

Organosoluble Poly(ether imide)s from Phthalimidine Based and Trifluoromethyl Substituted Bis(ether amine)

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ABSTRACT: A series of new organosoluble and optically transparent poly(ether imide)s (PEIs) were synthesized by the polycondensation of trifluoromethyl substituted and phthalimidine cardo group based bis(ether amine), 3,3-bis-[4-(2'-trifluoromethyl 4'-(4''-aminophenyl)phenoxy)phenyl]-2-phenyl-2, 3-dihydro-isindole-1-one with different fluorinated and non-fluorinated aromatic dianhydrides (2a–e). All the PEIs were well characterized by elemental analysis, NMR, FTIR spectroscopy, and gel permeation chromatography (GPC). The synthesized PEIs showed moderate to high inherent viscosity

0.41–0.61 dL/g and excellent solubility at room temperature in different organic solvents. All the transparent yellow films showed cut-off length upto 425 nm. They exhibited high tensile strengths upto 98 MPa, excellent thermostability upto 554°C for 5% weight loss, high glass transition temperature upto 327°C, and water uptake value less than 0.6%. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1550–1559, 2009

Key words: poly(ether imide); cardo group; phthalimidine; solubility; thermal stability

INTRODUCTION

Aromatic polyimides are considered as a class of high performance polymers because of their number of outstanding properties such as excellent thermal, mechanical, and electrical properties which lead to their application in several robust fields like aerospace and electronic industries as well as for fibers, adhesives, and in matrixes for composite material.^{1,2} In addition to the above properties, polyimides are endowed with high thermo-oxidative stability, chemical, and solvent resistive properties leading to many membrane-based applications such as gas separation, pervaporation *etc.*^{3,4}

However, high softening temperature and poor solubility in different organic solvents of these polymers lead to the difficulty in processing in both melt and solution condition. Incorporation of flexible linkages,⁵ bulky side groups or bulky units^{6,7} in the polymer backbone, or noncoplanar⁸ or alicyclic monomers⁹ in the main chain has been investigated in an attempt to ease the processing. In the 1970s, Korshak et al. first introduced the incorporation of bulky cyclic side groups (termed as “cardo groups”) in the polymer backbone to make polyimides soluble

without compromising the higher glass transitions temperatures (T_g) and thermomechanical resistance.¹⁰ All these approaches are made to reduce several types of polymer interchain interactions, chain packing, and the charge transfer electronic polarization interactions or charge transfer complex (CTC) formation. Incorporation of hexafluoroisopropylidene or pendent trifluoromethyl groups is also of great interest which increases the free volume of the polyimides, thereby improving various properties such as solubility, electrical insulating properties, and gas permeabilities without forfeiture of thermal stability. These groups decrease crystallinity, color, water absorption as well as increase optical transparency, environmental stability, and flame resistance.^{11–13} Optical transparency of polyimide membranes is an important property because of its demand in many optoelectronic devices.¹⁴

Accordingly, considerable attention has been devoted to the preparation of new classes of fluorinated polymers. We have already reported a number of poly(arylene ether)s, poly(ether amide)s, and poly(ether imide)s (PEIs) containing pendent trifluoromethyl groups.^{15–18}

Phenolphthalein is a very cheap bis-hydroxy compound and can be used as a cardo group. Phthalimidine made from phenolphthalein has been widely used as cardo group for poly(ether ether ketone)s, poly(arylene ether)s, poly(arylene ether sulfone)s, and polyesters.^{19–22} Unfortunately, it has not been exploited to make polyimides or PEIs. Recently, Yang and coworkers have reported several soluble PEIs containing different cardo groups.^{23–25}

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In our present study, we have prepared a series of novel fluorinated PEIs using 3,3-bis-[4-{2'-trifluoromethyl 4'-(4''-aminophenyl) phenoxy} phenyl]-2-phenyl-2,3-dihydro-isindole-1-one as bis(ether amine) (1) monomer based on cardo phthalimidine group. The detail characterizations of these new polymers are also reported.

EXPERIMENTAL

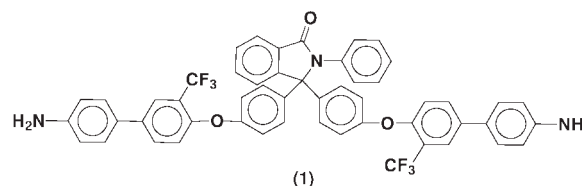
Measurements

Carbon, hydrogen, and nitrogen content of the compounds were analyzed by pyrolysis method using Vario EL (Elementar, Germany) elemental analyzer. FTIR spectra of the monomers and polymers were recorded from a NEXUS 870 FTIR (Thermo Nicolet) spectrophotometer at room temperature and humid free atmosphere using KBr pellets. $^1\text{H-NMR}$ and proton decoupled $^{13}\text{C-NMR}$ of monomers and polymers were recorded on a Bruker 500 MHz instrument (Switzerland), using CDCl_3 as solvent and TMS as reference. Inherent viscosities of the polymer solutions of 0.5 g/dL concentration in DMF were measured using an Ubbelohde viscometer at $(29 \pm 1)^\circ\text{C}$. Differential scanning calorimetry (DSC) were carried out under nitrogen using NETZSCH DSC 200PC differential scanning calorimeter at a heating rate of $20^\circ\text{C min}^{-1}$. Glass transition temperatures (T_g) were taken at the center of the step transition in the second heating run. Thermal decomposition behavior of these polymers was measured on a TGA Q 5000 of TA Instruments thermogravimetric analyzer at a heating rate of 10°C min under both nitrogen and synthetic air. The dynamic mechanical properties of the thin polymer films ($42\text{--}55\ \mu\text{m}$) of dimensions $30 \times 6\ \text{mm}^2$ were analyzed on a TA instrument DMA-2980 model (USA) under tension mode at a heating rate of $10^\circ\text{C min}^{-1}$ and were run at single frequency of 1 Hz for the temperature range of $50\text{--}350^\circ\text{C}$. Tensile strength and elongation at break of thin polymer films were tested using a Hounsfield H10KS-0547 at room temperature at 5% strain rate of the specimen length; five specimens were used for the measurements. Water absorptivity values were calculated from the weight gain of the polymer films after immersing in distilled water for 72 h, the samples were kept in a temperature bath at $(29 \pm 2)^\circ\text{C}$. Wide angle X-ray diffractograms were recorded by Rigaku, Ultima III X-ray diffractometer using a CuK_α ($\beta = 0.154\ \text{nm}$) source, operated at 40 kV and 40 mA. The range of 2θ for XRD studies was $5^\circ\text{--}50^\circ$. Gel permeation chromatography was performed with a Waters gel permeation chromatography (GPC) instrument. THF was used as eluent (flow rate

0.5 mL/min, polystyrene was used as standard and RI detector was used to record the signal.

