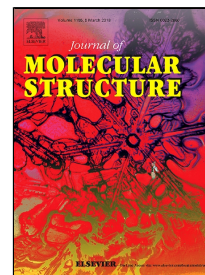


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Synthesis of polyimides from α,α' -bis(3-aminophenoxy)-p-xylene: Spectroscopic, single crystal XRD and thermal studies



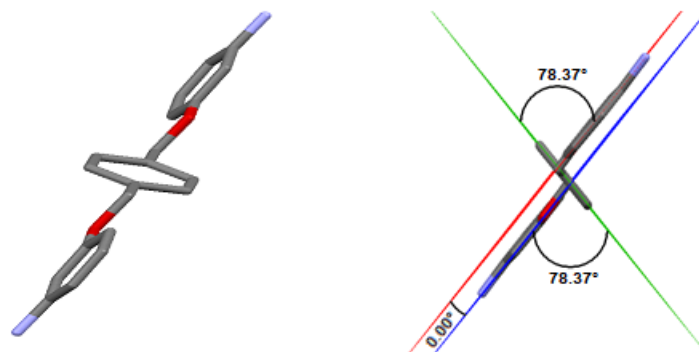
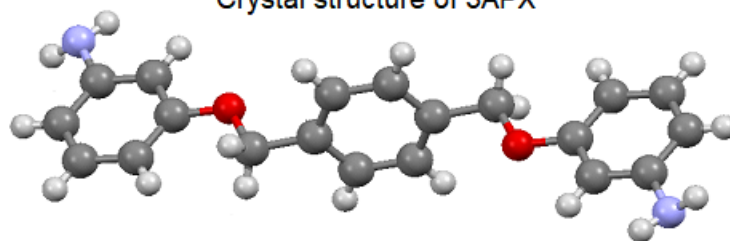
Ahmad Raza Ashraf, Zareen Akhter, Leonardo C. Simon, Vickie McKee, Charles Dal Castel

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Crystal structure of 3APX



Orientations of benzene rings

Synthesis of polyimides from α,α' -bis(3-aminophenoxy)-p-xylene: Spectroscopic, single crystal XRD and thermal studies

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Abstract

The meta-catenated ether-based diamine monomer α,α' -bis(3-aminophenoxy)-p-xylene (3APX) was synthesized from dinitro precursor α,α' -bis(3-nitrophenoxy)-p-xylene (3NPX). FTIR, ^1H and ^{13}C NMR spectroscopic studies accompanied by elemental analysis were performed for structural elucidations of 3NPX and 3APX. The spatial orientations of 3APX were explored by single crystal X-ray diffraction analysis. Its crystal system was found to be monoclinic, adopting the space group $P2_1/c$. The synthesized diamine monomer (3APX) was used for preparation of new series of polyimides by reacting with three different dianhydrides (BTDA, OPA, 6FDA). The relevant copolyimides were developed via incorporation of 4,4'-methylenedianiline (MDA) in the backbone of afore-synthesized polyimides. The structures of polyimides and copolyimides were verified by FTIR and ^1H NMR spectroscopic techniques. Their properties were evaluated by dynamic and isothermal TGA (nitrogen and air atmospheres) and WAXRD studies. Polyimides displayed significantly high thermal stability as their degradation started around 400 °C and it was improved further by execution of copolymerization strategy with MDA. The 5% weight loss temperature (T_5) of polyimides under nitrogen atmosphere was in the range of 425-460 °C while for copolyimides it increased to 454-498 °C. Thermal decomposition in air was slower than nitrogen between 400-550 °C however it was accelerated above 550 °C. Isothermal TGA disclosed that copolyimides have the ability to endure elevated temperatures for extended period. WAXRD analysis showed the amorphous nature of polyimides and copolyimides.

Keywords: Meta-catenated diamine; Single crystal analysis; Polyimides; Copolyimides; Thermal stability

1. Introduction

The diamines are valuable building blocks for the preparation of polymers like polyimides, polyamides and polyureas etc. These polymers are widely used in the modern technologies intended to reduce the cost of most demanding industrial processes by replacing metal, ceramic or glass. Polyimides have received special attention of scientists and engineers in the aerospace, automobile, microelectronics, optoelectronics and other advanced manufacturing industries as coatings, foams, matrices and gas separation membranes [1–3]. The broad spectrum applications of polyimides is attributed to excellent combination of several beneficial properties: exceptionally high thermal stability and glass transition temperature, excellent mechanical strength and stiffness at elevated temperatures [4,5], low dielectric constant and refractive index, good chemical and radiation resistance [6–8] etc. These properties depend upon chemical structure, composition, conformation, aggregation and inter/intra molecular interactions of polyimide chains, hence can be improved further or attuned as required. This can be achieved mainly through structural modifications of monomers so as to endow the chains with new moieties as well as execution of copolymerization strategy for manipulating composition, aggregation or interactions. Much research has been carried out by development of new monomers (dianhydride or diamine) capable of endowing resulting polyimides with unique features e.g. i) Troger's base, cardo, carbazole, benzoxazole or benzimidazole moieties [9–13], ii) special linkages like sulphone, siloxane, azomethine, thioether, ether, ketone or methylene [14–20], iii) high fluoride contents [21] or iv) kink in structure through ortho or meta catenation instead of para [22–24]. The isomeric monomers are capable of introducing asymmetry in the structure hence can affect the properties of resulting polymers to a large extent.

