ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 3669–3676

polymer

www.elsevier.com/locate/polymer

Synthesis and characterization of polyimides and co-polyimides having pendant benzoic acid moiety

Mahesh Kulkarni[a], Sandeep Kothawade[a], Girish Arabale[b], Deepali Wagh[b], K. Vijayamohanan[b], R.A. Kulkarni[a], S.P. Vernekar[a,*]

[a]*Polymer Chemistry Division, National Chemical Laboratory, Dr Homi Bhabha Road, Pashan, Pune 411008, India*
[b]*Physical and Materials Chemistry Division, National Chemical Laboratory, Dr Homi Bhabha Road, Pashan, Pune 411008, India*

Received 6 July 2004; received in revised form 31 August 2004; accepted 1 March 2005
Available online 2 April 2005

Abstract

A novel diamine monomer, 2,4-diamino-4′-carboxy diphenyl ether had been synthesized. Several polyimides were prepared by reacting this diamine with commercially available dianhydrides, such as benzophenone tetracarboxylic acid dianhydride (BTDA), 4,4′-bis{hexafluoroisopropylidene bis (phthalic anhydride)}(6-FDA), oxydiphthalic anhydride (ODPA) and 3,3′,4,4′-biphenyltetracarboxylic acid dianhydride (BPDA). Furthermore, copolymers from the resulting diamine and oxydianiline (ODA) with 6 FDA were also synthesized. The inherent viscosities of the polymers were 0.42–0.67 dl g^{-1}. The polymers have good solubility in polar aprotic solvents, high thermal stability up to 410 °C in nitrogen and high glass transition temperatures (T_g) ranging from 260–330 °C. These polymers formed tough flexible films by solution casting.

Keywords: Polyimides with pendant benzoic acid; Diamine with pendant benzoic acid; Co-polyimides

1. Introduction

Polyimides, due to their outstanding thermal behavior combined with their excellent mechanical, chemical, physical and electrical properties [1,2], have found wide usage as high temperature insulators and dielectrics, coatings, adhesives, matrix resins, gas separation membranes, polymer electrolytes and several other applications.

In general, most conventional fully aromatic polyimides are infusible, insoluble and processed with difficulty into their end use forms. Several structural modifications have been reported to modify the properties of polyimides to suit end use applications [3,4]. Thus, introduction of flexible bridging units as well as bulky or cardo groups into the rigid polyimide backbone in main chain or attachment of bulky side or pendant group have been widely used to improve processability and solubility in solvents [5–9]. Thus, polyimides with pendant bulky groups or alkyl silane groups are potential candidates for gas separation membranes with improved gas permeability and selectivity [10,11]. Restricted mobility of chain segments in combination with the presence of bulky groups preventing tight packing of the polymer chains should lead to membrane materials with improved selectivity without loss of permeability [12–14]. Coatings of polyimides with long alkyl group in side chain are found to have high pretilt angle for use in liquid crystal display devices [15,16]. The presence of functional group also modifies the properties of polyimides and expands the scope of their applications. For example, the presence of nitrile group improves adhesion of polyimide to copper [17,18]. Introduction of sulfonic acid group in polyimide modifies gas separation properties significantly [19,20]. The co-polyimides having the pendant carboxyl group have many uses such as micro filtration membranes, ion exchange resins and photosensitive materials [21–23]. The positive-patterning process using an aqueous alkaline developer is presently practiced for LSI manufacturing in terms of environmental issues. Kubota et al. [24,25], reported first positive photosensitive poly(amic acid) in which the pendant carboxylic acids were blocked with

---

[*] Corresponding author. Tel.: +91 2025893400x2070; fax: +91 2025893234.
E-mail address: vernekar@poly.ncl.res.in (S.P. Vernekar).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.03.001

O-nitro benzyl moieties as photosensitive functional group. Thus, carboxyl group, being reactive, offers further scope for the attachment of photosensitive and other groups by chemical reactions to modify properties of polyimides suitable for specific applications.

Considering the importance of carboxyl group in polyimides, in this paper, we report synthesis of a new diamine monomer, containing pendant benzoic acid group and the properties of the resulting polyimides and co-polyimides based on this diamine. Though, the polyimides containing carboxyl groups are reported in literature, carboxyl group in these polymers is attached to aromatic ring in main chain. Carboxyl group attached to aromatic ring in side chain should have more flexibility and easy access to further modifications by chemical reactions to introduce desired groups in side chain for specific applications. Thus, the objective of this work is to synthesize and characterize polyimides and co-polyimides containing carboxyl group in side chain and study the effect of pendant benzoic acid group on solubility, thermal property and film forming properties of polyimides.

2. Experimental

2.1. Reagents and solvents

ODPA, 6FDA, BPDA and BTDA were purchased from Aldrich and purified by sublimation. *N*-methyl-2-pyrollidinone (NMP), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethyl formamide (DMF) were distilled over CaH_2. Chloroform ($CHCl_3$), methanol, 4-hydroxy benzaldehyde, 1-chloro-2,4-dinitro benzene were purchased from s.d. fine-Chem Ltd and used without further purification. *m*-Cresol purchased from s.d fine-Chem Ltd, India, was distilled under reduced pressure and stored on molecular sieves.