Starting materials

All reagents were purchased from Fluka, Aldrich, and Acros Chemical Company and used as received unless otherwise noted. Benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA) was recrystallized from acetic anhydride. 4,4'-(4,4'-Isopropylidenedi-phenoxy)bis(phthalic anhydride) (BPADA), 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane (6FDA), 4,4'-oxydiphthalic anhydride (ODPA), and benzene-1,2,4,5-tetracarboxylic dianhydride (PMDA) were heated at 120°C for overnight prior to use. NMP and DMF (E. Merck, India) were purified by stirring with NaOH and distilled twice from P_2O_5 under reduced pressure. Aniline (E. Merck, India) was purified by distillation with constant stirring over KOH. Toluene (E. Merck, India) was dried by refluxing over sodium metal. The bis(ether amine) monomer (1) was prepared starting from phenolphthalein by following the procedure as reported in our previous communication.²⁶



Polymerization

The polymerization of the synthesized bis(ether amine) with five different aromatic dianhydrides were achieved in two conventional stages. A representative polymerization reaction of the bis(ether amine) (1) with bisphenol-A dianhydride (BPADA) is described below and shown in Figure 1.

In the first stage, in a 25-mL round bottomed flask equipped with a guard tube BPADA (0.26 g, 0.506 mmole) was added in portions into the solution of bis(ether amine) (0.44 g, 0.506 mmol) in dry DMF (6.0 mL). The mixture was left for stirring at room temperature until it transformed to a highly viscous solution of polyamic acid (PAA) (generally, it takes 45–60 min).

In the second stage, viscous PAA solution was spread onto a clean and dry flat bottomed glass petridish and kept in oven initially at 80°C for the slow removal of the solvent. Finally, the thermal cyclization of the PAA to PEI was achieved by sequential heating at 120, 150, 180, 200, and 220°C , each for half an hour and at 250°C for 15 min in an oven under nitrogen.

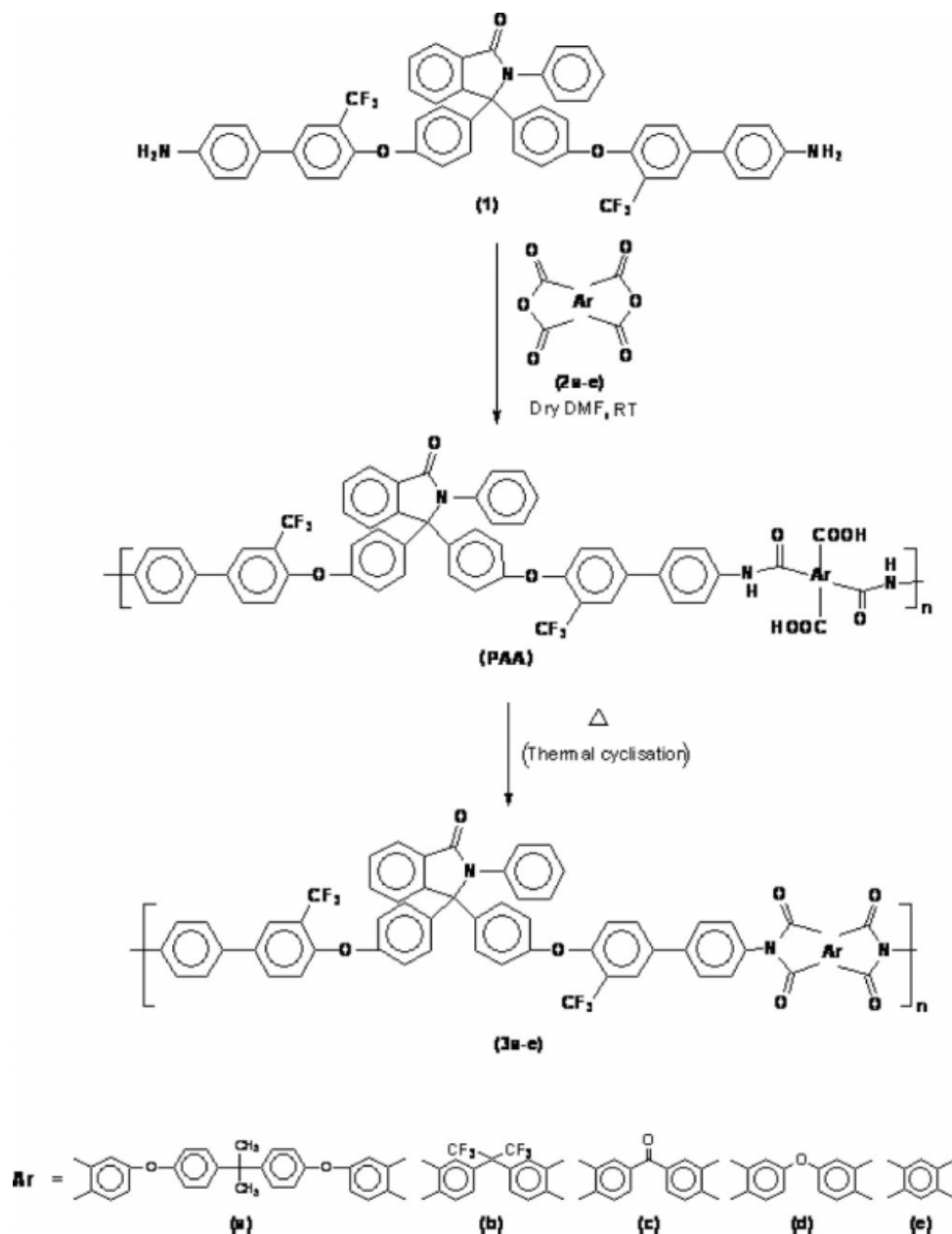
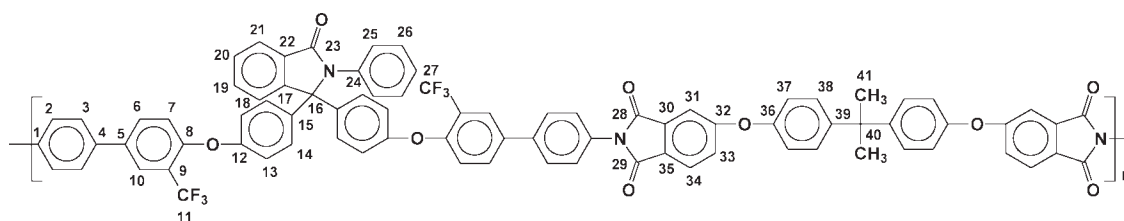


