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Synthesis and properties of fluorinated polyimides. 3. Derived from novel 1,3-bis[3′-trifluoromethyl-4′(4″-amino benzoxy) benzyl] benzene and 4,4-bis[3′-trifluoromethyl-4′(4-amino benzoxy) benzyl] biphenyl

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Abstract

Novel diamine monomers, 1,3-bis[3′-trifluoromethyl-4′(4″-amino benzoxy) benzyl] benzene (IV) and 4,4-bis[3′-trifluoromethyl-4′(4-amino benzoxy) benzyl] biphenyl (V) have been synthesized. These monomers lead to several novel fluorinated polyimides on reaction with different commercially available dianhydrides like pyromellatic dianhydride (PMDA), benzophenone tetracarboxylic acid dianhydride (BTDA) or 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane (6FDA). The polyimides prepared from above two monomers on reaction with 6FDA are soluble in several organic solvents such as *N*,*N*-dimethyl formamide (DMF), *N*,*N*-dimethyl acetamide (DMAc) and tetrahydrofuran (THF). The polyimides prepared from PMDA/IV is soluble in DMF and *N*-methyl pyrollidone (NMP) on heating, whereas V/PMDA is insoluble in all solvents. BTDA/IV polyimide is also soluble in NMP, DMF and DMAc. These polyimide films have low water absorption rate 0.2–0.7% and low dielectric constant 2.74–3.2 at 1 MHz. These polyimides showed very high thermal stability even up to 531 °C for 5% weight loss in synthetic air and glass transition temperature up to 316 °C (by DSC) in nitrogen. All polyimides formed tough transparent films, with tensile strength up to 148 MPa, a modulus of elasticity up to 2.6 GPa and elongation at break up to 31% depending upon the exact repeating unit structure.

Keywords: Poly(ether imide)s; Solubility; High strength

1. 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 find wide-spread applications as electrical insulating material as interlayer dielectrics/inter metal dielectrics (ILD/IMD). The PMDA–ODA based polyimide exhibit very high glass transition temperature ($T_g \sim 390$ °C), 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) is 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 imidizied 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 self life of the poly(amide acid) and emission of volatile byproducts (e.g. water) during imidization.

The search for new polyimides with improve 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 the BPDA [bisphenol-A di(phthalic anhydride)] and MPD (meta phenylene diamine) [7]. These material posses excellent flow characteristics and melt stability, because of flexible ether linkages in the main chain and serve as true high performance engineering thermoplastic. At the same time high flexibility affects its glass transition temperature ($T_g \sim 217$ °C). Hence, it is of great interest to have a material, which has the properties of

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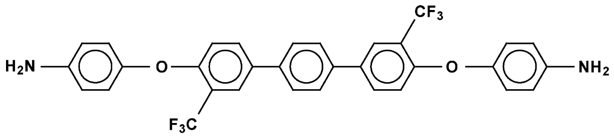
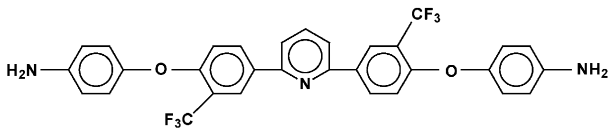
Kapton with improve processability and low dielectric constant.

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 non-coplanar [15,16] or alycyclic units [17]. Semifluorinated polyimides have got great attention in this regard from both academia and industry [18–23]. Polyimides containing hexafluoroisopropylidine group (6F), trifluoromethyl or trifluoromethoxy groups serves to increase the free volume, thereby improving various properties including enhance solubilities of the fully cyclized polyimide, lowers dielectric constant without forfeiture of thermal stability and concomitant decrease in crystallinity. The positive effect of fluorinated substituents is reduced moisture absorption due to the non-polar character of fluorocarbon groups, which vis-à-vis reduces the dielectric constant. NASA had reported one interesting fluoro polyethers imide, LARCTM-CPI, based on 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 2,2′-bis[4-(4-aminophenoxy) diphenylhexafluoropropane [24]. It was commercialized through licensing. However, it is not currently available commercially.

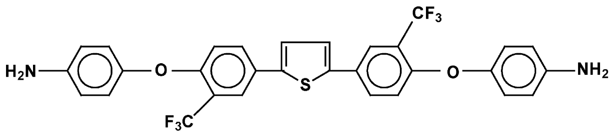
Our group is also working on the preparation of novel polyimides with improved processability and low dielectric constants for ILD/IMD applications. We have reported a number of polyimides based on the following novel diamines [25,26].



Monomer I

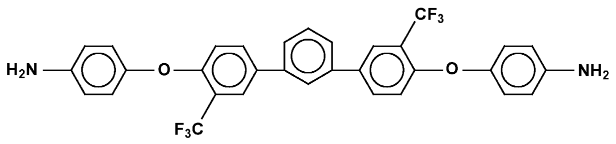


Monomer II

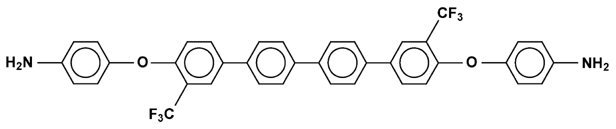


Monomer III

In this paper we would like discuss the properties of six novel poly(ether imide)s based on the following two new diamines and a comparison of properties with the previously reported poly(ether imide)s:



Monomer IV



Monomer V

2. Experimental section

2.1. General considerations

Carbon and hydrogen of the compounds were analyzed by Prejel method and nitrogen was analyzed by KJeldhal method. ^{1}H NMR (400 MHz), ^{13}C NMR (75 MHz) and ^{19}F NMR (100 MHz) spectra were recorded on a Bruker ARX 400 instrument (reference 0 ppm with TMS (^{1}H and ^{13}C NMR) or $CFCl_3$ (^{19}F NMR)). IR spectra of the polymer films were recorded with a Nicolet-Impact-410 spectrophotometer with KBr pellets. Gel permeation chromatography was performed 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 taken at the middle of the step transition in the second heating run. Thermogravimetry was measured 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 instrument in the tension mode on thin film (80–100 μm) 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 by the parallel plate capacitor method with a YHP 4278 capacitance meter at 1 MHz at a temperature 25 °C and relative humidity 45. Water absorption rates of the films were measured.by a Mettler micro balance of sesitivity of 10^{-6} g after immersing the films in a double distilled water for 72 h, at 30 °C.

