-NMR (CDCl$_3$): δ(ppm) 166.70, 163.92, 155.91, 155.45, 155.05, 153.97, 152.75, 150.90, 148.53, 147.63, 146.73, 139.04, 134.76, 134.50, 134.28, 131.65, 131.30, 128.80, 128.17, 127.60, 126.90, 125.81, 125.07, 123.97, 123.41 (q, J = 271.2 Hz, C11), 123.12, 121.38 (q, J = 31 Hz, C9), 120.03, 119.33, 119.13, 118.57, 116.46, 111.95, 59.60, 50.48, 42.61, 41.5, 33.6, 31.04, 30.87, 30.54.

Figure 1 Reaction scheme and structure of the diamine monomer.

RESULTS AND DISCUSSION

Synthesis of diamine monomer

The diamine monomer (**3**) was synthesized starting from commercially available BPA. In the first step, BPA was converted to the key bishydroxy monomer, 3-(4-Hydroxy-phenyl)-1, 1, 3-trimethyl-indan-5-ol (BPI) according to the procedure reported by Dai and co-workers[48] However, we did not get the desired BPI after filtration of the reaction mixture from formic acid. The white solid we got was not matching with the BPI characteristics. Instead, BPI was recovered after distilling off formic acid followed by purification of the crude solid product through silica gel chromatography using ethyl acetate-hexane (20:80) as eluent.

The 3-trifluoromethyl-4-fluoro-4'-nitrobiphenyl was synthesized via Suzuki coupling of 4-nitro bromobenzene and 4-fluoro-3-trifluromethyl phenyl boronic acid.[41] This compound was reacted with the BPI to form dinitro derivative. Finally, the new diamine monomer was achieved after catalytic hydrogenation of the dinitro compound. The detailed reaction scheme of the synthesis of the diamine monomer is shown in Figure 1.

The complete characterizations of the BPI, intermediate dinitro compound and the diamine monomer were done by elemental analyses, IR and NMR techniques, which are in very good agreement with the structure as shown in Figure 1. Analytical details are given in experimental section.
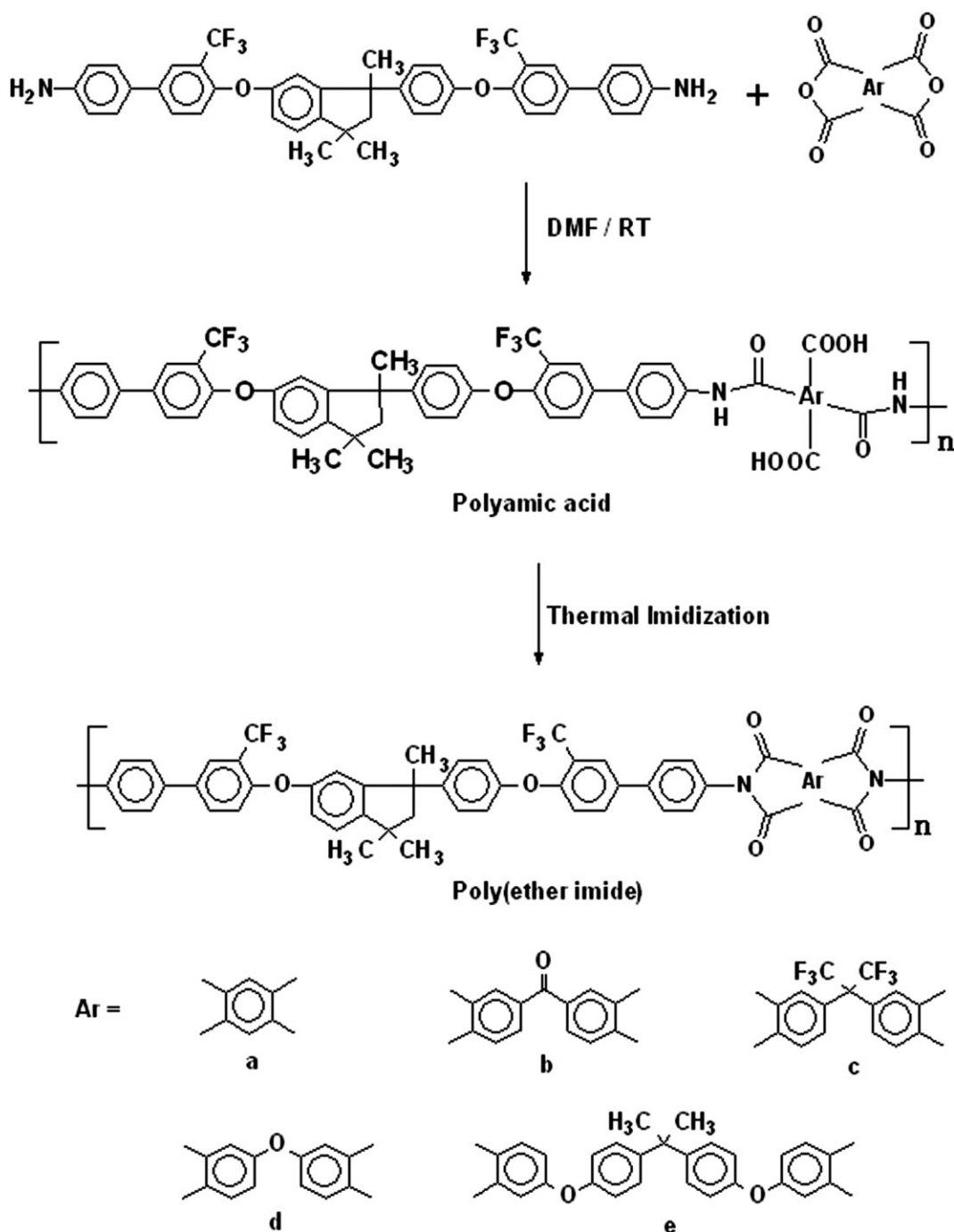
Synthesis of the poly(ether imide)s