Figure 1 Polymerization and structure of poly(ether imide)s.

Poly(ether imide) 3a



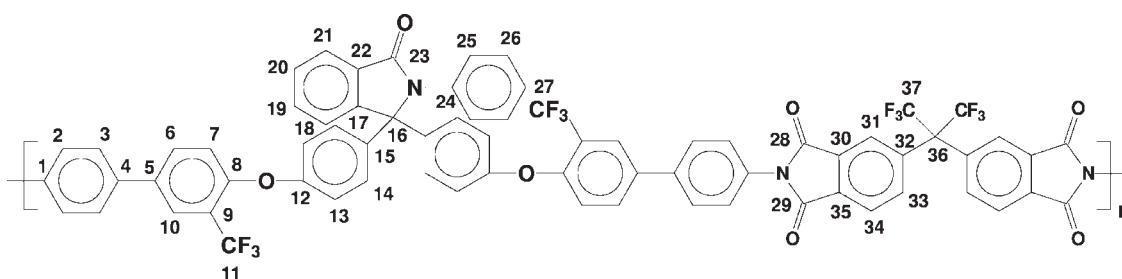
FTIR (KBr, cm^{-1}): 3067 (aromatic C—H stretching), 2971 (aliphatic C—H stretching), 1777 (asymmetric imide C=O stretching), 1722 (symmetric imide

C=O stretching), 1602 (aromatic C=C stretching), 1489, 1373 (aromatic C—N stretching), 1249 (asymmetric C—O—C stretching), 1135 (C—F stretching),

and 1054 (symmetric C—O—C stretching). $^1\text{H-NMR}$ (CDCl_3 , 500 MHz, δ ppm): 8.05 (d, $J=7.3$ Hz, 1H, H^{21}); 7.94 (d, $J=8.5$ Hz, 2H, H^{34}); 7.92 (s, 2H, H^{31}); 7.72 (d, $J=8.6$ Hz, 2H, H^{25}); 7.70 (d, $J=7.5$ Hz, 4H, H^2); 7.61 (d, $J=7.0$ Hz, 1H, H^{27}); 7.56 (d, $J=8.5$ Hz, 4H, H^3); 7.48 (s, 2H, H^{10}); 7.40 (d, $J=10.2$ Hz, 2H, H^6); 7.38 (d, $J=8.5$ Hz, 4H, H^{14}); 7.30–7.25 (m, 9H, H^{19} , H^{20} , H^{18} , H^{26} , H^7 , H^{33}); 7.08 (d, $J=8.35$ Hz, 4H, H^{38}); 7.02 (d, $J=8.1$ Hz, 4H, H^{13}); 6.99 (d, $J=8.6$ Hz, 4H, H^{37}); 1.80 (s, 6H, H^{41}). $^{13}\text{C-NMR}$ (CDCl_3 , 125

MHz, δ ppm): 169.0 (C^{23}); 166.8 (C^{28}); 166.7 (C^{29}); 164.0 (C^{32}); 156.3 (C^{12}); 154.4 (C^8); 152.7 (C^{36}); 151.0 (C^{17}); 147.7 (C^1); 138.8 (C^{30}); 137.0 (C^{24}); 135.7 (C^{15}); 135.6 (C^{39}); 134.3 (C^4); 132.9 (C^{22}); 131.8 (C^6 and C^5); 131.5 (C^{19}); 130.5 (C^{14}); 130.2 (C^{18}); 128.8 (C^{38}); 128.7 (C^{34}); 127.7 (C^3); 127.6 (C^{35}); 126.9 (C^2); 126.0 (C^{26}); 125.9 (C^{33}); 125.0 (C^{25}); 124.7 (C^{21}); 124.0 (C^{20}); 123.2 (q, $J=271.3$ Hz, C^{11}); 123.2 (C^{10}); 121.9 (C^{27}); 120.3 (q, $J=31$ Hz, C^9); 120.0 (C^{13}), 119.9 (C^7); 118.9 (C^{37}); 111.9 (C^{31}); 77.7 (C^{16}); 42.6 (C^{40}); 31.0 (C^{41}).