The copolymerization strategy i.e. preparation of copolyimides from two/three different dianhydrides or diamines goes along with the contribution from other authors looking at further enhancing and tailoring the properties of polyimides [25,26]. For example, Eichstadt et al. used a combination of aromatic, aliphatic and cycloaliphatic diamines in different proportions with 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA) and monitored the variation in thermal, mechanical and dielectric properties of resulting copolyimides [27].

The ambition of the research presented here is to evaluate the properties of polyimides obtained from meta-catenated diamine and determine the effect of ether, ketone and $-CF_3$ groups in dianhydrides (BTDA, ODPA, 6FDA) on properties of polyimides. Moreover, it is planned to enhance the thermal stability of polyimides by introducing 4,4'-methylenedianiline (MDA) as co-diamine in the structure. Main theme is to influence the charge transfer complex (CTC) formation between alternating electron-acceptor (dianhydride) and electron-donor (diamine) moieties of polyimide chains, since it triggers their properties.

In our previous study, polyimides and copolyimides were prepared from ortho-catenated diamine namely α,α' -bis(2-aminophenoxy)-p-xylene (2APX) [28]. It was observed that properties of polyimides were influenced by structural variations. In continuation of our efforts to investigate the monomer architecture effect on polyimide properties, this article is contributing with synthesis of meta-catenated diamine monomer α,α' -bis(3-aminophenoxy)-p-xylene (3APX), corresponding polyimides and copolyimides. It describes the: i) detailed structural characterization of synthesized materials by FTIR and NMR spectroscopic techniques along with elemental and single crystal X-ray diffraction analyses, ii) properties evaluation of polyimides and copolyimides by TGA (dynamic and isothermal under nitrogen and air atmospheres) and WAXRD techniques. The goals of the study were to firstly determine the thermal stability of

polyimides derived from meta-catenated diamine and secondly to monitor the effect of dianhydride structure variation and 4,4'-methylenedianiline (MDA) incorporation on thermal stability and morphology of polyimides.

2. Experimental

2.1. Materials

All chemicals and reagents used for the synthesis of diamine, polyimides and copolyimides were of highest purity and were used as received. Potassium carbonate (anhydrous), 3-nitrophenol, α,α' -dichloro-p-xylene and 4,4'-methylenedianiline (MDA) were obtained from Sigma Aldrich Germany. Palladium on activated carbon (5%), hydrazine hydrate (80%) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) were purchased from VWR Canada. 4,4'-oxydiphthalic anhydride (ODPA) and 4,4'-hexafluoroisopropylidenebisphthalic anhydride (6FDA) were procured from Akron Polymer Systems USA. Solvents ethanol, N,N-dimethylacetamide (DMAc) and N,N-dimethylformamide (DMF) obtained from various commercial sources were dried before use.

2.2. Instrumentation and measurements

Melting temperatures of the aromatic dinitro compound and diamine were determined in a capillary tube using Gallenkamp Electrothermal melting point apparatus. Labstar's Mbraun glove box was used for weighing and addition of dianhydrides under dry and inert atmosphere of nitrogen. VWR air circulating oven and Lindberg/Blue M furnace equipped with UP 150 controller were used for thermal curing of prepolymer (polyamic acid). Fourier transform infrared (FTIR) spectra ($400\text{-}4000\text{ cm}^{-1}$) of monomer and polymers were recorded using Thermo Nicolet-6700 spectrophotometer. Nuclear magnetic resonance (NMR) spectra of dinitro and diamine were recorded in deuterated DMSO- d_6 at room temperature using a Bruker

spectrometer operating at 300 MHz for ^1H NMR and at 75 MHz for ^{13}C NMR. Single crystal X-ray crystallographic data were collected at 150(2)K on a Bruker Apex II CCD diffractometer using Mo- $K\alpha$ radiation ($\lambda = 0.71073\text{\AA}$). The structure was solved by direct methods and refined on F^2 using all the reflections [29]. Thermogravimetric analysis (TGA) were carried out on TA instrument Q500 at a heating rate of 20 $^\circ\text{C}/\text{min}$ in a nitrogen and air atmospheres up to a maximum temperature of 800 $^\circ\text{C}$ for dynamic studies. For isothermal TGA, polymers were kept at 400 $^\circ\text{C}$ for 30 minutes under air atmosphere (ramping up at 50 $^\circ\text{C}/\text{min}$ from room temperature). TGA data was collected in terms of weight loss (%) as a function of temperature and time for dynamic and isothermal studies respectively. Wide-angle X-ray diffraction (WAXRD) analysis were carried out at room temperature on Bruker D8 FOCUS diffractometer using nickel-filtered Cu- $K\alpha$ radiation ($\lambda = 1.542\text{\AA}$, operating at 40 kV and 40mA) between 2 theta range of 5-50 $^\circ$ at an increment of 0.05 $^\circ$ with scan speed of 3 sec/step.