2.2. Measurements

Melting points were determined in capillary on Buchi melting point instrument. IR spectra were recorded on a Perkin–Elmer 16 PC FT-IR spectrophotometer. The ^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer. Inherent viscosity of polymers was determined at a concentration of 0.5 g dl^{-1} at 30 °C using an Ubbelohde viscometer. Elemental analysis was carried out on Elementar vario EL. Thermo gravimetric analysis (TGA) was performed on Perkin–Elmer TGA 7 analyzer and the thermal stability of samples was determined in N_2 by measurement of the weight loss during heating at a rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer DSC 7 analyzer. T_g of the polymers were determined with DSC at a heating rate of 10 °C min^{-1} in N_2 atmosphere.. The X-ray diffraction experiments were performed using Rigaku Dmax 2500 diffractometer. The system consists of a rotating anode generator with a copper target and a wide-angle powder goniometer having diffracted beam graphite monochromator.

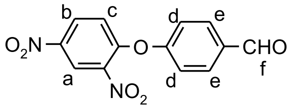
*2.3. Preparation of 2,4-dinitro-4′-formyl diphenyl ether (**I**)*

4-Hydroxy benzaldehyde (12.2 g, 0.1 mol) and 1-choro-2,4-dinitrobenzene (20.25 g, 0.1 mol) were dissolved in acetone (150 ml) in a 250 ml round bottomed flask fitted with a reflux condenser. Triethylamine (16.66 ml, 0.12 mol) was added to this solution and mixture was heated to reflux for 36 h. with stirring. Solvent acetone and excess triethylamine were distilled off and the residue was dissolved in chloroform (250 ml). The chloroform solution was washed with 5% HCl, 2% NaOH and repeatedly with water till free from alkali in a separating funnel and then dried with anhydrous Na_2SO_4. The solution, after filtration, was treated with activated charcoal, filtered and cooled. The compound separated was dried in a vacuum oven at 50 °C. Yield was 26 g (90%). Mp 120 °C.

Elemental analysis, calculated for $C_{13}H_8N_2O_6$: C, 54.16%; H, 2.77%; N, 9.72%. Found: C, 54.09%; H, 2.80%; N, 9.75%.

FT-IR (neat, cm^{-1}): 1710 (C=O); 1532, 1346 (NO_2 stretching) 1280, 1070 (C–O–C stretching) 1616, 1572 (aromatic).

^{1}H NMR ($CDCl_3$) δ: 10.9 (S, 1H, H_f); 9.2 (d, 1H, H_a); 8.7 (d, 1H, H_b); 8.3 (d, 2H, H_e); 7.8 (dd, 2H, H_d); 7.7 (dd, 1H, H_c).



I

*2.4. Preparation of 2,4-dinitro-4′-carboxyl diphenyl ether (**II**)*

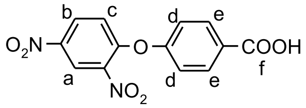
2,4-Dinitro-4′-formyl diphenyl ether (20.16 g, 0.07 mol) was dissolved in acetone (100 ml) in a 500 ml round bottomed flask. Sodium dichromate (36.55 g, 0.319 mol) dissolved in water (82 ml) was added to above solution. H_2SO_4 (60 ml) was added dropwise to this solution in 1 h and stirred overnight at room temperature. The reaction mixture was poured in 1 L of water. The precipitate was filtered and dissolved in 5% aqueous NaOH solution. The solution was filtered and neutralized with 10% H_2SO_4 solution. The precipitate obtained was filtered and washed with water. The product was recrystallized from methanol. Yield was 15.96 g (70%). Mp 260–263 °C.

Elemental analysis, calculated for $C_{13}H_8N_2O_7$: C, 51.31%; H, 2.63%; N, 9.21%. Found: C, 51.19%; H, 2.69%; N, 9.29%.

FT-IR (neat, cm^{-1}): 1680 (C=O); 1532, 1346 (NO_2

stretching) 1280, 1070 (C–O–C stretching) 1616, 1572 (aromatic).

^{1}H NMR ($CDCl_3$) δ: 9.25 (d, 1H, H_a); 8.78 (d, 1H, H_b); 8.38 (d, 2H, H_e); 7.68(dd, 2H, H_d); 7.6(d, 1H, H_c).



II

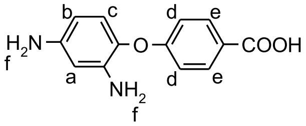
2.5. Preparation of 2,4-diamino-4′-carboxyl diphenyl ether (*III*)

A pressure vessel (Parr reactor), was charged with 2,4-dinitro-4′-carboxyl diphenyl ether (10.0 g, 0.04 mol) dissolved in methanol (150 ml) and 5% Pd/C (0.5 g). The reactor was flushed with hydrogen 2–3 times. The mixture was heated at 80 °C with stirring for 4 h. under 700 psi of hydrogen pressure. The reactor was cooled to room temperature. The solution was filtered to remove catalyst, treated with activated charcoal and filtered. The filtrate was concentrated by distilling off methanol and cooled. The solid separated was filtered, washed with ice-cold methanol and dried under vacuum at 50 °C. Yield was 8.5 g (85%). Mp 186 °C.