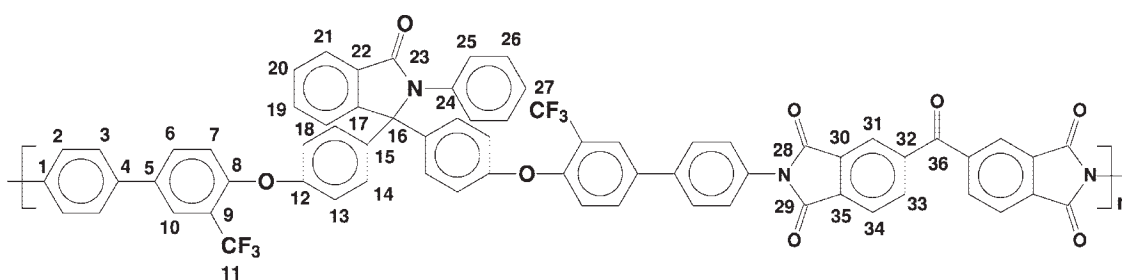
Poly(ether imide) 3b



FTIR (KBr , cm^{-1}): 3062 (aromatic C—H stretching), 1783 (asymmetric imide C=O stretching), 1725 (symmetric imide C=O stretching), 1611 (aromatic C=C stretching), 1490, 1374 (aromatic C—N stretching), 1253 (asymmetric C—O—C stretching), 1139 (C—F stretching), and 1054 (symmetric C—O—C stretching). $^1\text{H-NMR}$ (CDCl_3 , 500 MHz, δ ppm): 8.08 (d, $J=7.9$ Hz, 2H, H^{34}); 8.02 (d, $J=7.4$ Hz, 1H, H^{21}); 7.97 (s, 2H, H^{31}); 7.91 (d, $J=8.2$ Hz, 2H, H^{25}); 7.90 (s, 2H, H^{10}); 7.70 (m, 6H, H^2 , H^{33}); 7.59 (d, $J=7.4$ Hz, 1H, H^{27}); 7.55 (d, $J=8.1$ Hz, 4H, H^3); 7.27–7.23 (m, 9H, H^6 , H^{26} , H^{19} ,

H^{20} , H^{18} , H^7); 7.00 (d, $J=8.6$ Hz, 4H, H^{14}); 6.96 (d, $J=8.7$ Hz, 4H, H^{13}). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz, δ ppm): 169.0 (C^{23}); 166.1 (C^{29}); 165.9 (C^{28}); 156.3 (C^{12}); 154.5 (C^8); 151.0 (C^{17}); 139.4 (C^1); 139.3 (C^{15}); 137.0 (C^{24}); 136.1 (C^{22}); 135.8 (C^{30}); 135.5 (C^4); 132.9 (C^{19}); 132.7 (C^{33}); 132.4 (C^6); 131.8 (C^5); 131.0 (C^{35}); 130.5 (C^{14}); 130.2 (C^{18}); 128.8 (C^{26}); 128.7 (C^{31}); 127.8 (C^3); 127.6 (C^{32}); 127.0 (C^2); 126.5 (C^{21}); 126.1 (C^{20}); 125.5 (C^{10}); 124.7 (C^{27}); 124.3 (C^{34}); 125.1 (q, $J=259.6$ Hz, C^{11}); 122.2 (C^{37}); 122.1 (C^{25}); 121.9 (q, $J=30.5$ Hz, C^9); 119.9 (C^7); 118.9 (C^{13}); 77.7 (C^{16}); 65.0 (C^{36}).

Poly(ether imide) 3c



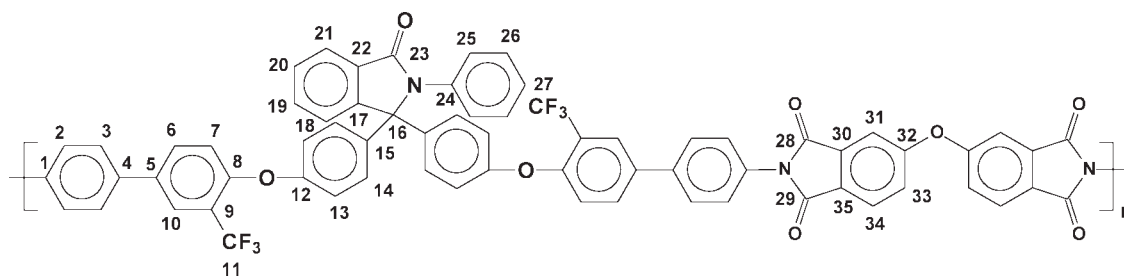
FTIR (KBr , cm^{-1}): 3054 (aromatic C—H stretching), 1780 (asymmetric imide C=O stretching), 1725 (symmetric imide C=O stretching), 1601 (aromatic C=C stretching), 1490, 1375 (aromatic C—N stretching), 1252 (asymmetric C—O—C stretching), 1135 (C—F stretching), and 1054 (symmetric C—O—C stretching). $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ (ppm): 8.32 (s,

2H, H^{31}); 8.28 (d, $J=7.2$ Hz, 2H, H^{34}); 8.16 (d, $J=7.6$ Hz, 2H, H^{33}); 8.02 (d, $J=6.95$ Hz, 1H, H^{21}); 7.90 (s, 2H, H^{10}); 7.71 (m, 6H, H^2 , H^{25}); 7.58 (d, $J=7.65$ Hz, 4H, H^3); 7.53 (d, $J=7.3$ Hz, 1H, H^{27}); 7.27–7.23 (m, 9H, H^6 , H^{19} , H^{26} , H^{20} , H^{18} , H^7); 7.00 (d, $J=8.56$ Hz, 4H, H^{14}); 6.97 (d, $J=8.45$ Hz, 4H, H^{13}). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz, δ ppm): 192.8 (C^{36}); 169.0 (C^{23});

166.0 (C²⁸ and C²⁹), 156.3 (C¹²); 154.5 (C⁸); 151.0 (C¹⁷); 142.0 (C³²); 139.3 (C¹); 137.0 (C²⁴); 135.9 (C¹⁵); 135.7 (C³⁵); 135.4 (C³³); 135.1 (C⁴); 133.0 (C²²); 132.2 (C³⁰); 131.8 (C⁶); 131.0 (C⁵); 130.5 (C¹⁴); 130.2 (C¹⁸); 128.8

(C³¹); 128.7 (C²⁶); 127.8 (C³); 127.6 (C²¹); 126.9 (C²); 126.1 (C³⁴); 124.8 (C¹⁰); 124.7 (C²⁰); 124.5 (C²⁵); 124.03 (C²⁷); 123.2 (q, $J=271.3$ Hz, C¹¹); 122.2 (C¹⁹); 121.9 (q, $J=31.5$ Hz, C⁹); 119.9 (C⁷); 118.9 (C¹³); 77.8 (C¹⁶).