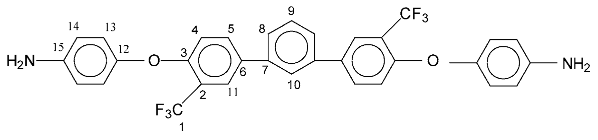
UV–visible spectra were recorded on Specord 200 UV–vis spectophotometer.

2.2. Starting materials

All reagents were purchased from Fluka, Lancaster and Acros Chemical Company and used as received unless otherwise noted. PMDA and BTDA (Fluka, Switzerland) were purified by sublimation under reduced pressure. 6FDA (99%) was purchased from Lancaster chemical company and was heated at 180 °C prior use. NMP (Fluka) and DMF (E Marck, India) was purified by stirring with NaOH and distilled twice from P_2O_5 under reduced pressure. Detail synthesis of the 1,3-bis(4′-fluoro-3′-trifluoromethyl benzyl) benzene and 4,4-bis (4′-fluoro-3′-trifluoromethyl benzyl) biphenyl have already been reported in our previous article [27–29].

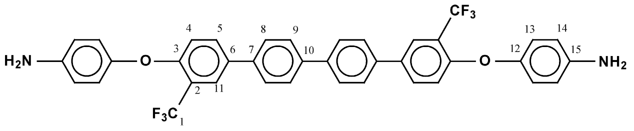
2.3. Synthesis of diamino monomers

1,3-Bis[3′-trifluoromethyl-4′(4″-amino benzoxy) benzyl] benzene. 1,3-Bis (4′-fluoro-3′-trifluoromethyl benzyl) benzene (3 g, 7.4574 mmol), 4-aminophenol (2.0345 g, 18.642 mmol), anhydrous K_2CO_3 (3.092 g, 22.372 mmol), NMP (18 ml) and toluene (90 ml) were taken in a three necked round-bottom flask equipped with a stir bar, a Dean-Stark trap fitted with condenser and nitrogen inlet. The reaction mixture was stirred at 130–140 °C (oil bath temperature for 5 h as water was removed azeotropically with toluene. After removing the toluene the reaction temperature was increased to 150 °C and maintained for another 4 h. After cooling to room temperature the reaction mixture was added to sufficient amount water to precipitate an off-white solid, which was collected by filtration and dried under vacuum at 80 °C for overnight. The product was recrystallized from water/ethanol (10/90) mixture.



Yield: 3 g (70%). Melting point: 173.55 °C (DSC, heating rate 20 °C/min). Anal. calcd for $(C_{32}H_{22}F_6O_2N_2)_n$ $(580.5258\ \mathrm{gmol}^{-1})_n$: C, 66.20; H, 3.81; N, 4.82. Found: C, 66.04; H, 5.23; N, 4.89 IR (KBr): (cm^{-1}) 3440, 3334, 1617, 1503, 1478, 1327, 1246, 1124, 1052, 840, 665, 507. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.817–7.811 (d, $J = 2$ Hz, 2H, H4); 7.64–7.62 (m, 3H, H10 & H11) 7.57–7.54 (m, 3H, H8 & H9); 6.87–6.83 (m, 6H, H5 & H13); 6.64–6.62 (d, $J = 8$ Hz, 4H, H14) 3.63 (s, 4H, NH_2). ^{13}C NMR ($CDCl_3$): δ (ppm) 157.76 (C15); 148.76 (C12); 144.40 (C3); 141.24 (C7); 135.45 (C9), 132.47 (C6); 130.40 (C5); 126.90 (C11), 126.65 (C10), 126.33 (C8), 128.40, 125.68, 122.95, 120.28 (q, C1, $J = 272$ Hz); 122.27 (C13), 121.70, 121.40, 121.10, 120.80 (q, $J = 30$ Hz, C2); 118.85 (C4), 117.01 (C14). ^{19}F NMR ($CDCl_3$): δ (ppm)-62.24 (F1).

4,4-Bis[3′-trifluoromethyl-4′(4-amino benzoxy) benzyl] biphenyl. 4,4-Bis (4′-fluoro-3′-trifluoromethyl benzyl) biphenyl (4.2 g, 8.779 mmol), 4-aminophenol (2.395 g, 21.946 mmol), anhydrous K_2CO_3 (3.6372 g, 26.317 mmol), NMP (25 ml) and toluene (125 ml). Procedure is same as stated above.

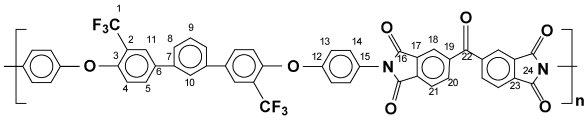


Yield: 4.5 g (85%). Melting point: 173.55 °C (DSC, heating rate 20 °C/min). Anal. calcd for $(C_{38}H_{26}F_6O_2N_2)_n$ $(656.6258\ \mathrm{gmol}^{-1})_n$: C, 69.50; H, 3.99; N, 4.26. Found: C, 69.55; H, 3.52; N, 4.29. IR (KBr):(cm^{-1}) 3386, 2924, 1618, 1508, 1483, 1331, 1249, 1130, 1052, 815, 505. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.83–7.82 (d, $J = 4$ Hz, 2H, H11); 7.66–7.52 (m, 10H, H5, H8 & H9); 6.8–6.9 (m, 6H, H4 & H13); 6.67–6.63 (m, 4H, H14); 3.56 (s, 4H, NH_2). ^{13}C NMR ($CDCl_3$): δ (ppm) 157.76 (C15); 148.76 (C12); 144.40 (C3); 141.24 (C7); 135.45 (C9), 132.47 (C6); 130.40 (C5), 126.90 (C11), 126.65 (C10), 126.33 (C8), 128.40, 125.68, 122.95, 120.28 (q, C1, $J = 272$ Hz); 122.27 (C13), 121.70, 121.40, 121.10, 120.80 (q, $J = 30$ Hz, C2); 118.85 (C4); 117.01 (C14). ^{19}F NMR ($CDCl_3$): δ (ppm)-62.24 (F1).

