

# Synthesis and Characterization of Fluorine and Nitrile Containing Polyimides

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Received 22 December 2005; accepted 7 February 2006

DOI 10.1002/app.24347

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A series of polyimides were synthesized from new diamine, Bis [4,4'-amino-5,5' trifluoromethyl phenoxy-(hexafluoro isopropylidene) phenoxy phenyl] benzonitrile [BATFB] and various aromatic tetracarboxylic anhydrides by thermal and chemical imidization routes. The BATFB was synthesized in two steps by nucleophilic displacement reaction of 2,6-dichloro benzonitrile, 4,4'-(hexafluoro isopropylidene) diphenol and 2-amino-5-fluoro benzotrifluoride in the presence of anhydrous potassium carbonate in *N,N'*-dimethyl acetamide (DMAc) and the structure was confirmed by FTIR spectroscopy and CHNSO analyzer. The polymers were characterized by FTIR spectroscopy and thermal analysis were performed by differen-

tial scanning calorimetry and thermogravimetric analysis methods. The prepared polyimides had glass transition temperatures between 230 and 290°C and their 10% weight loss were recorded in the range 550–590°C in N<sub>2</sub> atmosphere. Majority of polymers are found to be soluble in most of the organic solvents such as DMSO, DMF, DMAc, *m*-cresol, and THF even at room temperature and few becomes soluble on heating. The prepared polyimides showed water uptake values 0.34–0.54 wt % at room temperature. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3455–3461, 2006

**Key words:** BATFB; poly(amic acid); polyimide; thermal stability; imidization

## INTRODUCTION

Aromatic polyimide is one of the most useful and important polymers because of their excellent thermal stability, good chemical resistance, good mechanical, and electrical properties. Because of these properties, they have been widely used in aerospace, microelectronic, aviation, defense, and separation industries.<sup>1–4</sup> However, their applications were limited in many fields because the wholly aromatic polyimides were insoluble and intractable. Many efforts have been made to synthesize organo soluble polyimides by incorporating different moieties to enhance their intrinsic permeability and tractability. Flexible links (e.g. —O—, —SO<sub>2</sub>—, —CH<sub>2</sub>—) or bulky groups (trifluoride, hexafluoroisopropylidene, etc.) are commonly employed as solubilizing moieties, but it often costs a desirable in thermal stability and chain stiffness of polyimides.<sup>5–7</sup> In the polyimide family, fluoro-polyimides containing 4,4'-(hexafluoro isopropylidene) diphthalic anhydride [6FDA] have been identified as a potential candidate for many demanding applications. This is because of the rigid molecular structure and bulky CF<sub>3</sub> groups inhibit efficient chain packing and reduce local segmental mobility of polyimides.<sup>8–14</sup>

In this article, we have studied a polyimide having nitrile and CF<sub>3</sub> groups. The incorporation of the ether and CF<sub>3</sub> groups into the polyimide chain generally leads to an enhancement of the solubility and processability without affecting the thermal properties. In addition, the pendant nitrile group appears to promote adhesion of the polymer to many substrates possibly through polar interaction with other functional groups. A new diamine, i.e. bis [4,4'-amino-5,5' trifluoromethyl phenoxy-(hexafluoro isopropylidene) phenoxy phenyl] benzonitrile [BATFB], was synthesized from 2,6-dichloro benzonitrile, 4,4'-(hexafluoro isopropylidene) diphenol, and 2-amino-5-fluoro benzotrifluoride by nucleophilic addition reaction. Polyimides were synthesized using the above diamine with various aromatic tetracarboxylic dianhydrides. The infrared spectra of poly(amic acid) and poly(imide)s were taken. The solubility, moisture uptake, and thermal properties of the polyimide were investigated.

## EXPERIMENTAL

### Materials

2,6-Dichloro benzonitrile (Aldrich), 4,4'-(hexafluoro isopropylidene) diphenol (Aldrich), and 2-amino-5-fluoro benzotrifluoride (Aldrich) were used as received. Pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), 4,4'-oxydiphthalic anhydride (ODPA), 3,3',4,4'-biphe-

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nyl tetracarboxylic anhydride (BDA), 3,3',4,4'-diphenylsulphone tetracarboxylic dianhydride (DSDA), and 4,4'-(hexafluoro isopropylidene) diphthalic anhydride (6FDA) were recrystallized from acetic anhydride before use. *N,N'*-dimethylacetamide (DMAc) and *N*-methyl 2-pyrrolidone (NMP) were purified by distillation under reduced pressure over phosphorous pentoxide and stored over 4 Å molecular sieves.