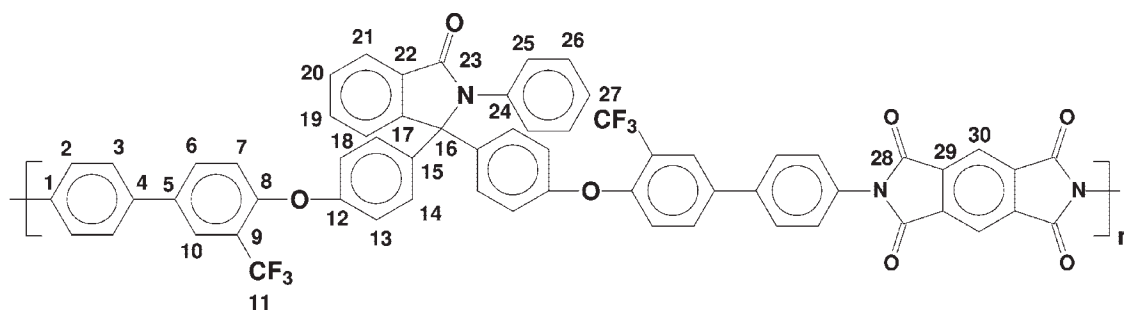
Poly(ether imide) 3d



FTIR (KBr, cm⁻¹): 3071 (aromatic C—H stretching), 1770 (asymmetric imide C=O stretching), 1724 (symmetric imide C=O stretching), 1609 (aromatic C=C stretching), 1489, 1372 (aromatic C—N stretching), 1251 (asymmetric C—O—C stretching), 1135 (C—F stretching), and 1054 (symmetric C—O—C stretching). **¹H-NMR (CDCl₃, 500 MHz, δ ppm):** 8.03 (d, $J=7$ Hz, 2H, H¹⁴); 8.02 (s, 1H, H²¹); 7.89 (s, 2H, H³¹); 7.70 (d, $J=7.5$ Hz, 4H, H²); 7.68 (d, $J=7.3$ Hz, 2H, H²⁵); 7.59–7.49 (m, 10H, H³, H⁶, H¹⁰, H²⁶); 7.27–7.23 (m, 8H, H¹⁹, H²⁷, H²⁰, H¹⁸, H⁷, H³³); 7.0 (m, 8H, H¹⁴,

H¹³). **¹³C-NMR (CDCl₃, 125 MHz, δ ppm):** 169.0 (C²³); 166.2 (C²⁸); 166.1 (C²⁹); 161.3 (C³⁰ and C³⁵); 156.4 (C³²); 154.5 (C¹²); 151.0 (C²⁴); 139.1 (C⁸); 137.0 (C¹); 135.7 (C¹⁵); 135.6 (C¹⁷); 134.7 (C⁴); 133.0 (C²²); 131.8 (C²⁰); 131.3 (C⁵); 130.5 (C¹⁴); 130.1 (C²¹); 128.8 (C²⁵); 128.7 (C²⁶); 127.7 (C²); 127.6 (C²⁷); 127.3 (C¹⁹); 127.0 (C³); 126.4 (C³⁴); 126.1 (C¹⁰); 125.0 (C¹⁸); 124.7 (C⁶); 124.1 (C⁷); 123.2 (q, $J=270.8$, C¹¹); 122.0 (q, $J=31.9$ Hz, C⁹); 119.9 (C³³); 118.9 (C¹³); 114.1 (C³¹); 77.8 (C¹⁶).

Poly(ether imide) 3e



FTIR (KBr, cm⁻¹): 3045 (aromatic C—H stretching), 1778 (asymmetric imide C=O stretching), 1728 (symmetric imide C=O stretching), 1603 (aromatic C=C stretching), 1490, 1371 (aromatic C—N stretching), 1251 (asymmetric C—O—C stretching), 1134 (C—F stretching), and 1053 (symmetric C—O—C stretching). **¹H-NMR (CDCl₃, 500 MHz, δ ppm):** 8.47 (s, 2H, H³⁰); 8.01 (s, 1H, H²¹); 7.90 (d, $J=8.14$ Hz, 2H, H²⁵); 7.72–7.68 (m, 6H, H², H¹⁰); 7.58–7.53 (m, 6H, H⁶, H³); 7.26–7.22 (m, 8H, H¹⁹, H²⁶, H²⁰, H¹⁸, H²⁷,

H⁷); 6.97–6.96 (m, 8H, H¹⁴, H¹³). **¹³C-NMR (CDCl₃, 125 MHz, δ ppm):** 169.1 (C²³); 165.0 (C²⁸ and C²⁹); 156.3 (C¹²); 154.6 (C⁸); 151.0 (C¹⁷); 139.5 (C²⁴); 137.2 (C¹); 137.0 (C¹⁵); 135.8 (C²⁹); 135.3 (C²²); 133.0 (C⁶); 131.8 (C⁴ and C¹⁹); 130.6 (C⁵); 130.5 (C¹⁴); 130.1 (C¹⁸); 128.8 (C²⁶); 128.7 (C³⁰); 127.8 (C³); 127.6 (C²¹); 126.8 (C²); 126.1 (C²⁰); 124.7 (C¹⁰); 124.0 (C²⁷); 123.2 (q, $J=271.2$ Hz, C¹¹); 122.2 (q, $J=23.9$ Hz, C⁹); 119.9 (C²⁵); 119.4 (C⁷); 119.0 (C¹³); 77.8 (C¹⁶).