The poly (ether imide)s were prepared using the synthesized diamine monomer (**3**) and various aromatic dianhydrides in DMF under nitrogen atmosphere adapting the standard procedure of poly (amic acid) synthesis.[30] Totally, five poly(ether imide)s were prepared from the diamine monomer and using commercial dianhydrides like PMDA, BTDA, 6-FDA, ODPA, and BPADA. The reaction scheme of synthesis and structures of the poly(ether imide)s are shown in Figure 2.

Typically, the poly (amic acid)s were prepared by dissolving the diamine in measured amount of dry DMF and adding a molar equivalent of dianhydride monomers to it. In all cases, the reaction mixtures become highly viscous within 10–15 min indicating the formation of high molar masses, and the reactions were continued for 1 h at room temperature. The poly (amic acid) solutions were spread on glass plate and heated at 80°C for over night to remove the solvent. The imidization and removal of solvent and water (form during imidization) was carried out by sequential heating at 120°C, 150°C, 200°C for 1 h at each temperature and at 250°C for 30 min in a leveled temperature controlled vacuum oven. The glass plates containing the polyimide films were allowed to cool down to 150°C and were kept under vacuum for overnight to ensure the complete removal of any residual solvent in the polyimide film. The oven temperature was slowly brought down to room

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

temperature. The resulting polyimide films were removed from the glass plates. Transparent, yellowish films were obtained in all cases. All the polymer had been well characterized and analytical details are reported in experimental section.