### Monomer synthesis

*Bis [4,4'-hydroxy phenyl-(hexafluoro isopropylidene) phenoxy] benzonitrile [BHFB]*<sup>1</sup>: 4,4'-(Hexafluoro isopropylidene) diphenol (0.02 mol), 2,6-dichloro benzonitrile (0.01 mol), and dry anhydrous potassium carbonate (0.01 mol) in 50 mL of DMAc and 60 mL toluene were taken in three-necked round bottom flask equipped with a stir bar, a Dean-Stark trap fitted with condenser, and nitrogen inlet. The reaction mixture was refluxed for 4 h as water was removed azeotropically with toluene. After removing the toluene, the reaction mixture was refluxed with stirring for another 8 h. The reaction mixture was allowed to cool and then poured into 500 mL of methanol/water (1:1) to give a brown solid, which was collected, washed repeatedly with water, and dried. The crude product was recrystallized from ethanol to afford off-white crystals. Yield = 85%; mp = 164°C by differential scanning calorimetry (DSC); IR (KBr): 3450 (O—H stretching); 2218 (C≡N stretching); 1252, 1220, (C—O—C stretching); 1140, 1125 (C—F stretching); Anal. Calcd For C<sub>13</sub>H<sub>20</sub>F<sub>12</sub>NO<sub>4</sub> (774.39): C, 57.33%; H, 2.58%; N, 1.80%; Found: C, 56.83%; H, 1.98%; N, 1.64%.

*Bis [4,4'-amino-5,5' trifluoromethyl phenoxy-(hexafluoro isopropylidene) phenoxy phenyl] benzonitrile [BATFB]*<sup>2</sup>: A mixture of the obtained dihydroxy compound BHFB (0.01 mol), 2-amino-5-fluoro benzotrifluoride (0.02 mol), and dry anhydrous potassium carbonate (0.01 mol) in 50 mL of DMAc and 60 mL toluene were taken in three-necked round bottom flask equipped with a stir bar, a Dean-Stark trap fitted with condenser, and nitrogen inlet. The reaction mixture was refluxed for 4 h as water was removed azeotropically with toluene. After removing the toluene the reaction mixture was refluxed with stirring for another 6 h. The reaction mixture was allowed to cool and then poured into 500 mL of distilled water to give off-white solid, which was collected, washed repeatedly with water, and dried. The crude product was recrystallized from ethanol to give pure BATFB (2). Yield = 87%; mp = 182°C by DSC; IR (KBr): 3342, 3226 (N—H stretching); 2219 (C≡N stretching); 1240, 1218, (C—O—C stretching); 1135, 1120 (C—F stretching); Anal. Calcd For C<sub>49</sub>H<sub>25</sub>F<sub>18</sub>N<sub>3</sub>O<sub>6</sub> (1094.73 g/mol<sup>-1</sup>): C, 53.71%; H, 2.78%; N, 3.94%; Found: C, 52.83%; H, 2.56%; N, 3.64%.

### Synthesis of polyimides

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

#### Thermal cyclodehydration

In a round-bottom flask equipped with a nitrogen inlet, a stir bar and Dean-Stark trap fitted with a condenser was charged with 0.01 mol of diamine (BATFB) and 20 mL of NMP. The solution was stirred until the diamine dissolved completely. Dianhydrides (6FDA; 0.01 mol) was added to this solution slowly. The reaction mixture was stirred under magnetic stirring for 24 h at room temperature forming a solution of poly(amic acid) in NMP. The poly(amic acid) solution was casted onto clean and dry glass plate by a doctor blade, and thermal imidization of the films were carried out in an oven by sequential heating at 110, 150, 200, 250, and 300°C for 30 min each. Polyimide films were removed by immersing the glass plates in boiling water.