TABLE I
Poly(ether imide)s from Various Anhydrides

Polymer	Formula (M_w)	Elemental analysis (%)			η_{inh} (dL/g) ^a	\overline{M}_n	PDI	
			C	H				N
3a	(C ₈₃ H ₅₁ F ₆ N ₃ O ₉) _n (1348.37) _n	Calcd.	73.93	3.82	3.12	0.46	35,400	3.2
		Found	73.66	3.79	3.18			
3b	(C ₇₁ H ₃₇ F ₁₂ N ₃ O ₇) _n (1272.11) _n	Calcd.	67.03	2.94	3.30	0.41	29,900	2.8
		Found	67.29	2.86	3.41			
3c	(C ₆₉ H ₃₇ F ₆ N ₃ O ₈) _n (1150.09) _n	Calcd.	72.05	3.25	3.65	0.61	50,400	3.4
		Found	72.18	3.19	3.74			
3d	(C ₆₈ H ₃₇ F ₆ N ₃ O ₈) _n (1138.08) _n	Calcd.	71.76	3.28	3.69	0.48	36,800	2.6
		Found	71.39	3.39	3.63			
3e	(C ₆₂ H ₃₃ F ₆ N ₃ O ₇) _n (1045.98) _n	Calcd.	71.19	3.19	4.02	0.44	30,700	3.1
		Found	71.44	3.06	4.19			

^a Measured at a concentration of 0.5 g/ dL in DMF at (29 ± 1)°C. \overline{M}_n , number average molecular weight; PDI, polydispersity index.

RESULTS AND DISCUSSION

Polymer synthesis

A novel series of PEIs (3a–e) was synthesized using pendent trifluoromethyl and cardo phthalimidine group containing bis(ether amine), and various fluorinated and non-fluorinated aromatic dianhydrides (2a–e) by the conventional ring opening polyaddition of bis(ether amine) to cyclic anhydrides to form poly(amic acid)s followed by thermal cyclization to poly(ether imide)s. All the films obtained in quantitative yields were yellowish, transparent, and flexible in nature. Thin films of thickness values in the range of 42–55 μm, were removed from the petridishes after soaking in hot water. The inherent viscosities were measured using Ubbelohde viscometers in DMF and the values were in between 0.41 and 0.62 dL/g. Elemental analyses of the polymers obtained were in good agreement with the calculated values. The elemental analyses data, viscosity values, and GPC analyses are tabulated in Table I.

Polymer solubility

All the polymers were soluble at room temperature in various high boiling polar organic solvents, such

as DMAc, NMP, DMF, and DMSO as well as in many low boiling solvents like THF, DCM, and CHCl₃ at room temperature. The solubility behavior of the PEIs are presented in Table II.

Spectroscopy

Complete imidization of the PEIs were confirmed by FTIR spectroscopy. The FTIR spectra of all the polymers showed absorption at 1780 cm⁻¹ (C=O asymmetric stretching) and 1720 cm⁻¹ (C=O symmetric stretching) which are characteristic of the imide bands. The FTIR spectra showed the absorption band at 1249–1253 cm⁻¹ corresponding to asymmetric Ph–O–Ph stretching, 1601–1611 cm⁻¹ to aromatic C=C stretching and 1135–1139 cm⁻¹ to C–F stretching. Representative proton decoupled ¹³C-NMR spectrum of polymer '3d' is shown in Figure 2. All the polymers showed exact number of desired ¹³C signals in both aliphatic and aromatic region. The C–F coupling constant values for each quartet of one bond coupling (¹J_{C–F}) were around 271 Hz. and for the two bond coupling (²J_{C–F}) were around 31.5 Hz. In the ¹H-NMR spectra no signal was observed above 10 ppm which again confirmed the complete imidization.

TABLE II
Solubility of the Poly(ether imide)s

Polymer	DMAc	NMP	DMF	THF	DCM	CHCl ₃	DMSO	Acetone
3a	+	+	+	+	+	+	±	–
3b	+	+	+	+	+	+	±	–
3c	+	+	+	+	+	+	±	–
3d	+	+	+	+	+	+	±	–
3e	+	+	+	+	+	+	±	–

(+), soluble at room temperature; (–) insoluble; (±), soluble after heating.

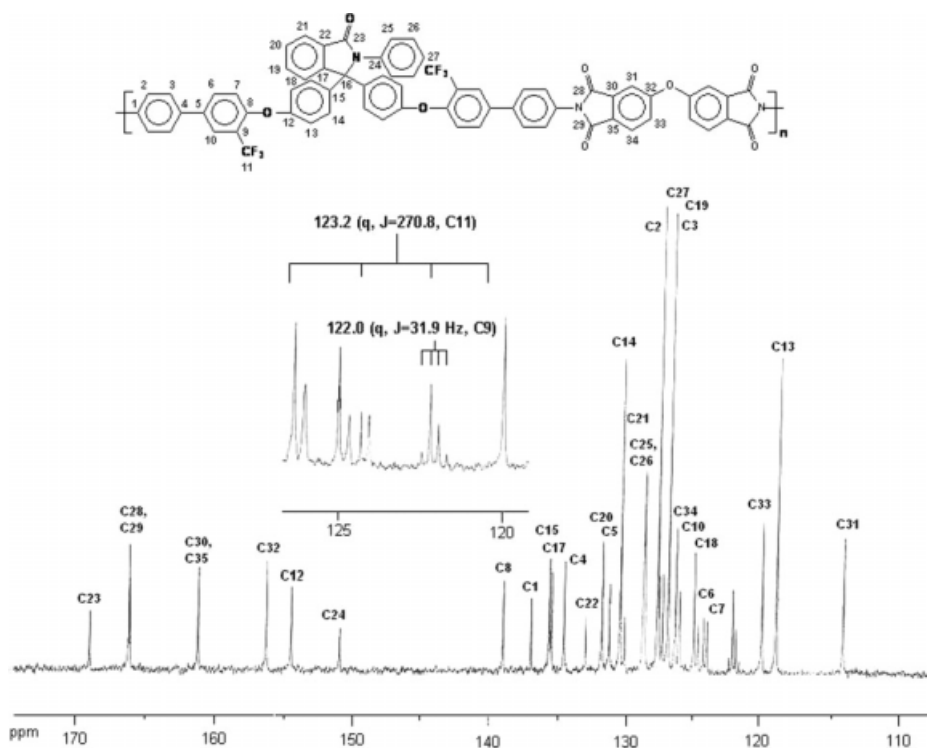


Figure 2 ^{13}C -NMR spectrum of poly(ether imide) '3d'.