Elemental analysis, calculated for $C_{13}H_{12}N_2O_3$: C, 63.93%; H, 4.91%; N, 11.47%. Found: C, 63.85%; H, 4.95%; N, 11.54%.

FT-IR (neat, cm^{-1}): 1670 (C=O); 3376 (N–H stretching) 1604 (N–H deformation) 1280, 1070 (C–O–C stretching) 1616, 1572 (aromatic).

^{1}H NMR ($CDCl_3$) δ: 7.8 (d, 2H, H_e); 7.6 (d, 2H, H_d); 7.55 (d, 1H, H_c) 6.75 (d, 1H, H_b); 6.5 (m, 1H, H_a); 5.4 (s, 4H, NH_2).



III

2.6. Preparation of polyimides (PI_1, PI_2, PI_3 and PI_4)

In a 50 ml three necked round-bottom flask, equipped with a magnetic stirrer; N_2 inlet and guard tube, 2,4-diamino-4′-carboxyl diphenyl ether (0.3 g, 1.22 mmol) was dissolved in *m*-cresol (3 ml) in nitrogen atmosphere. To this solution, oxydiphthalic anhydride (0.378 g, 1.22 mmol) and *m*-cresol (3.8 ml) were added with stirring under N_2 atmosphere. The reaction mixture was heated to 190 °C in 1 h and stirred for 8 h at this temperature. The viscous solution was cooled to room temperature and poured in methanol (300 ml) while stirring. The precipitated white fibrous polymer was filtered off, washed thoroughly with methanol several times to remove *m*-cresol by decantation, filtered and dried in a vacuum oven at 150 °C overnight. Yield 0.613 g (95%), η_{inh} −0.49 dl g^{-1} in DMAc).

Elemental analysis calculated for $(C_{29}H_{14}O_8N_2)_n$: C, 67.18%; H, 2.70%; N, 5.40%. Found: C, 66.70%; H, 2.64%; N, 5.20%.

Other polymers of this diamine with different dianhydrides were prepared following same procedure.

PI$_2$ was prepared as a white fibrous solid in 94% yield by reacting with 6-FDA (η_{inh} −0.50 dl g^{-1} in DMAc).

Elemental analysis calculated for $(C_{32}H_{14}O_7N_2F_6)_n$: C, 58.89%; H, 2.14%; N, 4.29%. Found: C, 57.69%; H, 2.54%; N, 4.23%.

PI$_3$ was prepared as a yellow fibrous solid in 97% yield by reacting with BPDA (η_{inh} −0.59 dl g^{-1} in DMAc).

Elemental analysis calculated for $(C_{29}H_{14}O_7N_2)_n$: C, 69.32%; H, 2.78%; N, 5.57%. Found: C, 69.00%; H, 2.84%; N, 5.23%.

PI$_4$ was prepared as a yellow fibrous solid in 95% yield by reacting with BTDA (η_{inh} −0.61 dl g^{-1} in DMAc).

Elemental analysis calculated for $(C_{30}H_{14}O_8N_2)_n$: C, 67.42%; H, 2.64%; N, 5.28%. Found: C, 67.10%; H, 2.74%; N, 5.23%.

2.7. Preparation of co-polyimides (CPI_1, CPI_2, CPI_3 and CPI_4)

In a 50 ml three necked round-bottom flask equipped with a magnetic stirrer, N_2 inlet and guard tube 2,4-diamino-4′-carboxyl diphenyl ether (0.27 g, 1.098 mmol) was dissolved in *m*-cresol (3 ml) in nitrogen atmosphere. To this solution, 4,4′-bis{hexafluoroisopropylidene bis(phthalic anhydride}(6-FDA) (0.542 g, 1.22 mmol) and *m*-cresol (2 ml) was added. The solution was stirred under N_2 atmosphere for half an hour and to this 4,4′-oxydianilne(ODA) (0.024 g, 0.122 mmol) and *m*-cresol (2 ml) was added. The reaction mixture was heated to 190 °C in 1 h and stirred for 8 h at this temperature. The viscous solution was cooled to room temperature and poured in methanol (300 ml) while stirring. The precipitated white fibrous polymer was filtered off, washed thoroughly with methanol several times to remove *m*-cresol by decantation, filtered and dried in a vacuum oven at 150 °C overnight. Yield 0.810 g (97%), η_{inh} 0.42 dl g^{-1} in DMAc. The ratio of 2,4-diamino-4′-carboxyl diphenyl ether and 4,4′-oxydianiline in this copolyimide is 90:10 mol%.

Other co-polyimides of 6-FDA with different ratio of 2,4-diamino-4′-carboxyl diphenyl ether and ODA were prepared following similar procedure.

CPI$_2$ was prepared as a white fibrous solid in 96% yield by reacting 70:30 ratio of 2,4-diamino-4′-carboxyl diphenyl ether and 4,4′-oxydianiline with 6-FDA (η_{inh} −0.48 dl g^{-1} in DMAc).