2.3. Monomer synthesis

The synthesis of the diamine monomer consists of two steps as shown in Fig. 1. The first step involves the preparation of precursor dinitro compound α,α' -bis(3-nitrophenoxy)-p-xylene (3NPX) which was reduced to the corresponding diamine α,α' -bis(3-aminophenoxy)-p-xylene (3APX) in the second step. The detailed description of each phase is given below:

2.3.1. Synthesis of α,α' -bis(3-nitrophenoxy)-p-xylene (3NPX)

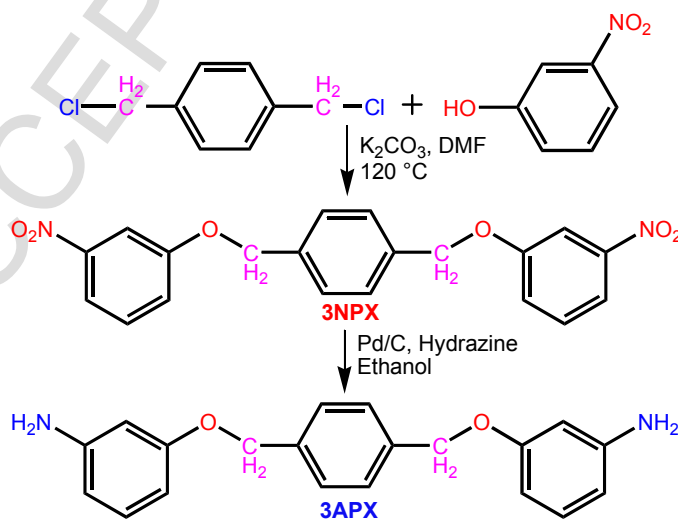
3NPX was synthesized by the Williamson's etherification reaction of 3-nitrophenol with α,α' -dichloro-p-xylene. For this purpose, a 250 mL two-neck round-bottom flask equipped with reflux condenser, nitrogen tube and magnetic stirrer was charged with 11.13 g (80 mmol) 3-nitrophenol, 7.00 g (40 mmol) α,α' -dichloro-p-xylene, 11.06 g (80 mmol) potassium carbonate (anhydrous) and 70 mL of DMF. The resulting mixture was heated at 120 $^\circ\text{C}$ for 16 hrs. The

color of solution changed from yellow to dark brown. Then solution was cooled to room temperature and poured into 800 mL of ice cold water. Light yellow precipitates were formed which were filtered, washed firstly with water and then with ethanol before drying. The product was obtained in 82% yield with melting temperature of 190 °C.

2.3.2. Synthesis of α,α' -bis(3-aminophenoxy)-p-xylene (3APX)

For the synthesis of 3APX, 3.0 g (7.89 mmol) of the obtained dinitro compound (3NPX), 0.10 g of 5% Pd/C and 70 mL ethanol were introduced into a 250 mL two-neck round-bottom flask and suspension was heated at 70 °C for 30 minutes. Then 10 mL of hydrazine hydrate (80%) was added dropwise at this temperature in 1 hr. The reaction was continued with stirring at reflux temperature for 12 hrs. The resultant clear, darkened solution was filtered while hot (applying vacuum filtration technique) to remove Pd/C, concentrated on rotary evaporator and cooled to get the solid product. The crude product was washed with water to remove any trapped hydrazine and finally recrystallized from ethanol. The diamine was obtained in 70% yield having melting point at 183 °C. The crystals suitable for single crystal X-ray diffraction analysis (SCXRD) were grown by slow evaporation of ethanol at room temperature.