Thermal properties

The thermo gravimetric analyses of all the PEIs were investigated in nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$ and the thermograms are shown in Figure 3. Thermal analysis reveals that the phthalimidine containing PEIs have outstanding thermal stability. Despite the amorphous structure, all these PEIs showed excellent heat resistance which is considerably higher than that of other polyimides.^{24,25} In Table III, the initial decomposition temperatures for 5 and 10% weight losses ($T_{d,5}$ and $T_{d,10}$) are summarized. These polymers showed 5% weight loss ranging from 521 to 554°C and 10% weight loss from 539 to 578°C. The polymers showed char residues more than 60 wt % at 800°C under nitrogen atmosphere.

The glass transition temperatures (T_g) of the PEIs were analyzed by DSC and DMA. DSC plots of the synthesized polymers are shown in Figure 4. The glass transition temperature values observed were in the range of 243–327°C. These polymers did not show any melting or crystallization temperature upto 350°C. All the PEIs in this series showed high glass transition temperatures, possibly due to the presence of rigid phthalimidine moiety in the main chain.¹⁰ Polymer '3a' showed the lowest T_g among the series. This may be attributed to the presence of extra flexible ether linkages in BPADA unit whereas highest T_g is observed for the PMDA unit containing polymer '3e' due to the rigidity in the polymer back-

bone. The T_g values obtained from DSC followed the same trend with DMA. The order is in good agreement with the increasing order of rigidity and polarity of the polymer chains. Polymer '3b' containing two extra $-\text{CF}_3$ group from the dianhydride 6FDA was found to be as higher T_g material in comparison to the very similar structure of polymer '3d'.

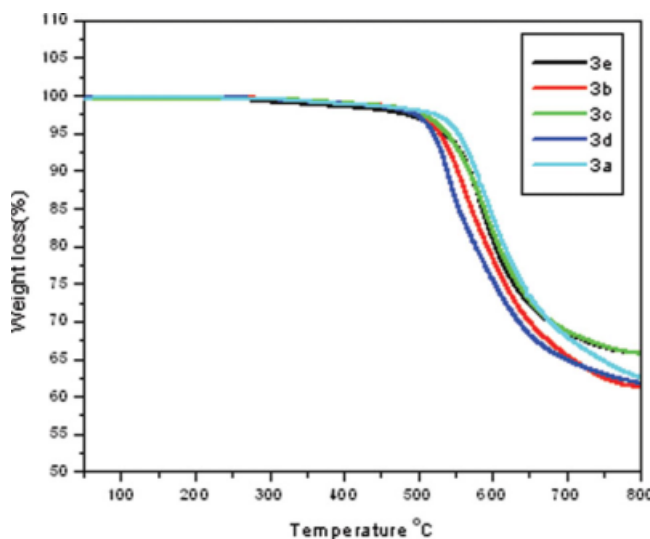


Figure 3 TGA thermograms of poly(ether imide)s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Thermal Analysis Data of the Poly(ether imide)s

Polymer	T_g (°C)		T_d (°C)		Residual mass at 600°C (%)
	DSC	DMA	T_{d5} (°C) ^a	T_{d10} (°C) ^b	
3a	243	234	500	533	65
3b	292	297	496	530	39
3c	280	268	337	516	58
3d	276	277	455	538	60
3e	327	311	424	524	53

^a 5% weight loss temperature measured by TGA in synthetic air.

^b 10% weight loss temperature measured by TGA in synthetic air.

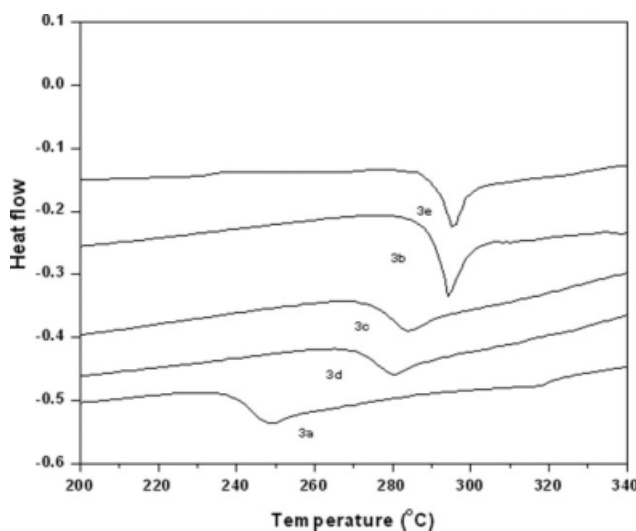


Figure 4 DSC thermograms of the poly(ether imide)s.

Mechanical properties

The mechanical properties of the thin PEI films cast from DMF are summarized in Table IV. The polymers exhibited good tensile strength upto 98 MPa and Young's modulus upto 1.7 GPa. Polymer '3c' showed the highest tensile strength among the series, probably due to the high-molecular development during polymerization as observed from the viscosity measurement (Table I). This high-molecular weight of this polymer may lead to better anchoring among the chains. The elongation at break for these

polymers ranges in between 6 and 9%. Low elongation at break values is observed because of the rigid phthalimidine moiety and absence of any extendable geometry in the polymer structures. Polymer '3e' made from PMDA showed least elongation and polymer '3a' from BPADA containing flexible ether linkages showed the highest elongation in the series. Representative DMA plot for the polymer '3d' is shown in Figure 5. The storage modulus values at 50°C were in the range of 1443–1121 MPa (Table IV). The DMA plots of these polymers indicate good retention of storage modulus upto 270°C.

XRD study

Representative wide-angle X-ray diffractograms of PEIs are given in Figure 6. All the polymers are amorphous in nature as shown by the broad peaks. The absence of well defined long ranged order or crystallinity in these polymers is expected because of the presence of bulky phthalimidine group, and pendent trifluoromethyl group in the main backbone. The cardo phthalimidine moiety and trifluoromethyl groups substantially reduce the interchain cohesion leading to the amorphous nature.