Polymer solubility

The solubilities of the poly(ether imide)s were tested in various solvent. The results are summarized in Table I. Attempt was made to obtain 10% (w/v) solution

of all the polymers in different organic solvents. These poly(ether imide)s showed excellent solubility in common organic solvents. All the polymers exhibited very good solubility in CHCl₃, THF, DCM, DMF, DMAc, and NMP at room temperature. They were soluble in DMSO on heating, except the polymer containing PMDA unit in the main chain. Generally, the enhanced solubility of fluorinated poly(ether imide)s can be attributed not only because of the flexible spacers like ether linkages but also because of bulky substituents like —CF₃ group, which inhibit close

TABLE I
Solubilities of the Poly(ether imide)s

Polymer	NMP	DMF	DMAc	THF	CHCl$_3$	DCM	Acetone	DMSO
a	+	+	+	+	+	+	−	−
b	+	+	+	+	+	+	−	+h
c	+	+	+	+	+	+	−	+h
d	+	+	+	+	+	+	−	+h
e	+	+	+	+	+	+	−	+h

+, Soluble at room temperature; +h, soluble on heating; −, insoluble at room temperature.

packing leading to reduction in polymer chain–chain interaction. The results indicate that the unsymmetrical flexible diamine moiety played an important role in obtaining good solubility of polymers in comparison with the previous reported polyimides from symmetrical diamine monomers.[30,36]

Spectroscopy

The complete imidization of poly(ether imide)s was confirmed by FTIR spectroscopy. FTIR spectra of all the polyimides prepared by thermal imidization method showed the absorption bands at about 3490 cm^{-1} (—N< stretching with low absorption), 1780 cm^{-1} (C=O asymmetric stretching), 1729 cm^{-1} (C=O symmetric stretching), 1370 cm^{-1} (C—N stretching), 825 cm^{-1} (C—N bending), corresponding to the characteristic of imide bands. No absorption bands were found at 3400–3200 cm^{-1} corresponding to amide (—NH), acid (—OH) stretching. ^{1}H NMR spectra of the polymers showed no amide and acid protons, indicating full imidization. A representative proton NMR spectrum is shown in Figure 3.
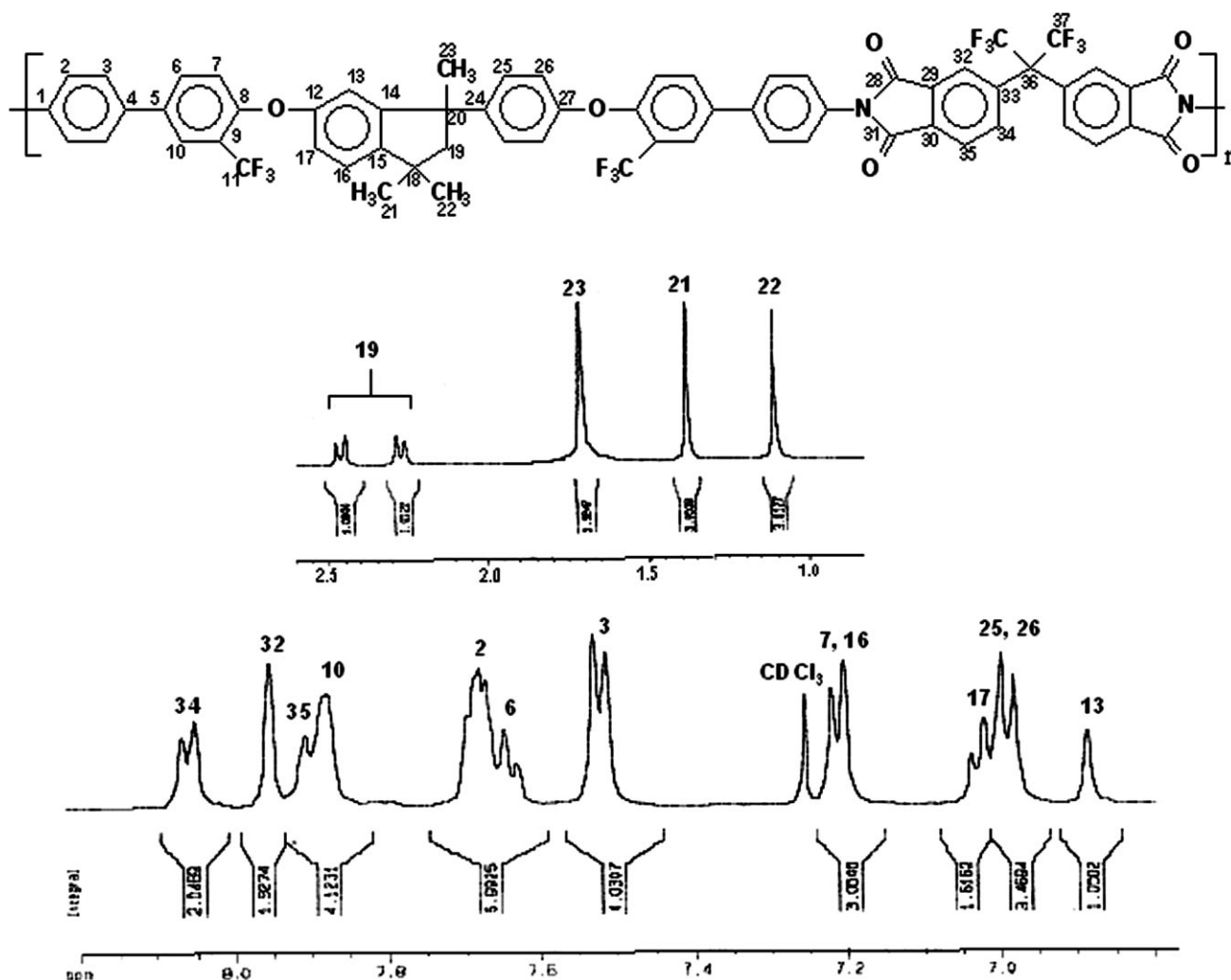