CPI$_3$ was prepared as a white fibrous solid in 98% yield by reacting 50:50 ratio of 2,4-diamino-4′-carboxyl diphenyl ether and 4,4′-oxydianiline with 6-FDA (η_{inh} −0.67 dl g^{-1} in DMAc).

CPI$_4$ was prepared as a white fibrous solid in 95% yield by reacting 30:70 ratio of 2,4-diamino-4′-carboxyl diphenyl ether and 4,4′-oxydianiline with 6-FDA (η_{inh} −0.51 dl g^{-1} in DMAc).

3. Results and discussion

3.1. Monomer synthesis

2,4-Diamino-4′-carboxyl diphenyl ether can be prepared by different routes. Conventional route could be condensation of *p*-cresol with 1-chloro-2,4-dinitrobenzene followed by oxidation of methyl group of resultant 2,4-dinitro-4′-methyl diphenyl ether to carboxyl group and subsequent reduction of nitro groups to amino groups. We attempted this route. However, the yield of pure acid after oxidation of 2,4-dinitro-4′-methyl diphenyl ether with alkaline potassium permanganate was low. So, in this work, the new diamine monomer, 2,4-diamino-4′-carboxyl diphenyl ether, which contains pendant benzoic acid group, was prepared by unconventional route in three steps starting from 4-hydroxybenzaldehyde according to the reaction sequence described in Scheme 1.

2,4-Dinitro-4′-formyl diphenyl ether (**I**) was readily synthesized in high yield (90%) from 1-chloro-2,4-dinitrobenzene and 4-hydroxy benzaldehyde as described in Section 2. 2,4-Dinitro-4′-formyl diphenyl ether (**I**) was oxidized with sodium dichromate and H_2SO_4 at room temperature to give 2,4-dinitro-4′-carboxyl diphenyl ether (**II**) in 70% yield. Dinitro compound was reduced to corresponding diamine monomer by hydrogenation in parr-reactor and the resulting diamine was recrystallized from methanol.

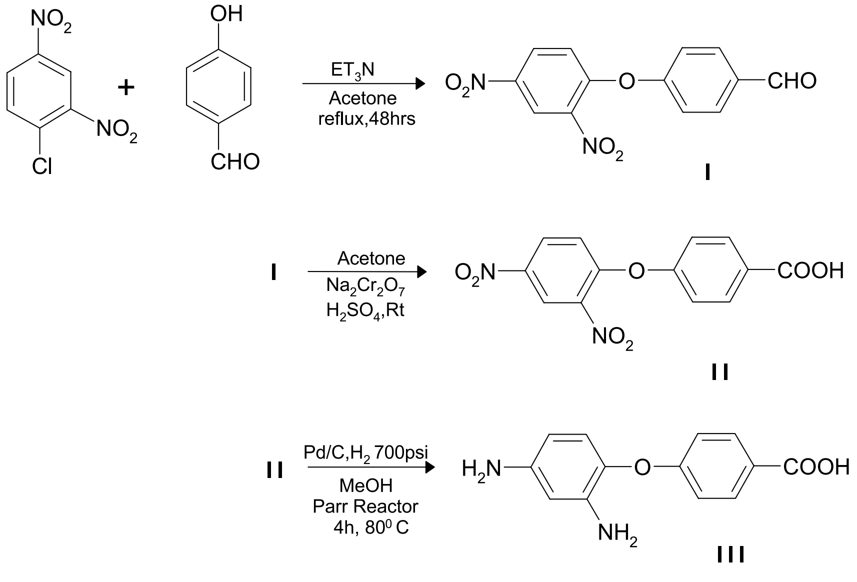
The FT-IR spectrum of 2,4-dinitro-4′-formyl diphenyl ether (Fig. 1 **I**) shows absorption bands at 1532 and 1346 cm^{-1} due to asymmetric and symmetric –NO_2 stretching vibration while 1280 and 1070 cm^{-1} bands are assigned to C–O–C asymmetric and symmetric stretching. Band at 870 cm^{-1} corresponds to aromatic C–N stretching vibration of C–NO_2 group. Characteristic absorption band of aldehyde due to (C=O) stretching is observed at 1710 cm^{-1}. After oxidation (Fig. 1 **II**), aldehyde peak at 1710 cm^{-1} disappears and peak at 1680 cm^{-1} of COOH group appears. The FT-IR spectrum of 2,4-diamino-4′-carboxyl biphenyl ether (Fig. 1 **III**) showed bands at 3381 cm^{-1} due to N–H stretching and the bands at 1532 and 1346 cm^{-1} of NO_2 group disappear. Bands at 1670 and 1216 cm^{-1} are due to carbonyl of COOH and ether linkage, respectively.