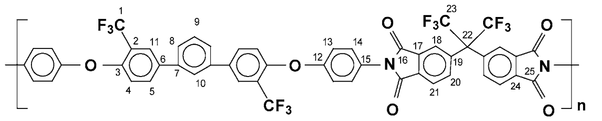
Polymerization. An equimolar amounts of diamine and dianhydride monomers were reacted in nitrogen atmosphere with constant flow. A representative polymerization procedure is as follows.

In a 50 ml round-bottom flask equipped with a nitrogen inlet, a stir bar and Dean-Stark trap fitted with a condenser, was charged with 0.6 g (1.0335 mmol) of 1,3-bis[3′-trifluoromethyl-4′ (4″-amino benzoxy) benzyl] benzene and 10 ml of DMF. The solution was stirred until the diamine dissolved completely, 0.2254 g (1.0335 mmol) PMDA was added to this solution slowly. The resulting highly viscous solution was stirred slowly and continuously for 3 h at room temperature. 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 15 min. Polyimide films were removed by immersing the glass plates in boiling water.

Polyimide 2a. Anal. calcd for $(C_{42}H_{20}F_6N_2O_6)_n$, $(762.6184\ \mathrm{g/mol})_n$: C, 66.14; H, 2.64; N, 3.67. Found: C, 66.10; H, 2.69; N, 3.82 IR (KBr): (cm^{-1}) 3658, 3494, 3054, 1778, 1731, 1608, 1508, 1451, 1330, 1055, 827, 722, 519.



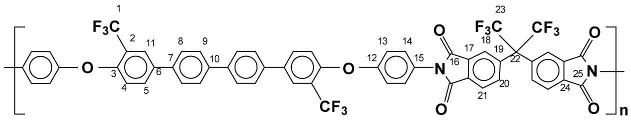
Polyimide 2b. Anal. calcd for $(C_{49}H_{24}F_6N_2O_7)_n$, $(866.7236\ g/mol)_n$: C, 67.90, H, 2.79; N, 3.24. Found: C, 68.05; H, 2.72; N, 3.47. IR (KBr): (cm^{-1}) 3658, 3062, 1725, 1501, 1377, 1330, 1250, 1210, 1133, 852, 721, 520. ^1H NMR ($CDCl_3$): δ (ppm) 8.19–8.22 (m, 4H, H21, H18); 8.07–8.12 (m, 2H, H5); 7.87 (s, 2H, H11); 7.65–7.75 (m, 4H, H4, H20); 7.51 (s, 2H, H9, H10); 7.05–7.40 (d, $J = 8$ Hz, 4H, H14); 7.05–7.15 (m, 6H, H14, H13).



Polyimide 2c. Anal. calcd for $(C_{51}H_{24}F_{12}N_2O_6)_n$, $(988.7466\ g/mol)_n$: C, 61.95; H, 2.44; N, 2.83. Found: C, 62.42; H, 3.01; N, 2.92. IR (KBr): (cm^{-1}) 3675, 3055, 1784, 1738, 1717, 1618, 1497, 1380, 1329, 1242, 1156, 1053, 891, 847, 723, 601, 519. ^1H NMR ($CDCl_3$): δ (ppm) 8.05 (d, $J = 8$ Hz, 2H, H21); 7.80–7.95 (m, 6H, H18, H20, H11); 7.68–7.78 (m, 6H, H5, H8); 7.55 (s, 2H, H10, H9); 7.45 (d, $J = 8$ Hz, 4H, H13); 7.10–7.18 (m, 6H, H4, H14). ^{13}C NMR ($CDCl_3$): δ (ppm) 166.11 (C16), 165.94 (C25), 156.53 (C12), 154.11 (C3), 140.79 (C7), 140.09 (C19), 139.22 (C24), 136.53 (C9), 132.61 (C6), 131.99 (C17), 129.75 (C5), 129.0 3(C20), 128.16(C13), 127.74 (C8), 123.17 (q, $J = 271$ Hz, C1), 126.93 (C11), 126.548 (C10), 125.73 (C18), 125.41 (C15), 124.19 (C21), 122.367 (q, $J = 31$ Hz, C2), 120.57 (C4), 119.58 (C14), C22, C23 (not found).

Polyimide 3a. Anal. calcd for $(C_{48}H_{24}F_6N_2O_6)_n$, $(838.716\ g/mol)_n$: C, 68.73; H, 2.88; N, 3.34. Found: C, 68.79; H, 2.92; N, 3.74. IR (KBr): (cm^{-1}) 3659, 3493, 3040, 1776, 1731, 1609, 1500, 1428, 1374, 1331, 1268, 1130, 1051, 820, 724, 520.

Polyimide 3b. Anal. calcd for $(C_{55}H_{28}F_6N_2O_7)_n$, $(942.8236\ g/mol)_n$: C, 70.06 H, 2.99; N, 2.97. Found: C, 71.02; H, 3.02; N, 2.99. IR (KBr): (cm^{-1}) 3656, 3490, 3051, 1780, 1731, 1677, 1508, 1426, 1204, 1160, 1052, 824, 522.