Figure 3 Representative 1H NMR spectrum of poly(ether imide), "c".
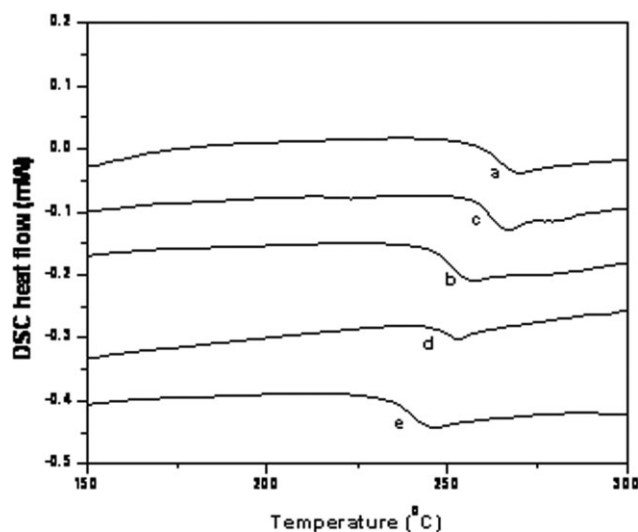
Figure 4 DSC curves of the poly(ether imide)s.

DSC measurement

The glass transition temperatures (T_g) of the poly (ether imide)s were evaluated by DSC. These polymers showed glass transition temperatures, which indicate amorphous or glassy morphology. The glass transition temperature of poly (ether imide)s were in the range of 241 to 265°C. No melting or crystallization transition of the polyimides observed. The DSC curves of the polymers are shown in Figure 4 and the T_g values are summarized in Table II. Glass transition temperatures of the polymers depend on many factors such as polymer symmetry, intermolecular force, and rigidity of polymer backbone. It is well known that with the increase in rigidity, glass transition temperature also increases. The higher T_g value of PMDA-based polyimide compared with other dianhydride-based polymers can be explained on the basis of rigid PMDA moiety. 6FDA-based polymers showed higher T_g value in comparison with BTDA-based polymer because of the presence of bulky 6F unit in the polymer backbone. The polyimide, which was derived from BPADA, showed lowest T_g in the series. This is because of the presence of additional flexible ether linkage, coming from the dianhydride moiety. The T_g values of this series of polymer are higher than many commercial poly (ether imide)s; e.g., Ultem 1000 ($T_g = 217$°C),