The ^{1}H NMR spectrum of 2,4-dinitro-4′-formyl diphenyl ether shows aromatic protons at 7.50–9.25 δ with expected multiples and integration. The single proton of aldehyde group appears at 10.9 δ (Fig. 2 **I**). The ^{1}H NMR spectrum of 2,4-dinitro-4′-carboxyl diphenyl ether (Fig. 2 **II**) shows aromatic protons at 7.50–9.25 δ with expected multiples and integration. Aldehyde proton disappeared. Protons of 2,4-diamino-4′-carboxyl diphenyl ether at 5.0–5.4 δ correspond to –NH_2 protons. Aromatic protons in the region 6.5–8.0 δ showed the expected multiplicity and integration values as shown (Fig. 2 **III**).

Elemental analysis values of C, H and N of all the compounds are close to theoretical values as described in Section 2. Thus FT-IR, NMR and Elemental analysis confirmed the structures of all these new compounds.

3.2. Polymer synthesis and characterisation

New polyimides containing pendant benzoic acid groups were prepared in good yields by condensing 2,4-diamino-4′-



Scheme 1. Synthesis of dinitro compounds **I**, **II**, and diamine **III**.

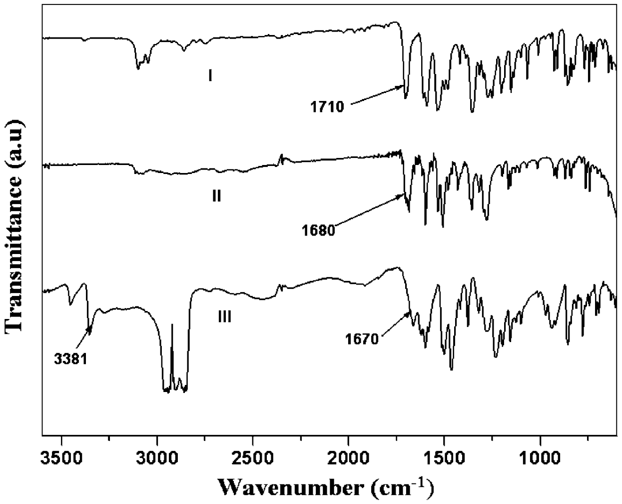


Fig. 1. FTIR spectra of dinitro compounds **I**, **II** and diamine **III**.

carboxyl diphenyl ether with commercially available aromatic dianhydrides (Scheme. 2), such as ODPA, BPDA, BTDA and 6-FDA in *m*-cresol by using the conventional one-step one-pot procedure as described in Section 2.

Co-polyimides of 2,4-diamino-4′-carboxyl diphenyl ether and oxydianiline in different mole ratio of (90:10, 70:30, 50:50 and 30:70.) with 6-FDA were synthesized in *m*-cresol in good yields as described in Section 2. All the polymers form thread like structure during precipitation with methanol. They form transparent, tough film on casting from solution.

The formation of polyimides was conformed by FT-IR spectroscopy. The FTIR spectra of PI_1, PI_2, PI_3 and PI_4 are shown in Fig. 3. The characteristic absorption bands of the imide ring appear near 1775 cm^{-1} corresponding to asymmetric C=O stretching, 1716 cm^{-1} due to symmetric C=O stretching, 1376 cm^{-1} of C–N stretching and 1092 and 739 cm^{-1} due to imide ring deformation. The absorption band at 1670 cm^{-1} due to COOH free group is not observed probably due to hydrogen bonding. These polymers are soluble in dilute sodium carbonate solution and can be precipitated on neutralization indicating the presence of carboxyl group.

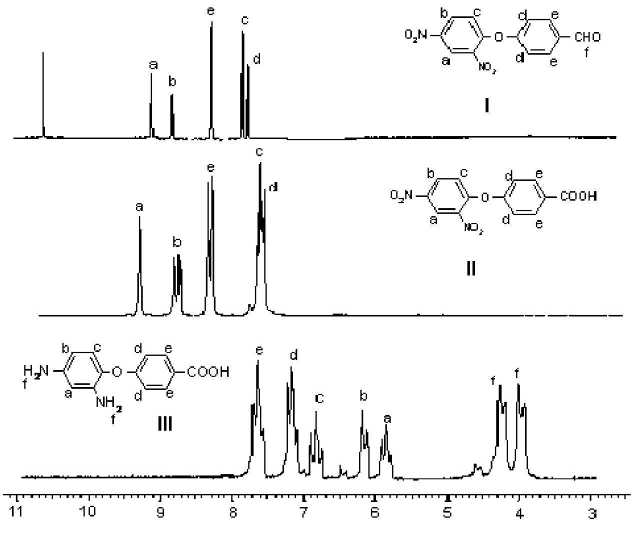


Fig. 2. NMR spectra of dinitro compounds **I**, **II** and diamine **III**.

The polymers displayed good solubility in polar aprotic solvents such as DMF, DMAc, DMSO and NMP (Table 1 and 2). However, these polymers are not soluble in common solvents such as chloroform, toluene, dioxane or tetrahydrofuran due to the presence of polar carboxyl group. They are soluble in *m*-cresol on heating. Compared to these polyimides, co-polyimides have better solubility in aprotic polar solvents. They are soluble in *m*-cresol at room temperature. The presence of flexible ether groups in main chain in co-polyimides improves the solubility. However, these polymers are also not soluble in common solvents. All the polymers are soluble in dilute aqueous $NaHCO_3$ solution on keeping overnight at ambient temperature due to the presence of free carboxyl group.