Polyimide 3c. Anal. calcd for $(C_{57}H_{28}F_{12}N_2O_6)_n$, $(1064.83\ g/mol)_n$: C, 64.29; H, 2.65; N, 2.63. Found: C, 65.02; H, 2.72; N, 2.69. IR (KBr): (cm^{-1}) 3494, 3040, 1731, 1500, 1491, 1376, 1331, 1268, 1146, 821, 723, 523. ^1H NMR ($CDCl_3$): δ (ppm): 7.99 (d, $J = 8$ Hz, 2H, H21); 7.82–7.89 (m, 6H, H18, H20, H11); 7.67–7.71 (m, 6H, H5, H8); 7.61 (d, $J = 8$ Hz, 4 H, H9); 7.37 (d, $J = 8$ HZ, 4H, H13); 7.03–7.18 (m, 6H, H4, H14). ^{13}C NMR ($CDCl_3$): δ (ppm) 166.12 (C16), 165.95 (C24), 156.61 (C12), 153.96 (C3), 139.98 (C19), 139.25 (C10), 138.28 (C7), 136.33 (C6), 135.96 (C20), 132.65 (C24), 132.36 (C17), 131.68 (C5), 128.16 (C13), 127.64 (C8), 127.44 (C9), 122.81 (q, $J = 273$ Hz, C1), 125.83 (d, $J = -5$ Hz, C11), 125.42 (C18); 124.81 (C15); 124.19 (C21); 122.37 (q, $J = 31$ Hz, C2), 120.59 (C4), 119.59 (C14), C22, C23 (not found).

3. Results and discussion

3.1. Synthesis of the bisamino monomers

The diamino monomers, 1,3-bis[3′-trifluoromethyl-4′(4″-amino benzoxy) benzyl] benzene (IV) and 4,4-bis[3′-trifluoromethyl-4′(4-amino benzoxy) benzyl] biphenyl (V) were prepared by the nucleophilic displacement of fluorine from 1,3-bis(4′-fluoro-3′-trifluoromethyl benzyl) benzene and 4,4-bis(4′-fluoro-3′-trifluoromethyl benzyl) biphenyl by 4-amino phenol as shown in Fig. 1. We have alredy proved that trifluoromethyl group is strong enough to activate the halogens towards nuclephilic displacement reaction with phenoxides [27–29]. The activation by this group is expected due to the stabilization of negative charges at the 2- or 4-position by hyper conjugation and by the negative inductive effect [30]. The critical condition of this reaction is that the reaction temperature should not exceed 160 °C, and the reaction is to be performed under completely oxygen free atmosphere. The detail characterizations on the diamine compounds were done by elemental analyses, IR and NMR techniques, which support unambiguously the structure shown in Fig. 1. The detail analytical data of the compounds are given in Section 2.

3.2. Synthesis of polymers

The diamino monomers were reacted with pyromellitic dianhydride (PMDA), benzophenone tetracarboxylic acid dianhydride (BTDA) and 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane (6FDA) to give the corresponding poly(imide)s as shown in Fig. 2.

The syntheses of polyimides were carried out via poly(amic acid) intermediate. The diamines were reacted with equimolar amount of PMDA, BTDA or 6FDA in DMF at room temperature. Initially, diamines were dissolved in

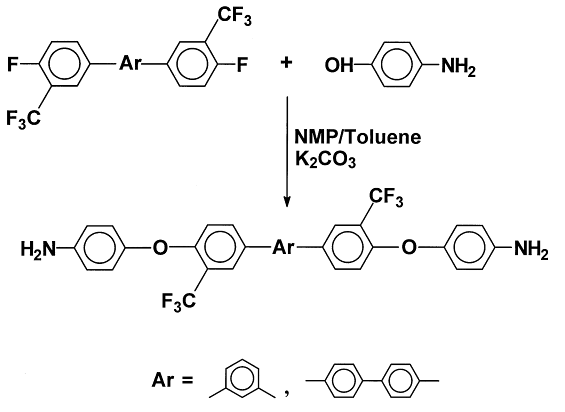


Fig. 1. Reaction scheme and structures of the diamino monomers.

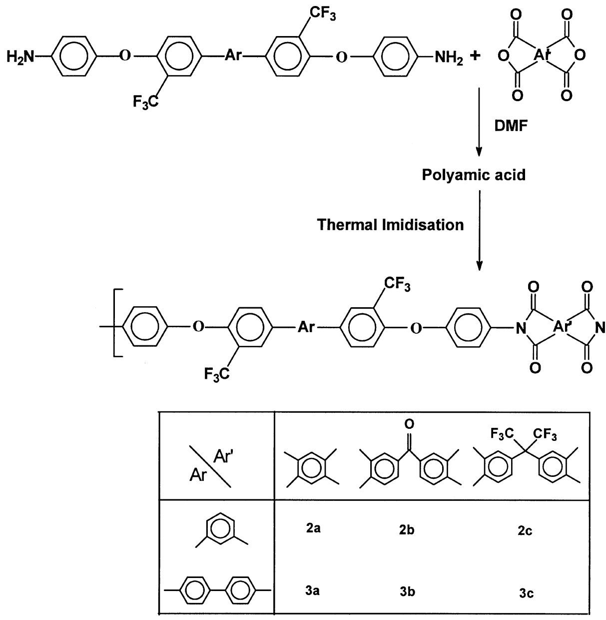


Fig. 2. Reaction scheme and structures of the polymers.

measured amount of dry DMF and the dianhydride monomers were added to it slowly. In all cases the reaction mixture become highly viscous within 10 − 15 min, the reactions were continued for 3 h. The inherent viscosities of the poly(amic acid)s shown in Table 1 indicated formation of high molar masses. The poly(amic acid) solutions were cast on clean glass plates and heated the film through various stages up to 350 °C to remove solvent and water formed by the imidization. The transparent, pale-yellowish, films were obtained in all cases. All polyimides films were tough.