#### Chemical cyclodehydration

Chemical cyclodehydration was carried out by adding a mixture of acetic anhydride and sodium acetate (volume ratio 2 : 1) into the above-mentioned poly(amic acid) solution with stirring at room temperature for 1 h, and then stirred at 100°C for 3 h. The polymer solution was poured into methanol to form a precipitate. The precipitate was collected by filtration, washed thoroughly with methanol and hot water, and dried at 100°C under vacuum.

The other polyimides were prepared in similar manner from BATFB and other tetracarboxylic dianhydrides.

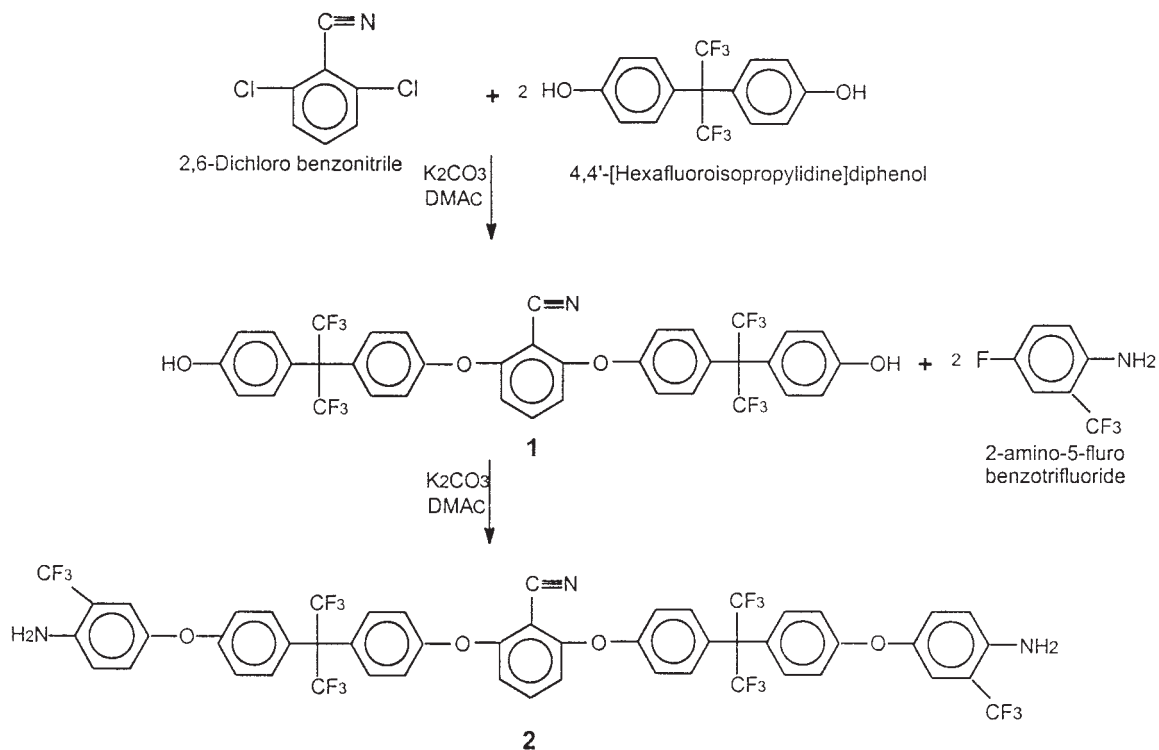
### Measurements

The infrared spectra were recorded using Nicolet 750 Fourier transform infrared spectrophotometer. Glass transition temperature ( $T_g$ ) was recorded using differential scanning calorimetry, using TA Instruments, USA (Model No. DSC 2910), at a heating rate 5°C/min under nitrogen atmosphere. The degradation temperature ( $T_d$ ) was recorded using Hi-Res TGA 2950 instrument at a heating rate of 10°C/min under N<sub>2</sub> atmosphere. Elemental analysis was made on a VARIO-EL ELEMENTAR (CHNSO) Analyser.

## RESULTS AND DISCUSSION

### Monomer synthesis

The CF<sub>3</sub> and C≡N containing diamine, BATFB (2) was prepared in two steps according to Scheme 1.