Fig. 1 Scheme for synthesis of 3NPX and 3APX

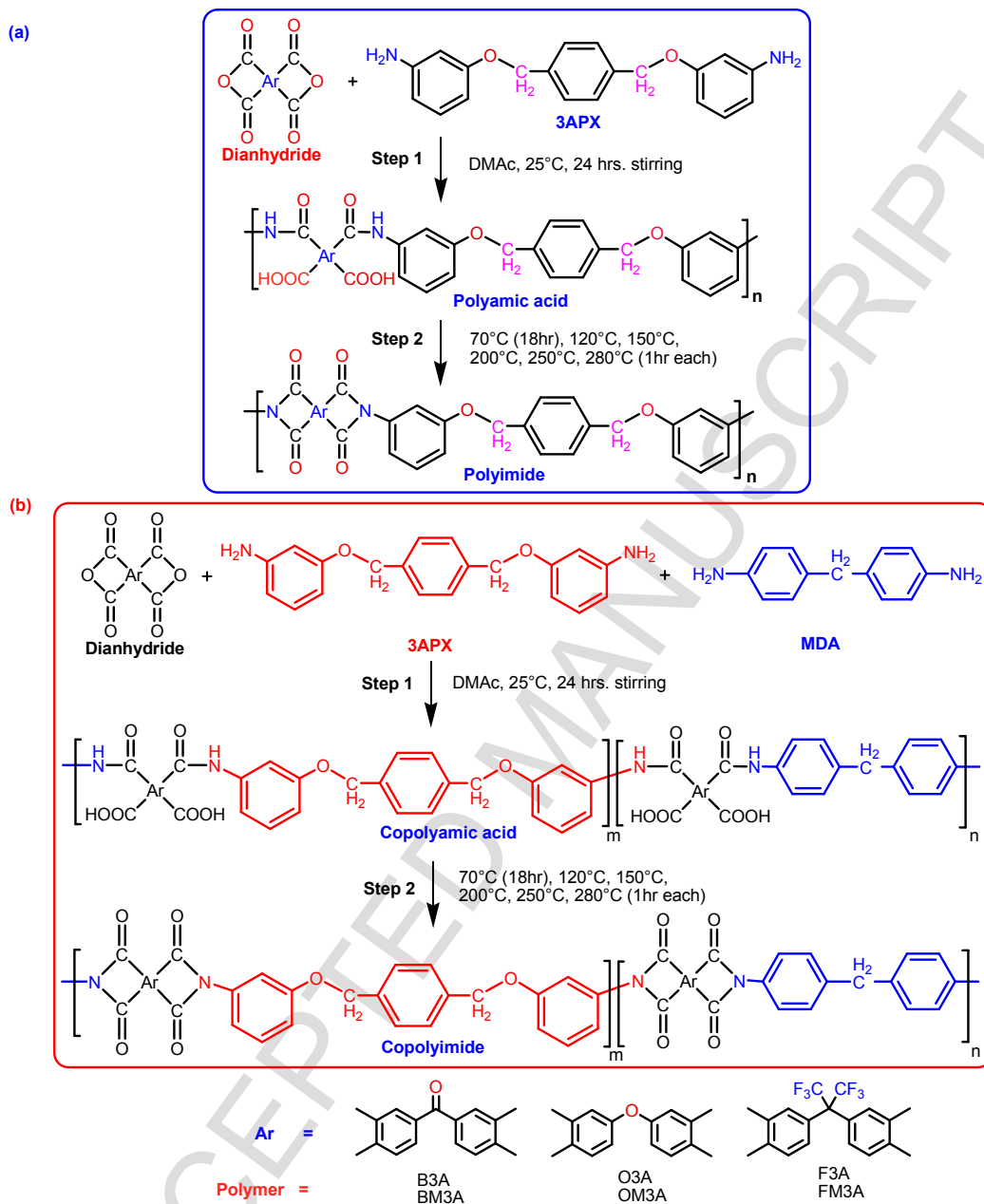


2.4. Synthesis of polyimides

A new series of polyimides (B3A, O3A, F3A) was developed by condensing the synthesized diamine 3APX with three different dianhydrides (BTDA, ODPA, 6FDA) via executing two-step route as shown in Fig. 2a. In the first step: diamine and dianhydride were reacted with each other to get the polyamic acid solution which was cyclodehydrated in second step to the corresponding polyimide. The synthesis of polyimide B3A is presented as an example for complete illustration of procedure: 0.320 g of 3APX (1 mmol) and 4 mL DMAc were introduced in a 50 mL two-neck round-bottom flask (prebaked on vacuum to exclude any moisture, equipped with nitrogen tube and magnetic stirrer) and a clear colorless solution was obtained after complete dissolution of diamine. Then equimolar amount of dianhydride BTDA (0.322 g, 1 mmol) was added to this solution in small portions with continuous stirring. In order to avoid the impurities due to side reactions of BTDA with moisture, weighing and addition was done in Labstar's Mbraun glove box having dry and inert atmosphere of nitrogen. The mixture was kept on stirring at room temperature for further 24 hrs to get the viscous polyamic acid solution. The resulting polyamic acid solution was thermally imidized by casting on a clean aluminum weighing dish followed by curing with a programmed procedure: 70 °C (18 hrs for solvent removal in air circulating oven), 120 °C, 150 °C, 200 °C, 250 °C, 280 °C (1hr each in furnace) to produce a fully imidized polyimide B3A. Similarly, 3APX was condensed with 4,4'-oxydiphthalic anhydride (ODPA) and 4,4'-hexafluoroisopropylidenebisphthalic anhydride (6FDA) for the preparation of O3A and F3A polyimides.