3.3. Polymer solubility

The solubilities of the resulting poly(imide)s by thermal imidization were investigated in different organic solvents. It was attempted to obtain 10% (w/v) solution of all polymers in different solvents as presented in Table 2. These polymers exhibited good solubility behavior in common organic solvents like the previously reported semi-fluorinated poly(ether imide)s [25,26] and poly(arylene ether)s [27–29,31]. A comparison of the solubility of 2c and 3c polymers with other polymers shows that these polymers have better solubility in $CHCl_3$, THF, DMF, DMAc, NMP, at room temperature. Insolubility of these polymers in DMSO, while their solubility in amide solvents, such as NMP, DMF, DMAc, at room temperature, (although these types of dipolar aprotic solvents have similar properties) indicates that polarity alone is not the only parameter sufficient for selecting a polymer solvent.

Table 1
Poly(ether imide)s from various anhydrides

Polymer	η_{inh}	$\lambda_{\text{Cut off values}}$	M_n	PDI	Film quality
2a	0.97	412	–	–	Clear, flexible
2b	0.92	428	–	–	Clear, flexible
2c	0.84	359	32,940	1.97	Clear, flexible
3a	1.12	414	–	–	Clear, flexible
3b	1.08	450	–	–	Clear, flexible
3c	1.01	372	24,760	1.87	Clear, flexible

η_{inh}, inherent viscosity of poly(amic acid) in DMF at 30 °C; λ, wave length, M_n, number average molecular weight; PDI, polydispersity index.

3.4. Spectroscopy

The formation of poly(ether imide)s was confirmed by FTIR spectroscopy. FTIR spectra of the polyimide films prepared by thermal imidization method show the absorption bands at about 1780 cm^{-1} (C=O asymmetric stretching) 1730 cm^{-1} (C=O symmetric stretching), 1378 cm^{-1}(C–N stretching), 721 cm^{-1} (C=O bending) corresponding to the characteristic of imide bands [25,26]. No absorption bands were found at 3400–2900 cm^{-1} corresponding to amide (–NH–) and acid (–OH) stretching, 1720 cm^{-1} corresponding to C=O cm^{-1} stretching of carboxylic acid, 1660 corresponding to C=O cm^{-1} amide stretching of the polyimides. ^1H NMR spectra of the polymer 2c and 3c showed no amide and acid protons, indicating full imidization. UV–visible spectroscopic studies of the polymers revealed that polymer 2c and 3c have greater transparency than the polymer 2a, 2b, 3a and 3b, which is directly related to the color intensity of the film. All the polymer films (thickness 30–40 μm) showed high optical transparency, a cut off wavelength at about 421, 449, 418 for 2a, 2b, 2c and 414, 450, 372 for 3a, 3b, and 3c, respectively.

3.5. DSC measurements

The poly(ether imide)s exhibited no crystallization or melting transition in DSC measurements. These polymers show glass transaction temperature, which indicate amorphous or glassy morphology. DSC curves of the polymers are shown in Figs. 3 and 4. The glass transition values are summarized in Table 3. The polymers 2a and 3a exhibited higher T_g values than other polymers, which can be explained on the basis of the presence of rigid PMDA moieties in the backbone [32].

It is interesting at this stage to compare the glass transition temperatures of the polymers shown in Table 3. The polyimides containing 4,4-diphenyl biphenyl (quadriphenyl) unit in the polymer backbone exhibited highest glass transition temperatures in comparison to the analogous polyimides containing 1,4-diphenyl benzene, 1,3-diphenyl benzene, 2,6-diphenyl pyridine and 2,5-diphenyl thiophene moieties, which is also expected. In general, an order on glass transition temperature is obtained: quadriphenyl > 1,4-diphenyl benzene > 2,6-diphenyl pyridine > 2,5-diphenyl thiophene ≥ 1,3-diphenyl benzene.

Table 2
Solubility of the poly(ether imide)s

Polymer	NMP	DMF	DMAc	DMSO	THF	$CHCl_3$	CH_2Cl_2	Acetone
2a	0	0	−	−	=	=	−	−
2b	+	+	+	−	+	0	=	−
2c	+	+	+	−	+	+	+	+
3a	−	−	−	−	−	=	−	−
3b	−	−	−	−	−	−	−	−
3c	+	+	+	−	+	+	+	+

+ , Soluble at room temperature; 0, soluble on heating; = , swelled; −, insoluble at reflux.

This order could be explained on considering three factors rigidity, catenation angle of the different groups and polarity. It is expected that if a macromolecule exhibit more extended geometry, i.e. higher catenation angle providing by the different building blocks, is expected to have higher glass transition temperature [27]. Similarly, if the polymer molecule is built up of rigid units, is expected to have higher glass transition temperature [33]. The trend of glass transition temperatures of the polyimides can be well explained when we take a look on the glass transition temperatures of the polyimides containing quadriphenyl, 1,4-diphenyl benzene and 1,5-diphenyl benzene units. The catenation angle between 4,4-diphenyl biphenyl and 1,4-diphenyl benzene is same, however, the polymers containing 4,4-diphenyl biphenyl units is exhibited higher T_g, is due to the rigidity of this unit. The polyimides containing 1,5-diphenyl benzene is expected to have lower glass transition temperature comparison to the above two, as it has less extended geometry (catenation angle 120°) and the same result obtained [27]. It will be more interesting to take a close look on the glass transition temperatures of the polyimides containing 1,6-phenyl pyridine and 1,5-phenyl thiophene units and their comparison to the polyimides containing 1,5-diphenyl benzene. Although the catenation angle of 1,6-diphenyl pyridine unit is 28° lower than 1,5-diphenyl thiophene unit (catenation angle for 1,6-diphenyl pyridine unit is 120° and for thiophene is 148°) [34], the T_gs of pyridine containing polymer is higher. The high T_g of polymer containing pyridine (10–25 °C) moiety may be due to the polarity of the pyridine ring [27]. Thiophene has a more extended geometry than pyridine at the same time pyridine has four times more polarity than thiophene ($\mu_{\text{pyridine}} = 7.4 \times 10^{-30}$ cm; $\mu_{\text{thiopene}} = 1.83 \times 10^{-30}$cm) [34], which are the probable reason of higher T_g for pyridine ring containing polymers.