Scheme 1

The diamine, BAFTB, was prepared by the nucleophilic displacement of fluorine from 2-amino-5-fluoro benzotrifluoride, bis [4,4'-hydroxy phenyl-(hexafluoro isopropylidene) phenoxy] benzonitrile in the presence of anhydrous potassium carbonate in DMAc. In the first step, aromatic nucleophilic chlorodisplacement of 2,6-dichloro benzonitrile with 4,4'-(hexafluoro isopropylidene) diphenol in the presence of potassium carbonate in DMAc resulted in the dihydroxy (1) compound. This intermediate compound was reacted with 2-amino-5-fluoro benzotrifluoride in the presence of anhydrous potassium carbonate by nucleophilic displacement. The trifluoromethyl group is strong enough to activate the halogens toward nucleophilic displacement reaction with phenoxides. The characterization of the diamine compound was done by IR spectroscopy and elemental analysis.

### Polyimide synthesis

The synthesis of polyimide was carried out via poly(amic acid) intermediate. The reaction procedure is shown in Scheme 2. The diamine (BATFB) was reacted with equimolar amount of PMDA, BTDA, ODPA, DSDA, BDA, or 6FDA in NMP at room temperature. Initially, diamines were dissolved in measured amount of dry NMP and the dianhydrides were added portion wise. The poly(amic acid) solutions were cast on clean glass plates and heated the film

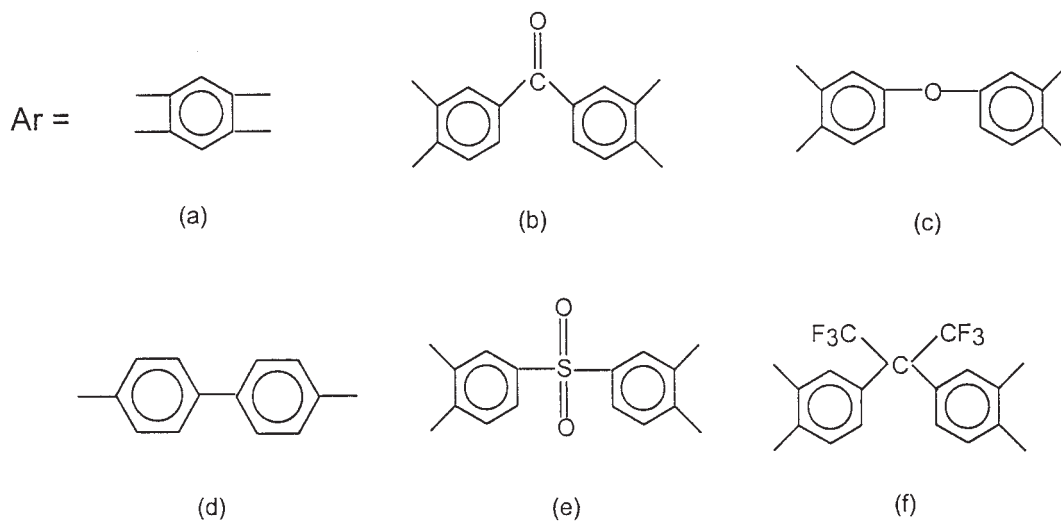
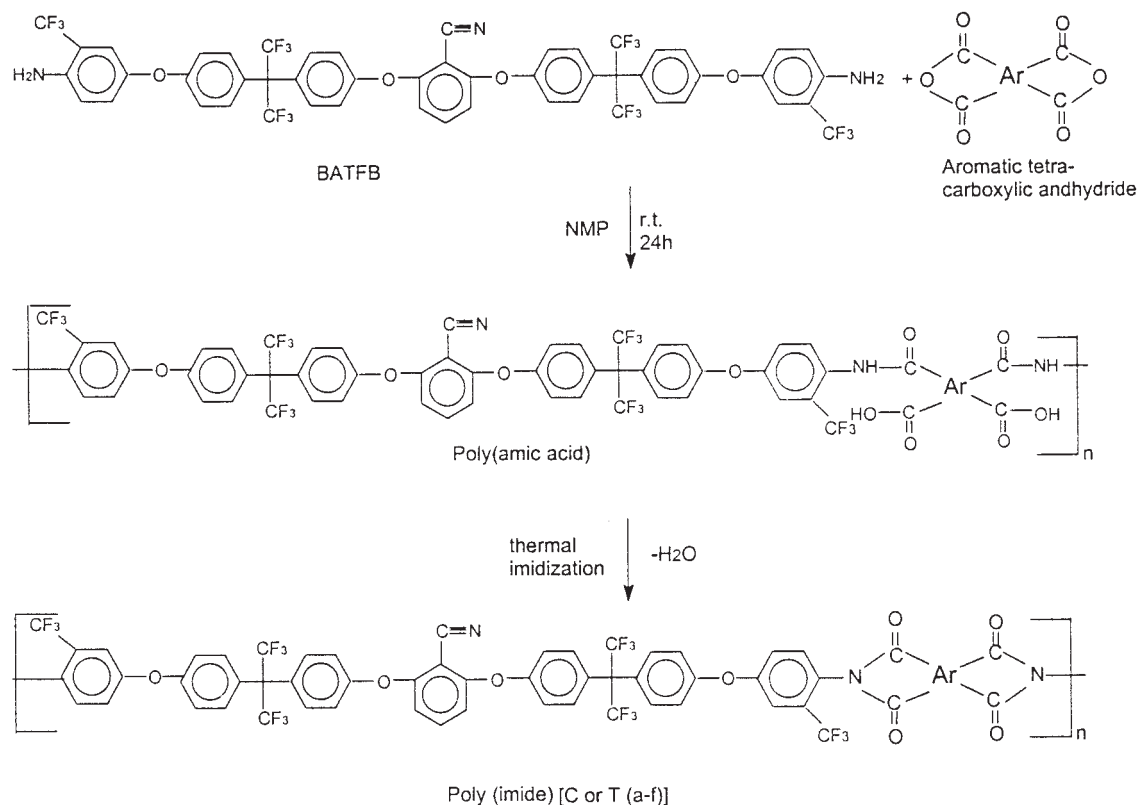
through various stages upto 300°C to remove solvent and water formed during cyclization process. The transparent, flexible films were obtained in thermal imidization.