2.5. Synthesis of copolyimides

For the synthesis of copolyimides (BM3A, OM3A, FM3A) dianhydrides were treated with two different diamines (3APX and MDA) simultaneously (Fig. 2b). The complete explanation of synthetic process is provided by taking the example of BM3A: a 50 mL two-neck round-bottom flask (prebaked under vacuum and nitrogen) was charged with 0.160 g 3APX (0.5 mmol) and 0.099 g 4,4'-methylenedianiline (MDA) (0.5 mmol). Both the diamines were dissolved completely in 4 mL DMAc and a transparent light brown solution was obtained. Then 0.322 g BTDA (1 mmol) was added to this solution in small portions with continuous stirring. Labstar's Mbraun glove box was used for weighing and addition of dianhydride under dry and inert atmosphere of nitrogen so as to get rid of side products (impurities) due to its reaction with moisture. The mixture was kept on stirring at room temperature for further 24 hrs and a viscous copolyamic acid solution was obtained which was casted on a clean aluminum weighing pan and cured with a programmed procedure to obtain fully imidized copolyimide: 70 °C (18 hrs. for solvent removal in air circulating oven), 120 °C, 150 °C, 200 °C, 250 °C, 280 °C (1hr each in furnace). Same approach was used for preparation of copolyimides OM3A and FM3A while changing the dianhydrides.

Fig. 2 Scheme for synthesis of polyimides (a) and copolyimides (b)

3. Results and discussion

3.1. Characterization of monomer

The meta-catenated ether-based diamine α,α' -bis(3-aminophenoxy)-p-xylene (3APX) was synthesized via two-step approach according to scheme presented in Fig. 1. Firstly, the dinitro precursor α,α' -bis(3-nitrophenoxy)-p-xylene (3NPX) was prepared by the Williamson's etherification of 3-nitrophenol with α,α' -dichloro-p-xylene in N,N-dimethylformamide catalyzed by anhydrous potassium carbonate. Then 3NPX was reduced to corresponding diamine 3APX with hydrazine hydrate and Pd/C in ethanol. The structures of these compounds were confirmed by FTIR, ^1H and ^{13}C NMR spectroscopic studies, elemental and single crystal X-ray diffraction analyses.

FTIR and NMR spectroscopic studies

Data obtained from FTIR and NMR (^1H , ^{13}C) spectroscopic techniques is summarized in Table 1. The FTIR spectrum of 3NPX exhibited the characteristic absorption bands for nitro functionality (NO_2) at 1579 cm^{-1} and 1347 cm^{-1} corresponding to asymmetric and symmetric stretches respectively. Formation of ether linkage was established by the presence of absorption peak at 1256 cm^{-1} which is attributed to C-O-C stretches. The reduction of 3NPX to 3APX was certified by the disappearance of NO_2 absorptions and appearance of typical N-H stretching bands for primary amines at 3445 and 3421 cm^{-1} in the spectrum of 3APX. Absorption signals around 3050 and 2880 cm^{-1} were assigned to aromatic and aliphatic C-H stretches respectively. Structures of nitro precursor (3NPX) and its amino derivative (3APX) were also elucidated by ^1H and ^{13}C NMR spectroscopic techniques: phenyl protons resonated between 7.82-6.15 ppm depending upon nature of substituents attached e.g. the protons of aromatic ring adjacent to nitro group ($\text{H}^{2,4}$) resonated farthest downfield (7.82-7.79 ppm) in the ^1H NMR spectrum of 3NPX due

to deshielding caused by electron withdrawing effect of NO_2 group. However in case of 3APX, resonance signals for these protons were shifted upfield (6.17-6.15 ppm) which is a clear evidence in favor of nitro group reduction to amine. Moreover, presence of amine functionality in the structure of 3APX was also confirmed by the advent of two proton singlet at 4.99 ppm in the ^1H NMR spectrum as shown in Fig. 3. The appearance of two proton singlets at 5.27 and 5.06 ppm for 3NPX and 3APX respectively due to methylene protons (CH_2) is consistent with the formation of ether linkage. ^{13}C NMR spectroscopic study also supported the structures of compounds as the characteristic signals for all the carbon atoms were observed, represented by the ^{13}C NMR spectrum of 3APX in Fig. 4. The carbon atoms of the aromatic rings attached directly to the oxygen and nitrogen atoms i.e. C^1 and C^3 were strongly deshielded and their signals were observed most downfield. A slight upfield shift observed for carbon atoms at ortho ($\text{C}^{2,4}$) and para (C^6) positions of $-\text{NH}_2$ group in the ^{13}C NMR spectrum of 3APX as compared to 3NPX is attributed to electron donating effect of amine group. This also supported the successful conversion of NO_2 group to NH_2 functionality.