The T_g values of these polymers are higher than commercial poly(ether imide), Ultem 1000 (T_g, 217 °C); based on BPADA [bisphenol-A(diphthalic anhydride)] and MPD (*m*-phenylene diamine) [32] and comparable to BTDA–ODA (T_g, 279 °C) [23] based polyimide. However, the T_g values of these polymers are lower than Kapton films derived from PMDA–ODA (T_g, 390 °C) [7].

3.6. Thermal stability

The thermal properties of the poly(ether imide)s were evaluated by TGA. The TGA curve for polymer is shown in Figs. 5 and 6. The thermal properties of the polymers are summarized in Table 3. The 5% weight loss temperature in air of these polymers is in the range of 491–516 °C for *m*-terphenyl ring containing poly(ether imide)s and 520–531 °C for biphenyl ring containing polymers. In general high thermal stability is due to the presence of rigid backbone structures as expected for polyimides. As 5% weight loss temperature does not provide much information about the suitability of a material for long term applications at high temperatures, the isothermal stabilities of the poly(ether imide)s were investigated at two different

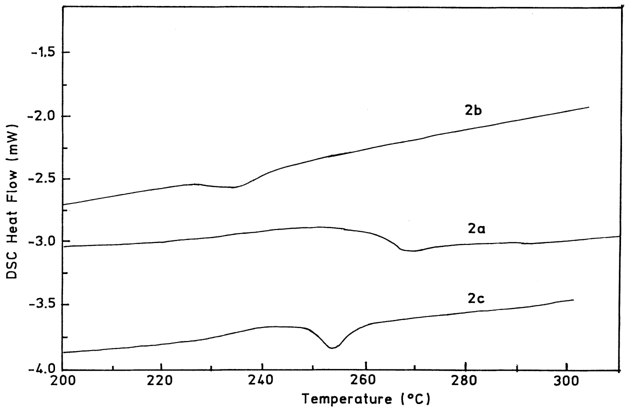


Fig. 3. DSC curves of the 1,3-phenyl ring containing poly(ether imide)s.

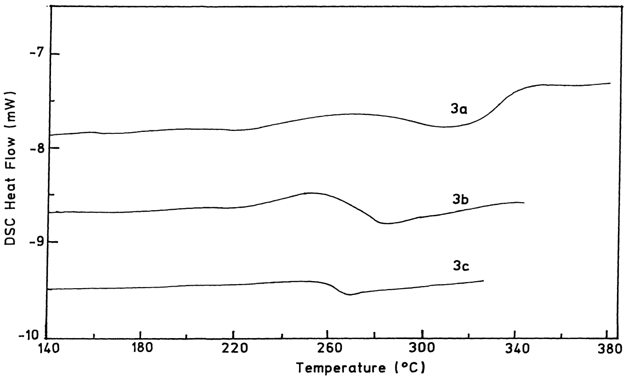
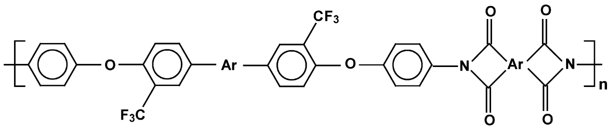


Fig. 4. DSC curves of the 4,4-biphenyl containing poly(ether imide)s.

Table 3
Glass transition temperatures (°C) and 5% weight loss temperature in air of the poly(ether imide)s, and their comparison with previously reported poly(ether imide)s [25,26]



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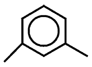
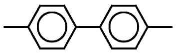
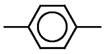
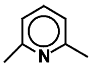
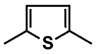
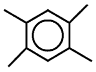
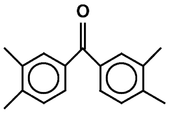
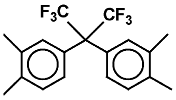
															
	T_g (°C)		T_d[a]	T_g (°C)		T_d[a]	T_g (°C)		T_d[a]	T_g (°C)		T_d[a]	T_g (°C)		T_d[a]
	DSC	DMA[b]		DSC	DMA[b]		DSC	DMA[b]		DSC	DMA[b]		DSC	DMA[b]	
	269	266	513	316	301	519	294	278	532	287	269	518	262	256	462
	234	231	491	262	263	531	272	236	525	253	239	513	242	229	468
	251	248	516	273	277	526	278	256	519	264	258	503	257	247	480

[a] 5% weight loss temperature in air.
[b] tan δ peaks at 10 Hz.

temperatures: 315 °C for 5 h and at 400 °C for 7 h in air. The polymers 2a, 2b, 2c, 3a, 3b and 3c showed only 0.6, 0.5, 0.7, 0.3, 0.3, 0.4% weight loss at 315 °C after 5 h and 7.2, 7.3, 7.0, 5.9, 6.3, 6.4% weight loss at 400 °C after 7 h, respectively.

3.7. DMA measurements

The dynamic mechanical behaviors of the polymers films are shown in Fig. 7. The T_gs taken from the tan δ peaks at 10 Hz are given in Table 3. These values are comparable to the calorimetric T_g values. The polymers retained mechanical properties up to T_gs as can be observed from the storage modulus plots of the polymers.

3.8. Mechanical properties

The mechanical properties of thin polyimides films cast from DMF are shown in Table 4. In general the mechanical properties of the polyimide films are excellent, exhibited very high tensile strength and modules. The polyimides containing most rigid quadriphenyl unit exhibited highest tensile strength up to 149 MPa and Young modulus up to 2.6. These polymers also exhibited very high elongation at break up to 29%, which is really very interesting. In general, the polyimides exhibit low elongation. Our previous experience with the poly(aryl ether)s containing quadriphenyl moieties exhibited higher tensile strength and higher elongation at break in comparison to the similar poly(aryl ether)s containing terphenyl moieties [27,28]. It is also observed from Table 4 that the polymers having more extended geometry results in more elongation at break than the polymers having less extended geometry. Polyimides containing 1,3-phenyl, 2,6-pyridine and 2,5-thiophene moieties exhibited very low elongation at break in comparison to the polymers containing 1,4-phenyl and 4,4-biphenyl moieties. Representative stress-strain plot of poly(ether imide) 3b is shown in Fig. 8

These values are comparable to those of many other commercially available polyimides (Ultem 1000: tensile 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].