TABLE II
Thermal Properties of the Poly(ether imide)s

Polymer	DSC T_g (°C)	T_d (°C) 5% weight loss	T_d (°C) 10% weight loss	Residual mass at 700°C
a	265	526	545	71
b	252	517	533	69
c	262	509	528	71
d	249	508	521	67
e	241	503	520	68

based on BPADA and MPD (*m*-phenylene diamine).[24,25]

Thermal stabilities

The thermal properties of the poly (ether imide)s were evaluated by TGA. The 5% weight loss temperature of these polymers in nitrogen was in the range of 503–526°C with 67–71% of char residue. All the polymers showed high thermal stability as expected in the case of polyimides. The 5% weight loss temperature for polymer "a" containing rigid PMDA moiety showed the highest value whereas for polymer "e" containing BPADA moiety with the maximum numbers of flexible ether linkages showed the lowest among this series. The TGA thermograms of the poly(ether imide)s are shown in Figure 5. The 5% weight loss and 10% weight loss temperature in nitrogen are summarized in Table II.

Mechanical properties

The mechanical properties of all the poly (ether imide)s films are shown in Table III. An average value of three repeated measurements is shown in the Table. A representative stress–strain plots of polyimide "d" is shown in Figure 6. The nature of the plot indicates the ductile behavior of the material. These poly (ether imide)s showed high tensile strength up to 85 MPa, Young's modulus up to 2.5 GPa and elongation at break up to 38% depending on exact polymer structure. The polyimide "e" exhibited the highest elongation at break because of its flexible nature. The poly(ether imide)s containing PMDA unit showed least elongation at break (3%) in the series. This can be attributed to the rigid nature of this polymer. However, to get a realistic picture of the mechanical properties of these polymers, it is
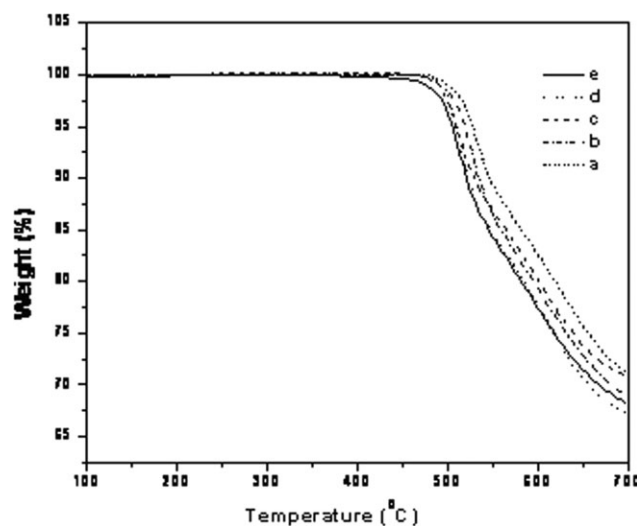

Figure 5 TGA thermograms of the poly(ether imide)s.

TABLE III
**Mechanical Properties, Viscosity, and GPC Data of the Poly(ether imide)s**

Polymer	Tensile break (MPa)	Modulus (GPa)	Elongation at break (%)	η (dL/g)	M_w	PDI
a	85	2.3	3	0.35	52,300	2.4
b	83	2.5	9	0.65	72,500	2.9
c	69	2.3	12	0.33	52,200	2.3
d	57	2.2	37	0.35	57,400	2.5
e	51	2.0	38	0.39	59,200	2.4

η, inherent viscosity; M_w, weight average molecular weight; PDI, poly dispersity index.

essential to evaluate the mechanical properties of the molded specimens. There are chances of formation of defect structure during preparation of dense solution cast film that may affect the final mechanical properties of the polymers.