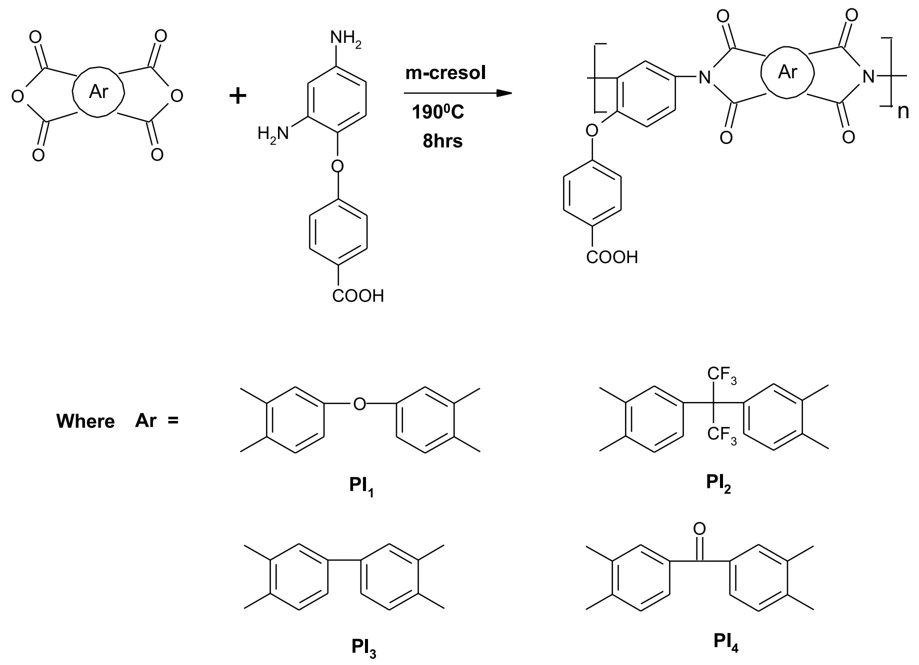
Thermal stability of these polymers was determined by thermogravimetric analysis (TGA) in nitrogen atmosphere at a heating rate of 10 °C min^{-1} (Table 3). Thermograms of these polymers are given in Figs. 4 and 5.

All the polymers show similar decomposition behavior. No weight loss was observed below 400 °C. The thermal decomposition takes place in two stages. Depending on the structure of dianhydride initial decomposition starts between 415 and 450 °C. Polymer based on ODPA shows highest IDT at 454 °C. First stage decomposition is mainly due to decarboxylation of carboxyl groups.

Temperature for 10% weight loss for these polyimides ranges from 495 to 580 °C depending on the structure of dianhydride. Polyimide based on ODPA has highest T_{10} of 580 °C. Maximum decomposition temp (T_{max}) of these polymers vary between 650 and 706 °C depending on structure of dianhydride. Polyimide based on ODPA shows high T_{max} of 706 °C where as PI based on BPDA shows low T_{max} of 650 °C. In general, these polyimides show good thermal stability. Co-polyimides also show similar behavior of decomposition. They decompose in two stages. IDT of these co-polyimides ranges from 410 to 418 °C depending on ODA content. T_{10} values range from 465 to 563 °C and these values increase with ODA content.

Glass transition temperature (T_g) of polyimides varies between 291 and 328 °C depending on structure of dianhydride. Thus, PI based on ODPA has lowest T_g due to flexible ether linkage, where as BPDA based polyimide has highest T_g due to rigid structure. Glass transition temperature of co-polyimides is influenced by ODA content. T_g of co-polyimides decreases with increase in ODA content due to the presence of flexible ether linkage in ODA.

Crystalline nature of these polymers was studied by X-ray diffraction. Fig. 6 represents typical X-ray



Scheme 2. Synthesis of polyimides.

Table 1
Inherent viscosity and film nature of polyimides and co-polyimides

Polymer code	Dianhydride	Diamine	Inherent viscosity η_{inh} (dl/g)	Film nature	Film colour
PI$_1$	ODPA	III	0.49	Flexible	Transparent
PI$_2$	6-FDA	III	0.50	Flexible	Transparent
PI$_3$	BPDA	III	0.59	Flexible	Light yellow
PI$_4$	BTDA	III	0.61	Semi flexible	Dark yellow
CPI$_1$	6-FDA	90% III/10% ODA	0.42	Brittle	Transparent
CPI$_2$	6-FDA	70% III/30% ODA	0.48	Flexible	Transparent
CPI$_3$	6-FDA	50% III/50% ODA	0.67	Flexible	Transparent
CPI$_4$	6-FDA	30% III/70% ODA	0.51	Flexible	Transparent