3.9. Dielectric properties and refractive index

The dielectric constant of the polymer films were determined from the refractive index values (using sodium D light, wavelength 589.3 nm) and from capacitance values using a capacitance meter 1 MHz at 25 °C under wet condition (RH 45%). The refractive index and dielectric constant values are presented in Table 5. These values are

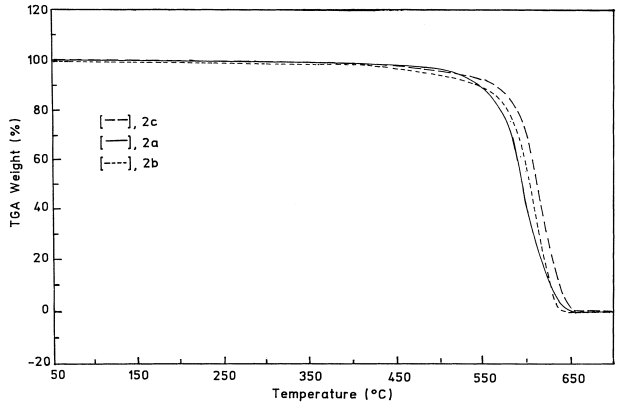


Fig. 5. TGA thermograms of the 1,3-phenyl ring containing poly(ether imide)s.

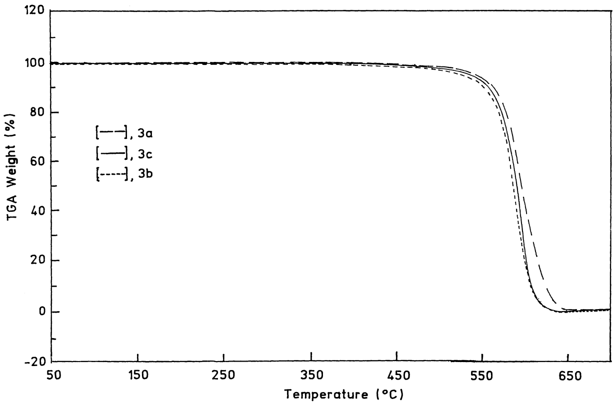


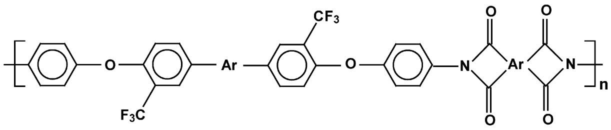
Fig. 6. TGA thermograms of the 4,4-biphenyl ring containing poly(ether imide)s.

compared with the theoritical dielectric constants values, calculated from the group increments given in Van Kravelen's book on properties of polymers [35]. The dielectric values obtained from three different methods are comaparable and expected to be showing the real properties of the se materials. Although, the dielectric constant have ben measured at RH 45%, due to very low water absorption of these poly(ether imide)s (0.2–0.7 wt%), do contribute much to the dielectric constant values. The vacuum dried films (dried at 200 °C, under vacuum for 4 h) were used for the measurements, however the measurement were done at ambient condition. The dielectric constant values largely depend on the fluorine content, the values decreases as the amount of fluorine content increases (Table 5). The dielectric constant values of these films are lower than Kapton H ($\varepsilon = 3.5$ at 1 kHz), Upilex R ($\varepsilon = 3.5$ at 1 kHz), Upilex S ($\varepsilon = 3.5$ at 1 kHz) and Ultem 1000($\varepsilon = 3.15$ at 1 kHz) type of polyimide materials and comparable to those of many semifluorinated poly(ether imide)s (6FDA–MPD: $\varepsilon = 3.0$; 6FDA–7FMDA: $\varepsilon = 2.9$; 6FDA–13FMDA: $\varepsilon = 2.7$) [23] (Fig. 8).

4. Conclusion

New diamine monomers, 1,3-bis[3′-trifluoromethyl-4′(4″-amino benzoxy) benzyl] benzene and 4,4-bis[3′-trifluoromethyl-4′(4-amino benzoxy) benzyl] biphenyl

Table 4
Mechanical properties of the polyimide, and their comparison with previously reported poly(ether imide)s [25,26]



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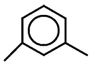
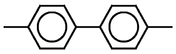
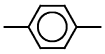
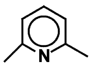
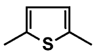
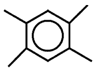
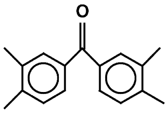
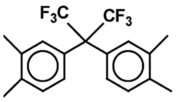
															
	TS (MPa)	Mod (GPa)	%E	TS (MPa)	Mod (GPa)	%E	TS (MPa)	Mod (GPa)	%E	TS (MPa)	Mod (GPa)	%E	TS (MPa)	Mod (GPa)	%E
	98	2.5	11	125	2.3	19	112	2.4	21	112	2.5	11	85	2.5	5
	87	2.3	9	148	2.6	31	100	3.0	17	115	2.5	12	75	2.9	4
	97	2.1	9	109	2.1	21	96	2.8	19	105	2.8	6	87	2.8	4