Optical properties and water absorption study

UV–visible spectroscopic studies (Fig. 7) of the polymers revealed that all the polymer thin films (thickness between 42 and 55 μm) showed high optical

TABLE IV
Tensile Properties of Poly(ether imide) Films

Polymer	Tensile strength/MPa (Variance/%)	Young modulus/GPa (Variance/%)	DMA storage modulus ^a /GPa	Elongation at break/% (Variance/%)
3a	61.5 (3.6)	0.82 (6.2)	1.12	9.3 (1.2)
3b	773 (3.8)	1.63 (6.3)	1.26	7.2 (1.1)
3c	98.4 (6.5)	1.74 (7.2)	1.34	8.2 (1.5)
3d	79.5 (4.9)	1.52 (5.9)	1.17	7.2 (1.3)
3e	70.2 (3.9)	1.61 (5.8)	1.24	6.1 (1.1)

^a Values from single measurement at 50°C.

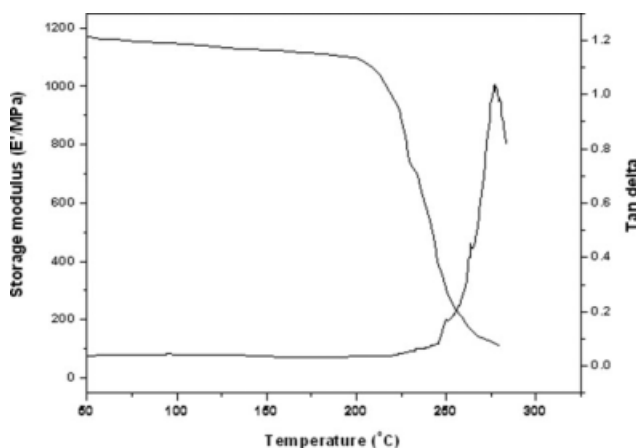


Figure 5 DMA plot of the poly(ether imide) '3d'.

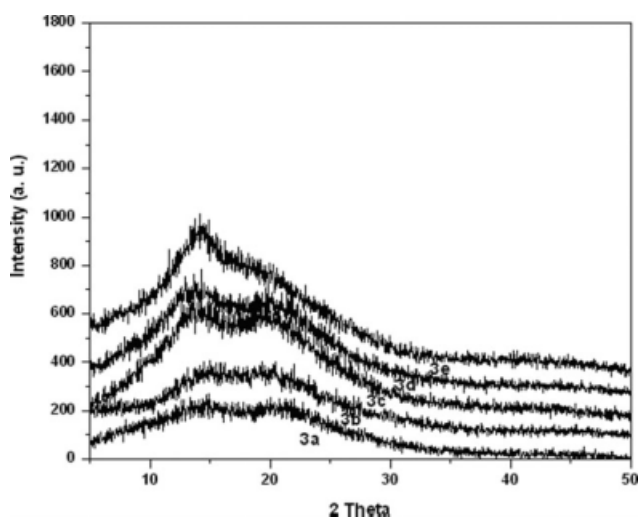


Figure 6 Wide-angle X-ray diffraction curves of poly(ether imide) films.

transparency and, a cut-off wavelength upto 425 nm depending on the thickness and exact structures, respectively. High optical transparency of these films can be attributed to the presence of flexible ether linkages, pendent trifluoromethyl group, and bulky cardo phthalimidine group in the polymer backbone which hinders the inter chain close packing as well

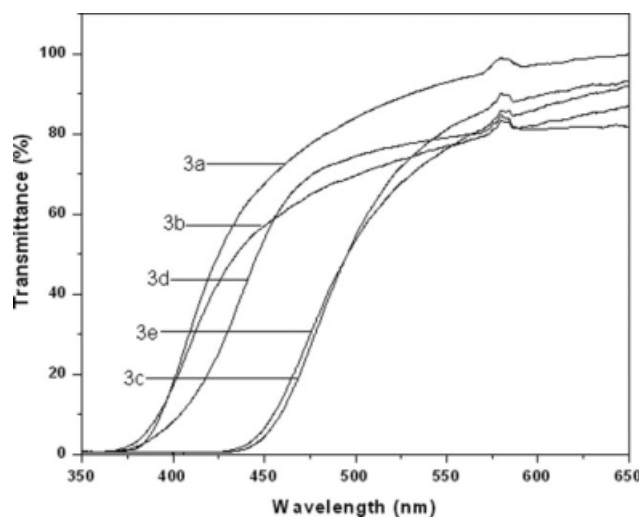


Figure 7 UV-visible spectra of the poly(ether imide)s.

as CTC formation. Again high optical transparency of these polymers proved that there was no thermal oxidation of the films during thermal imidization (upto 250°C).

Along with the high optical transparency, low water absorption is also an important criterion for application in optoelectronic devices. The water absorption of the polymers was calculated from the weight gain values of the polymer films using microbalance (sensitivity 10^{-6}) after immersion in distilled water for 72 h. The water absorption is found to be very low, in the range of 0.4–0.6%. The least water uptake value was observed for polymer '3b' among the series. This is most possibly due to the highest fluorine content in this polymer from 6FDA. The detailed values of water absorption and cut-off wavelength are summarized in Table V.

CONCLUSION

A novel series of highly soluble and colorless PEIs were prepared from the bis(ether amine) monomer, 3, 3-bis-[4-[2'-trifluoromethyl 4'-(4''-aminophenyl) phenoxy] phenyl]-2-phenyl-2, 3-dihydro-isoindole-1-

TABLE V
Cut-Off Wavelength and Water Absorption Data of the Poly(ether imide) Films

Polymer	Thickness (μm)	Cut-off wavelength (λ_0 nm)	Water absorption (%) ^a	Color and quality
3a	42	378	0.6	Yellow, flexible
3b	55	359	0.4	Yellow, flexible
3c	44	425	0.6	Yellow, flexible
3d	53	407	0.5	Yellow, flexible
3e	45	422	0.6	Yellow, flexible

^a After 72 h.

one, using various fluorinated and non-fluorinated aromatic dianhydrides by conventional two stage method. The introduction of cardo phthalimidine unit into the main chain remarkably improves the solubility, processibility, thermal properties as well as mechanical properties. All the polymers are amorphous in nature as indicated by wide angle X-ray data and have excellent thermal stability. These properties could make these polymers attractive for practical applications, such as processable high-performance engineering plastics and may find application in optoelectronic devices, pervaporation, and gas permeation.

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