### IR spectra

IR spectroscopy allows monitoring of the imide ring formation during thermal curing or chemical treatment. From the IR spectra, the characteristic absorption band of the imide ring was observed near 1780, 1720 (asymmetrical and symmetrical C=O imide stretching vibration), 1348 (C—N stretching vibration), 1087 and 788  $\text{cm}^{-1}$  (imide ring deformation), and those of amide and carboxyl groups in the regions of 3000–3500 and 1500–1700  $\text{cm}^{-1}$  disappeared, indicating a virtually completed conversion of the poly(amic acid) precursor into polyimide. The IR spectral data of various poly(amic acid) and poly(imide) s were represented in Table I.

### Solubility

The solubility of resulting polyimides was determined qualitatively in various organic solvents. The solubility was determined by using 2 mg sample taken in a 2 mL of solvent and the results are presented in Table II. The solvents like DMSO, DMF, DMAc, *m*-cresol, and THF are tested. Some polyimides are soluble on heat-



Scheme 2

ing, while some are slightly soluble and some are insoluble. This increase in solubility may be attributed to the bulky  $\text{CF}_3$  groups, which increased the disorder in the chain and hindered dense chain packing, thereby reducing dense chain interactions to enhance solubility. The polyimides obtained by chemical imi-

dization showed slightly higher solubility compared with those obtained by thermal imidization. The insolubility of the polyimides is attributed to the compact aggregation of the polymer chain occurred as imidization was carried out at a higher temperature.

TABLE I  
Infrared Spectroscopy Data of Poly(amic acid) and Poly(imide)s

Polymer code	Wave Number (cm <sup>-1</sup> )				
	Poly(amic acid)		Poly(imides)		
	Amide stretch	Carboxyl stretch	Imide C=O asymmetrical stretch	Imide C=O symmetrical stretch	C—N stretch
C-IIIa	3350	1640	1780	1724	1348
C-IIIb	3380	1650	1778	1724	1380
C-IIIc	3450	1620	1779	1725	1378
C-IIId	3390	1640	1781	1726	1365
C-IIIE	3420	1630	1780	1723	1370
C-IIIf	3350	1640	1781	1723	1367

### Density

The density of the polyimide was determined from

$$\rho = \rho_a M_1 / (M_1 - M_2)$$

where  $M_1$  and  $M_2$  are the masses of polymer film in air and ethanol respectively, and  $\rho_a$  is the density of pure ethanol at 25°C. The polyimides were showed density 0.8–1.32. The calculated densities of all polyimides were presented in Table III.