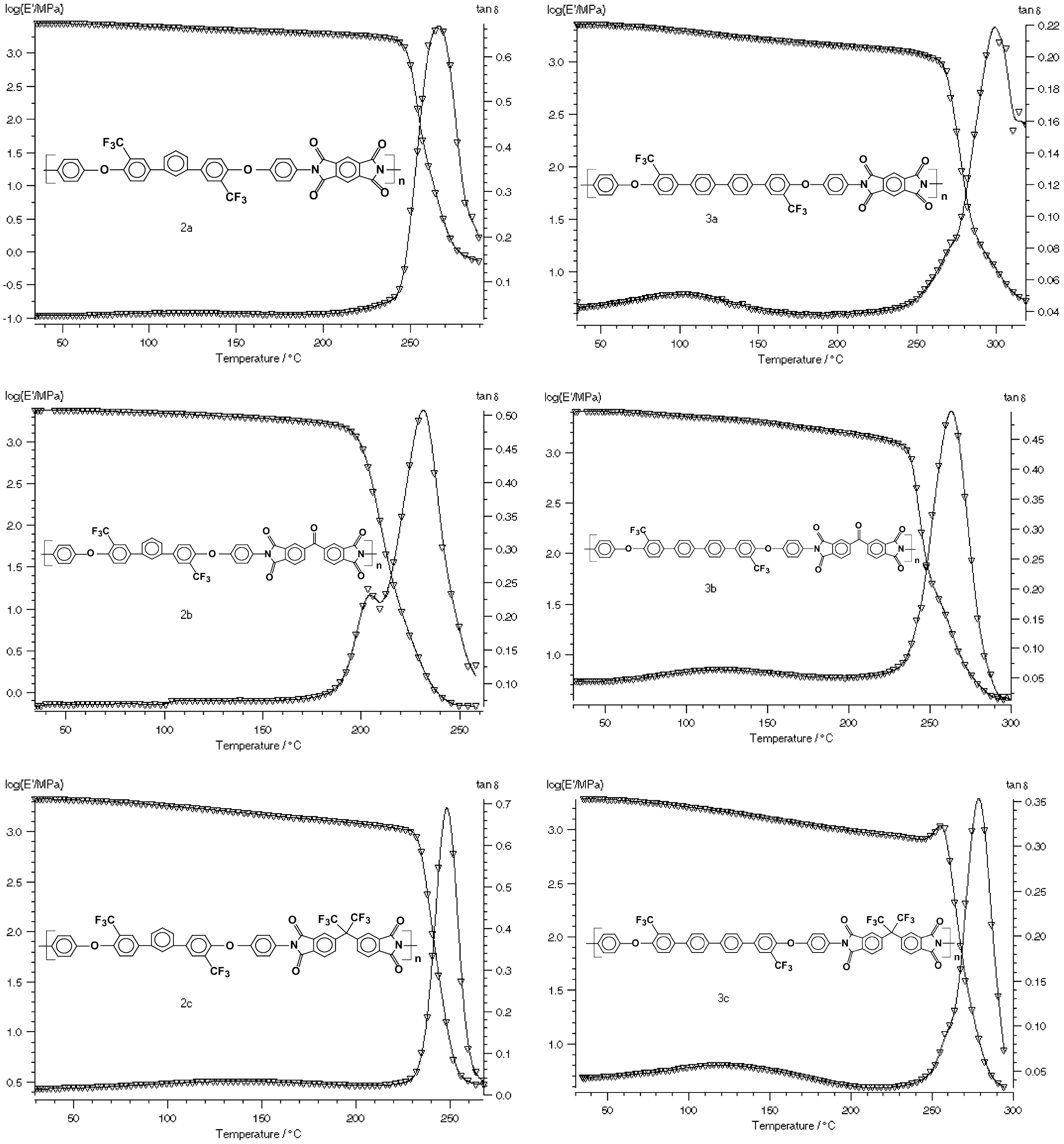


Fig. 7. DMA plots of the poly(ether imide)s.

Table 5
Dielectric and other physical properties of the poly(ether imide)s

Polymer	Fluorine content%	Water absorption%	RI	n^2	$\varepsilon_{\mathrm{wet}}$/1 MHz	$\varepsilon_{\mathrm{calculated}}$
2a	14.94	0.5	1.688	2.84	2.93	2.86
2b	13.16	0.7	1.782	3.17	2.97	2.90
2c	23.05	0.3	1.652	2.72	2.76	2.70
3a	13.59	0.5	1.685	2.83	2.91	2.86
3b	12.09	0.6	1.789	3.20	2.98	2.89
3c	21.41	0.2	1.657	2.74	2.74	2.71

n, refractive index, *ε*, dielectric constant.

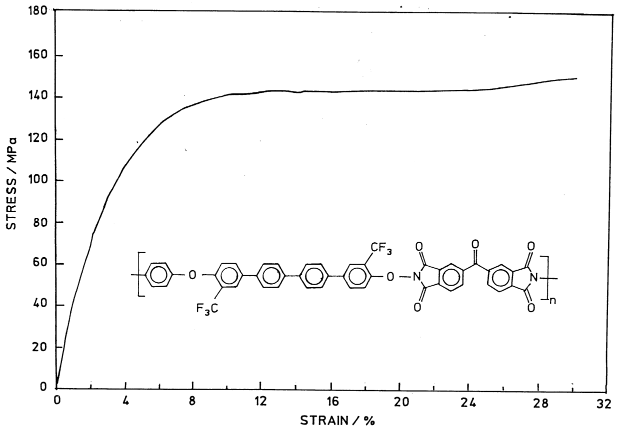


Fig. 8. Representative stress–strain plot of poly(ether imide), 3b.

have been synthesized, which lead to a number of novel fluorinated polyimides by thermal imidization routes, on reacting with different dianhydrides. The synthesized polymers exhibited good solubility in different organic solvents. The resulting poly(ether imide)s are amorphous, exhibited outstanding thermal stability in air like many other thermally stable polyimides without substituents. These polymers have high mechanical strength and high modulus. Poly(ether imide)s based on these materials shown to have valuable properties for electronic applications, such as low moisture absorption, low dielectric constant, and high optical transparency. These polymers may find use in plastics, fiber, and membrane for separation applications.

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