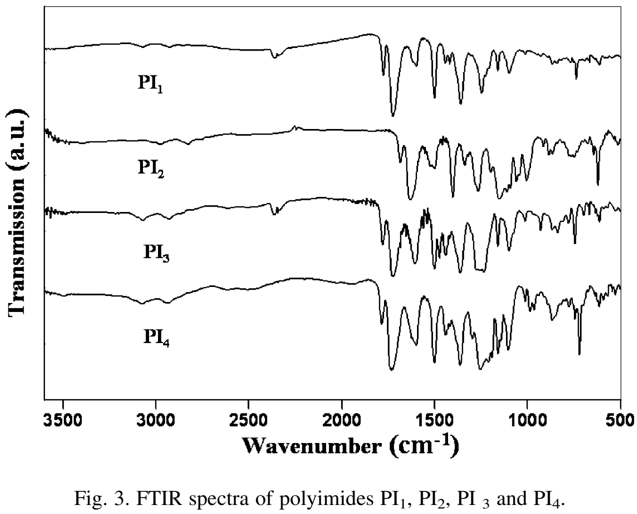


Fig. 3. FTIR spectra of polyimides PI$_1$, PI$_2$, PI $_3$ and PI$_4$.

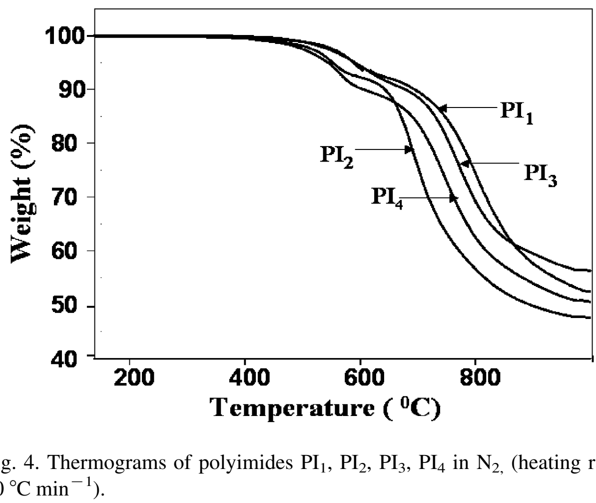


Fig. 4. Thermograms of polyimides PI$_1$, PI$_2$, PI$_3$, PI$_4$ in N$_2$, (heating rate 10 °C min^{-1}).

Table 2
Solubility behavior of polyimides and co-polyimides

Code	Dianhydride	Diamine	Solvents						
			DMF	DMAc	DMSO	NMP	H_2SO_4	*m*-cresol	Dioxane
PI_1	ODPA	III	++	++	++	++	++	+h	−−
PI_2	6-FDA	III	++	++	++	++	++	+h	−−
PI_3	BPDA	III	+h	++	++	++	++	+h	−−
PI_4	BTDA	III	+h	++	++	++	++	+h	−−
CPI_1	6-FDA	90% III/10% ODA	++	++	++	++	++	++	−−
CPI_2	6-FDA	70% III/30% ODA	++	++	++	++	++	++	−−
CPI_3	6-FDA	50% III/50% ODA	++	++	++	++	++	++	−−
CPI_4	6-FDA	30% III/70% ODA	++	++	++	++	++	++	−−

++, soluble at room temperature; +h, soluble at heating; and −−insoluble; DMF: *N*,*N*-dimethylformamide; DMAc, *N*,*N*-dimethyl acetamide; DMSO, dimethyl sulfoxide; NMP, *N*-methyl-2-pyrrolidone.

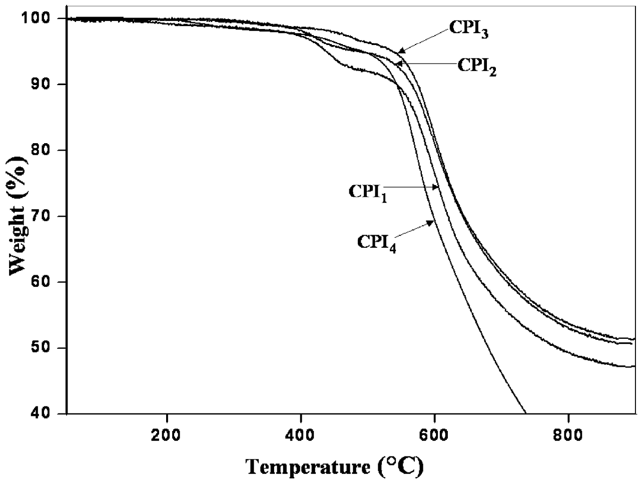


Fig. 5. Thermograms of co-polyimides CPI_1, CPI_2, CPI_3, CPI_4 in N_2, (heating rate 10 °C min^{-1}).

diffractograms for film specimen of polymers PI_1, PI_2, PI_3, CPI_1, CPI_2 and CPI_3. All the polymers are amorphous in nature.

4. Conclusions

New diamine monomer containing pendant benzoic acid moiety has been synthesized. Based on this diamine, new polyimides and co-polyimides containing pendant benzoic acid groups have been synthesized. Polyimides and co-polyimides have good solubility in aprotic polar solvents and they exhibit good thermal stability and high glass transition temperature. These polymers form tough, flexible and transparent films, which have potential applications in ion exchange membranes, gas separation membranes and immobilization of metal clusters for use as potential catalysts.