### Water uptake

Water uptake of the polyimide films were measured by immersing films into deionized water at 25°C for 24 h at room temperature. Then the films were taken out, wiped with tissue paper, and quickly weighed on a microbalance. The water uptake of the film was calculated from

$$\text{Water uptake (\%)} = \frac{W - W_0}{W_0} 100$$

$W_0$  is the initial weight of the polymer sample,  $W$  is the weight of the polymer sample after immersion in water for 24 h.

The results are presented in Table III. The polyimides showed low water uptake values 0.34–0.54 wt %. These exhibited the low water uptake because of the highest fluorine content in the repeat unit.

### Thermal analysis

The thermal behavior of the polymers was evaluated by the DSC and thermogravimetric analysis (TGA). Table III summarizes the thermal data for all polyimides. DSC measurements were conducted at a heating rate of 5°C/min. The polyimides had glass transition temperatures ( $T_g$ ) in the range of 230–290°C. The glass

TABLE II  
Solubility of Polyimides

Polymer Code <sup>a</sup>	Solvent						
	DMAc	DMF	DMSO	NMP	<i>m</i> -cresol	THF	CHCl <sub>3</sub>
C-IIIa	+	+	+	+	+	–	–
T-IIIa	+	+	+	+	+	±	±
C-IIIb	+	+	+	+	+	+	–
T-IIIb	+	+	+	+	+	+	±
C-IIIc	+	+	+	+	+	+	+
T-IIIc	+	+	+	+	+	+	±
C-IIId	+	+	+	+	+	–	–
T-IIId	+	+	+	+	+	±	±
C-IIIE	+	+	+	+	+	+	+
T-IIIE	+	+	+	+	+	+	±
C-IIIf	+	+	+	+	+	+	+
T-IIIf	+	+	+	+	+	+	+

(+), Soluble at room temperature; (±), soluble on heating; (–) partially soluble or swollen; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide, NMP, *N*-methyl-2-pyrrolidone; and THF, Tetrahydrofuran.

<sup>a</sup>Polyimides obtained by chemical cyclodehydration method are designated as C while those obtained by thermal means are designated as T.



TABLE III  
Physical and Thermal Data of Polyimides

Polymer code	Density $\delta$ , g/cm <sup>-3</sup>	Water uptake (%)	DSC <sup>a</sup> ( $T_g$ ) (°C)	TGA		Char yield <sup>d</sup> (%)
				$T_d^{5b}$ (°C)	$T_d^{10c}$ (°C)	
C-IIIa	1.314	0.42	290	560	588	58
C-IIIb	1.328	0.56	250	535	550	56
C-IIIc	1.322	0.54	240	546	562	52
C-IIId	1.316	0.48	285	560	590	64
C-IIIE	1.304	0.40	240	542	552	50
C-IIIf	1.302	0.34	230	566	580	60

<sup>a</sup>DSC measurements conducted at a heating rate of 5°C/min in nitrogen.  $T_g$  is the glass transition temperature of polyimides.

<sup>b</sup>Temperature at which 5% weight loss recorded by TGA at a heating rate 10°C/min in nitrogen.

<sup>c</sup>Temperature at which 10% weight loss recorded by TGA at a heating rate 10°C/min in nitrogen.

<sup>d</sup>Residual yield of polyimides at 800° C under nitrogen.

transition temperature of polyimides could be attributed to the higher free volume created by the fluorine groups and the presence of flexible ether groups. The polyimides containing phenyl and biphenyl unit in the polymer backbone exhibited highest glass transition temperature in comparison with the other analogous of polyimides containing BTDA, ODPDA, DSDA, and 6FDA moieties. The polymer molecule is built of rigid units and is expected to have higher glass transition temperature.<sup>15</sup> All polyimides showed clear transitions because of the presence of ether, and fluorine groups creates low intermolecular forces in bridging moieties.