Elemental analysis

The data for elemental analysis summarized in Table 1 showed that the measured ratios of carbon (C), hydrogen (H) and nitrogen (N) are in good agreement with the calculated proportions for each element in the synthesized compounds which is reinforcing the proposed structures of compounds (3NPX, 3APX).

Table 1 FTIR, NMR and Elemental analysis data of 3NPX and 3APX

Technique	3NPX	3APX
FTIR (cm ⁻¹)	3085 (Ar-H), 2883 (CH ₂), 1579 (NO ₂ asym), 1347 (NO ₂ sym), 1256 (C-O-C)	3445, 3421 (NH ₂), 3040 (Ar-H), 2875 (CH ₂), 1275 (C-O-C)
¹H NMR (ppm)	7.82-7.79 (2H, m, H ^{2,4}), 7.65-7.63 (1H, m, H ⁵), 7.59-7.52 (3H, m, H ^{6,9,10}), 5.27 (2H, s, CH ₂)	7.42 (2H, s, H ^{9,10}), 6.92-6.87 (1H, m, H ⁵), 6.22-6.20 (1H, m, H ⁶), 6.17-6.15 (2H, m, H ^{2,4}), 5.06 (2H, s, CH ₂), 4.99 (2H, s, -NH ₂)
¹³C NMR (ppm)	160.64 (C ¹), 152.37 (C ³), 138.27 (C ⁸), 130.43 (C ⁵), 128.27 (C ^{9,10}), 122.74 (C ⁶), 114.28 (C ⁴), 109.92 (C ²), 69.13 (C ⁷)	159.79 (C ¹), 150.46 (C ³), 137.40 (C ⁸), 130.02 (C ⁵), 128.01 (C ^{9,10}), 107.53 (C ⁴), 102.66 (C ⁶), 100.74 (C ²), 68.91 (C ⁷)
Elemental Analysis	% Calcd: C = 63.16, H = 4.21, N = 7.37 % Measd: C = 63.04, H = 4.16, N = 7.15	% Calcd: C = 75.00, H = 6.25, N = 8.75 % Measd: C = 74.60, H = 6.35, N = 8.50

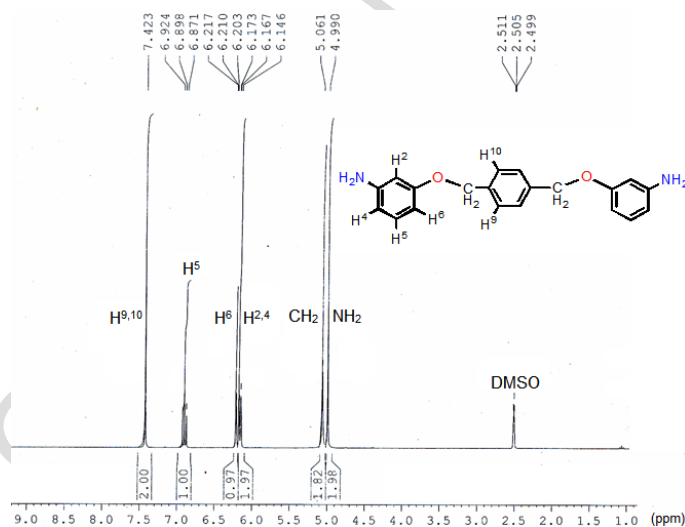
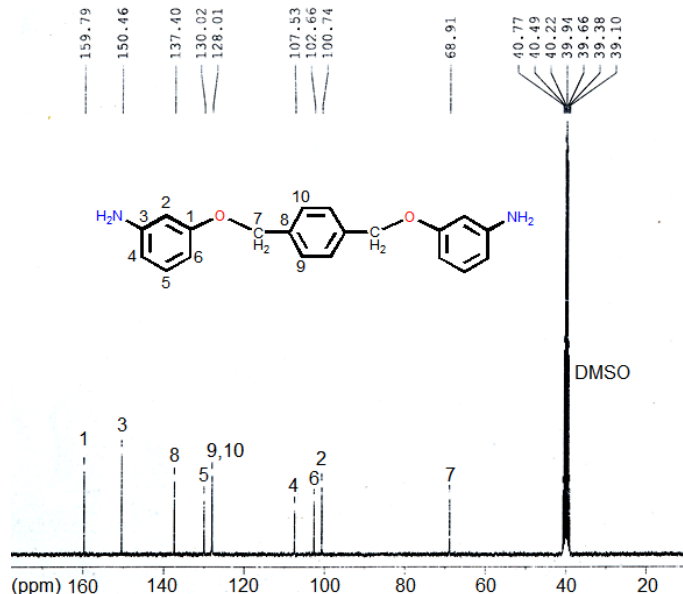
Fig. 3 ¹H NMR spectrum of 3APX