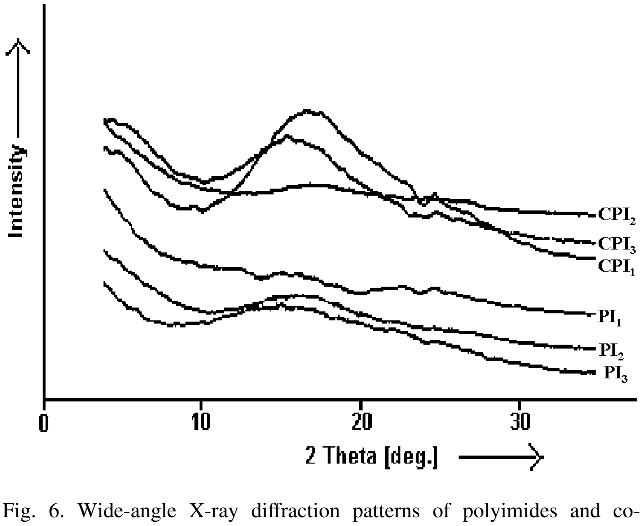


Fig. 6. Wide-angle X-ray diffraction patterns of polyimides and co-polyimides.

Table 3
Thermal properties of polyimides and co-polyimides

PI/CPI	Dianhydride	Diamine	IDT (°C)	T_{10} (°C)	$T_{\max}$ (°C)	T_g (°C)
PI_1	ODPA	III	454	580	706	291
PI_2	6-FDA	III	419	484	591	319
PI_3	BPDA	III	434	495	676	328
PI_4	BTDA	III	416	456	650	316
CPI_1	6-FDA	90% III/10% ODA	418	465	601	321
CPI_2	6-FDA	70% III/30% ODA	411	548	609	294
CPI_3	6-FDA	50% III/50% ODA	413	563	606	280
CPI_4	6-FDA	30% III/70% ODA	417	560	597	254

III: 2,4-Diamino-4′-carboxyl diphenyl ether. ODA: oxydianiline, IDT: initial decomposition temperature, T_{10} and $T_{\max}$: Temperature at which 10% and maximum weight loss of polymer takes place respectively, T_g: glass transition temperature.

Acknowledgements

The authors would like to thank Ministry of Nonconventional Energy Sources (MNES, New-Delhi) and CSIR-India for their financial support.

References

[1] Wilson D, Stenzenberger HD, Hergenrother PM, editors. Polyimides. New York: Chapman and Hall; 1990.
[2] Ghosh MK, Mittal KL, editors. Polyimides: fundamentals and applications. New York: Marcel Dekkar; 1996.
[3] Stroog CE, Endrey AL, Abramo SV, Berr CE, Edwards WM, Olivier KL. J Polym Sci Part A1 1965;3:1373.
[4] Sroog CE. J Polym Sci Macromol Rev 1976;11:161.
[5] Yang CP, Lin JH. J Polym Sci, Part A: Polym Chem 1993;31:2153.
[6] Bhowwik PK, Atkins EDT, Han H. ACS Polym Prepr 1995;31:2153.
[7] Li ZG, Meintgre JE, Tomka JG. Polymer 1993;34:551.
[8] Yang CP, Chen WT. Macromolecules 1993;26:4865.
[9] Eastmond C, paprotny J. J Mater Chem 1997;7:589.
[10] Roheson LM. J Membr Sci 1991;62:165.
[11] Freeman BD. Macromolecules 1991;32:375.
[12] Pixtan MR, Paul DR. Polymer 1995;36:3165.
[13] Me Hatties JS, Koros WJ, Paul DR. Polymer 1992;33:1701.
[14] Koros WJ, Fleming GK. J Membr Sci 1993;8:1.
[15] Lee SW, Kim SI, Park YH, Rim YN, Yoon HJ, Kim HC. Mol Cryst Sci Technol Sect A 2000;349:279.
[16] Lee KW, Pack SH, Lien A, Durning C, Fakura H. Macromolecules 1996;29:8894.
[17] Bauman D, Morgson A, Wolarz E. J Mol Struct 1994;135:169.
[18] Song D-m, Jung K-h, Moon J-h, Shin D-m. Opt Mater 2003;21(1–3):667.
[19] Kim YK, Park HM, Lee YM. Desalination 2002;145(1–3):389.
[20] Piroux F, Spuche EE, Mercier R, Pineri M, Gebel G. J Membr Sci 2002;209:241.
[21] Eastmond GC, M Gibbs M, Pacynko WF, Paprotny J. J Membr Sci 2002;207:29.
[22] Lee H-R, Lee. Y-D. J Polym Sci, Part A: Polym Sci 1989;27:1481.
[23] Fumushima T, Hosokawa K, Oyama T, Iijima Y, Tomoi M, Itataki H. J Polym Sci, Part A: Polym Chem 2001;39:934.
[24] Kubota S, Moriwaki T, Ando T, Fakami A. J App Polym Sci 1987;33:1763.
[25] Kubota S, Tanaka Y, Moriwaki T, Eto S. J Electrochem Soc 1991;138:1080.