Inherent viscosities and molecular weight

The poly(ether imide)s showed inherent viscosities ranged from 0.33–0.65 dL g^{-1}. The exact molecular weights are shown in Table III. The polymers derived from 6FDA, showed relatively low inherent viscosity in comparison to their respective molar masses. This is because of the fact that inherent viscosity decreases with an increasing number of trifluoromethyl groups in a repeat unit. This point is also illustrated with hydrodynamic volume which depends on molecular weight and structure of the polymer. The trifluoromethyl group decreases the interchain interaction with increasing fluorine atoms. This, in turn, affects the hydrodynamic volume of the polymer in solvent and show lower inherent viscosities.[36] The weight average molecular weight of the polymers in good agreement with the viscosity
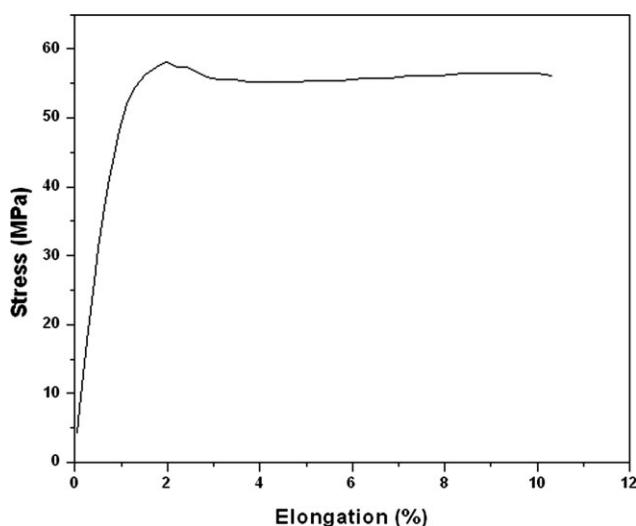
Figure 6 Representative stress–strain plot of the poly (ether imide), "d".

data and the polydispersity index values are in the range that is expected for condensation polymers.

Water absorption behavior

Water absorption study of the poly(ether imide)s were done by immersing the samples in water after taking the initial weight at room temperature. Final weight was taken after 72 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 is a great concern when the polymers are used in electronic packaging as dielectric insulation. The water absorption value for these series of polyimides lies between 0.19 to 0.30%. The exact values for different polymers are given in the Table IV. The 6FDA containing polyimides showed the lowest water absorption (0.19 wt %) that is due to the presence of higher fluorine content in the polymer structure. This is due to the fact that $-CF_3$ groups are hydrophobic in nature. Water absorption depends on the % fluorine content in the polymer, which is a characteristics of semifluorinated poly(ether imide)s. These values are observed to be less than Ultem 1000 which have water absorption of 1.52%[25] and Kapton (3%).[5]

X-ray diffraction analysis

The morphological structures of the polyimide films were analyzed by wide angle X-ray diffraction

TABLE IV
Optical Properties and Water Absorption Behavior of the Poly(ether imide)s

Polymer	Water absorption (%) after 72 h	Thickness (mm)	λ_0 (nm)	Film quality
a	0.22	0.10	420	Clear
b	0.24	0.08	385	Clear, flexible
c	0.19	0.07	350	Clear, flexible
d	0.27	0.07	370	Clear, flexible
e	0.30	0.09	365	Clear, flexible

λ_0, cut-off wavelength.

studies. The X-ray diffraction patterns for the polyimides are displayed in Figure 7. DSC measurement detected no melting or crystallization transition of the polyimides and the XRD data are in good agreement. All the polyimides exhibited amorphous diffraction patterns.[21,31] The broad peak in XRD data because of the unsymmetrical diamine monomer containing bulky $-CF_3$ groups reduces attraction between molecules and hinders molecules sterically. As expected this trend was not only seen in flexible dianhydride-based polyimide like BPADA and ODPA but also in comparatively rigid dianhydride BTDA and PMDA. This is because all polyimides contained fluorinated unsymmetrical diamine in the backbone.