Fig. 4 ^{13}C NMR spectrum of 3APX

Single crystal X-ray diffraction analysis

Further evidence of successful synthesis of diamine monomer (3APX) is offered from single crystal X-ray diffraction (SCXRD) analysis. Parameters for data collection and refinement are summarised in Table 2. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms were inserted at calculated positions using a riding model. The asymmetric unit of 3APX contains two independent half-molecules, each lying on a center of symmetry. One of these is shown in Fig. 5a. In both molecules the terminal aminophenoxy units are parallel to each other and approximately orthogonal to the central phenyl ring with interplanar angles of $78.37(5)^\circ$ and $79.97(5)^\circ$ for independent molecules. The Fig. 5b is demonstrating the orientations of benzene rings in one molecule. There are no unusual bond lengths or angles in either molecule. However, two different types of intermolecular hydrogen bonding i.e. amine-amine (Fig. 5c) and amine-ether along with other short contacts in the form of H-H and π -H interactions (Fig. 5d) are detected between the molecules. The data for hydrogen-bond geometries is presented in Table 3. This hydrogen bonding links the molecules

into a network composed of linked sheets of independent molecules in the bc plane as shown in Fig. 6.

Table 2 Single crystal data and structure refinement for 3APX.

Empirical formula	$C_{20} H_{20} N_2 O_2$	
Formula weight	320.38	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 9.319(3)$ Å	$\alpha = 90^\circ$
	$b = 17.855(6)$ Å	$\beta = 95.217(6)^\circ$
	$c = 10.136(4)$ Å	$\gamma = 90^\circ$
Volume	1679.5(10) Å ³	
Z	4	
F(000)	680	
Crystal description	orange block	
Reflections collected	16863	
Independent reflections	4181 [R(int) = 0.0224]	
Max. and min. transmission	0.9877 and 0.9693	
Goodness-of-fit on F ²	1.039	
Final R indices [I > 2σ(I)]	R1 = 0.0443, wR2 = 0.1112	
R indices (all data)	R1 = 0.0585, wR2 = 0.1204	
Largest diff. peak and hole	0.253 and -0.186 e.Å ⁻³	

Fig. 5 Molecular structure of one of the two independent, centrosymmetric molecules of 3APX (a), orientations of benzene rings in molecule (b), intermolecular amine-amine hydrogen bonding (c), intermolecular amine-ether hydrogen bonding, H-H and π -H interactions (d).

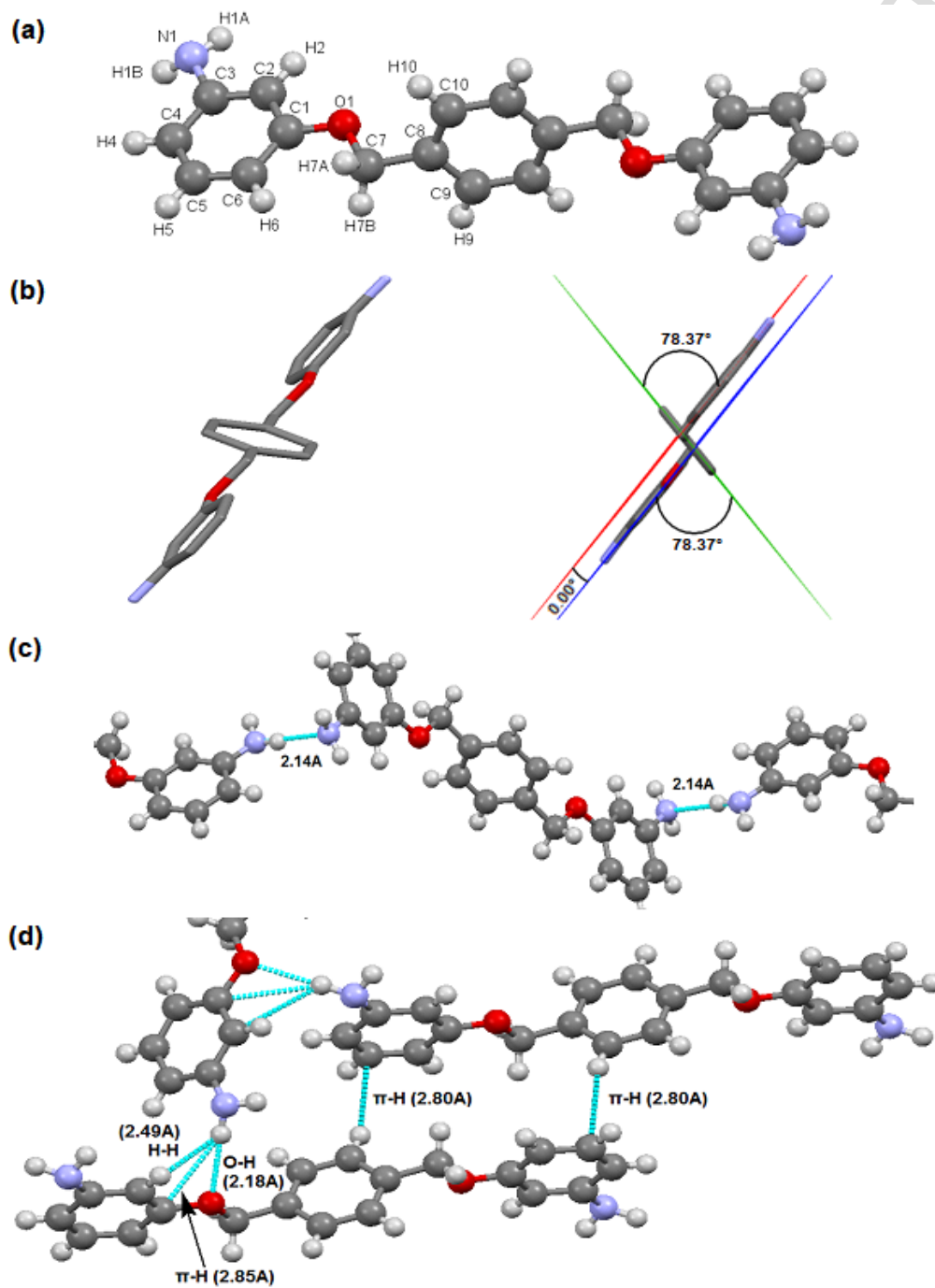
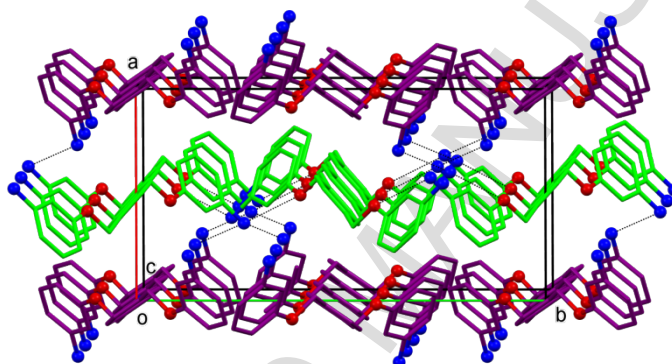