The decomposition temperatures ( $T_d$ ) were recorded using TGA measurements conducted at a heating rate 10°C/min under N<sub>2</sub> atm. The decomposition temperatures for 5% weight loss ( $T_d^5$ ) were observed in the range of 535–560°C and for 10% weight loss ( $T_d^{10}$ ) were observed in the range of 550–590°C. Thermal stability of the polyimides would vary depending upon the dianhydride moiety. Polyimides C-IIIa and C-IIId exhibited higher thermal stability when compared with other polyimides such as C-IIIb, C-IIIc, C-IIIE, and C-IIIf because of their rigid phenyl and biphenyl rings. High thermal stability is attributed to the

presence of rigid backbone structures, as expected for polymers. All polyimides had shown good thermal stability. The resulting polyimides had char yield 52–64% at 700°C.

#### Isothermal aging

The polyimides samples were placed in an air circulating oven at 250 and 300°C for 120 h. The samples were weighed at the scheduled aging time intervals. Figures 1 and 2 depict the thermo-oxidative stability of polyimides. In air, the polyimides lost more than 9–13% of its original weights after isothermal aging at 250 and 300°C for 120 h. The thermo-oxidative stability of the polyimides decreased in the following order C-IIId > C-IIIf > C-IIIc > C-IIIb. The relatively better thermo-oxidative stability obtained for C-IIId may be attributed to the presence of biphenyl in the backbone of polyimide chain. All polyimides showed good thermo-oxidative stability at 250 and 300°C for several hours.

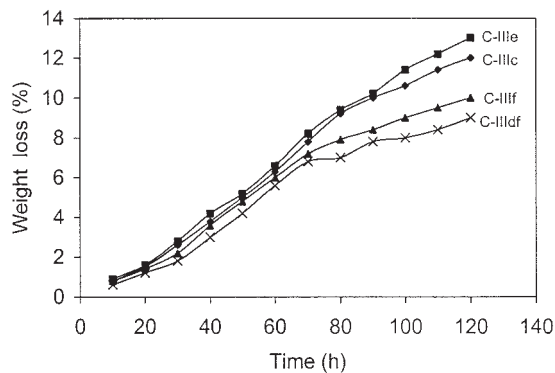


Figure 1 Thermo-oxidative stability of polyimides at 250°C.

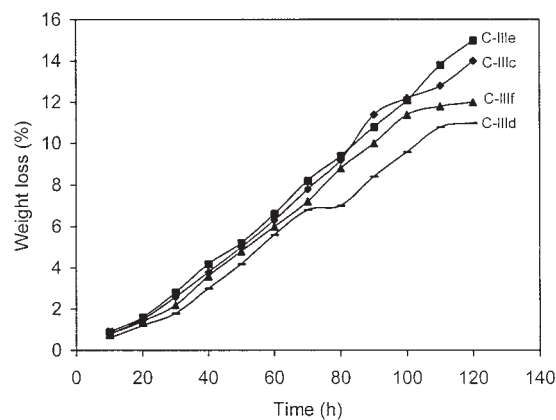


Figure 2 Thermo-oxidative stability of polyimides at 300°C.

### CONCLUSIONS

New diamine having  $\text{CF}_3$  and  $\text{C}\equiv\text{N}$  groups, BATFB (2) was successfully synthesized. Polyimides were synthesized using above diamine and various aromatic tetracarboxylic dianhydrides by thermal and chemical imidization routes. The polymers were characterized by IR spectroscopy and thermal analysis was performed by DSC and TGA methods. The prepared polyimides had glass transition temperatures between 210–290°C. The polyimides showed water uptake values 0.34–0.54 wt %. These have exhibited good solubility in various organic solvents such as NMP, DMF, DMAc, DMSO, *m*-cresol, and  $\text{CHCl}_3$ . The resulting polyimides exhibited outstanding thermal stability and good char yield.

The authors thank Dr. K. U. Bhaskar Rao, Director, DM-SRDE, Kanpur, India for accepting to publish this article and kind support to carryout this work successfully.

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