Optical properties

Transmission UV–Vis spectra were measured for all the thin polyimides films. Typical UV–Vis spectra are illustrated in Figure 8. All polyimide films exhibited cut-off wavelengths (λ_0) shorter than 420 nm and high optical transparency with the 80% transmission wavelength above 550 nm. The values of cut-off wavelength (λ_0) of the polyimides are shown in Table IV. The light colors of the polyimides with the $-CF_3$ groups in their unsymmetrical diamine moieties could be explained by the decreased intermolecular interactions and reduced packing density. The bulky and electron-withdrawing $-CF_3$ group in the diamine monomer is effective in decreasing CTC (charge transfer complex) formation between polymer chains through steric hindrance and the inductive effect (by decreasing the electron-donating property of diamine moieties).[31,34] BPADA, ODPA, and 6FDA produced fairly transparent and colorless polyimide films in contrast to BTDA and PMDA.
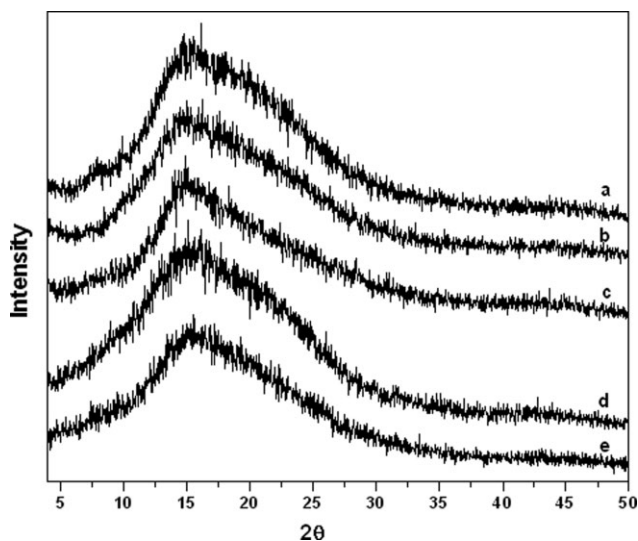

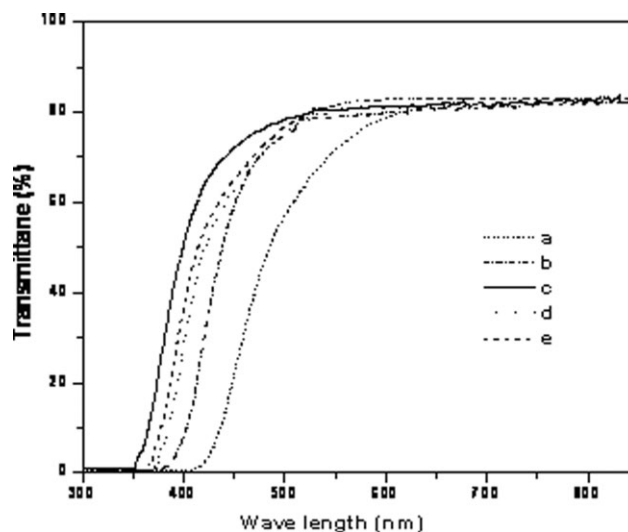**Figure 7**   X-ray diffractograms of the poly(ether imide)s.

Figure 8   UV–Vis spectra of the poly (ether imide)s.

These results are attributed to the ether linkages of BPADA and ODPA, and the $-CF_3$ group of 6FDA. They reduce the intermolecular CTC between alternating electron donor (diamine) and electron acceptor (dianhydride) moieties.

CONCLUSIONS

A new unsymmetrical diamine monomer has been synthesized, which led to a series of novel fluorinated polyimides by reacting with different dianhydrides followed by thermal imidization. All the synthesized polymers exhibited excellent solubility in different organic solvents including low boiling dichloromethane. The resulting poly(ether imide)s are amorphous and exhibited good thermal stability and good mechanical strength. These poly(etherimide)s are observed to have light colored with good optical transparency and low moisture uptake. Hence they are promising materials for optoelectronic applications and as gas separation membranes.

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