Table 3 Hydrogen-bond geometry (Å, °) for 3APX

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1B\cdots O1^i$	0.96	2.18	3.137 (18)	174
$N2-H2A\cdots N1^{ii}$	0.95	2.14	3.092 (2)	174
$N2'-H2'A\cdots O2^{ii}$	0.90	2.25	3.058 (7)	150

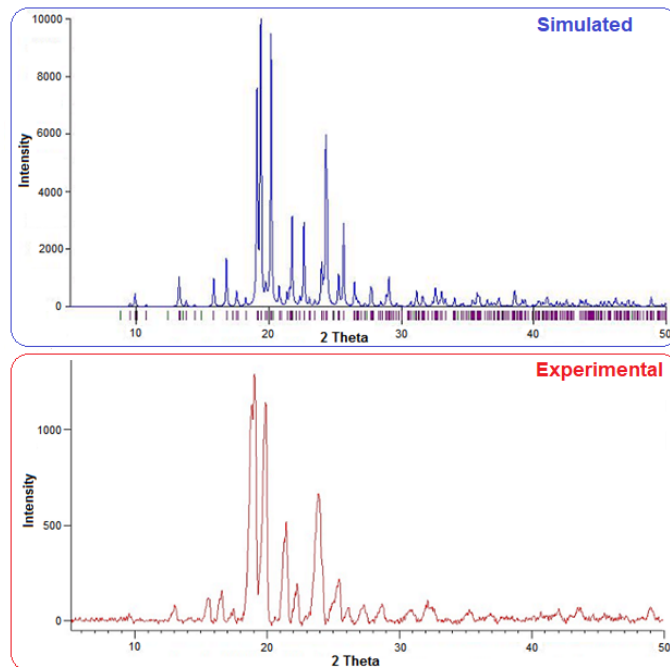
Symmetry codes: (i) $x, -y+1/2, z+1/2$; (ii) $x, -y+1/2, z-1/2$.

Fig. 6 Unit cell packing plot for 3APX. The carbon atoms of the two independent molecules are shown in green or purple, hydrogen bonds are shown as dashed lines.



Simulated and experimental powder XRD

The single crystal X-ray diffraction analysis was also used for structural verification of 3APX via comparing powder X-ray diffractograms (simulated and experimental). For this study, the simulated pattern was calculated from CIF file using Mercury software while experimental diffractogram was determined by analyzing the powder sample of synthesized compound (3APX) on wide angle X-ray diffractometer. The comparative simulated and the experimental diffractograms shown in Fig. 7 are showing reasonable matching with each other, thus further confirming the successful synthesis of diamine monomer.

Fig. 7 Simulated and experimental wide angle X-ray diffractograms for 3APX

3.2. Characterization of polyimides and copolyimides

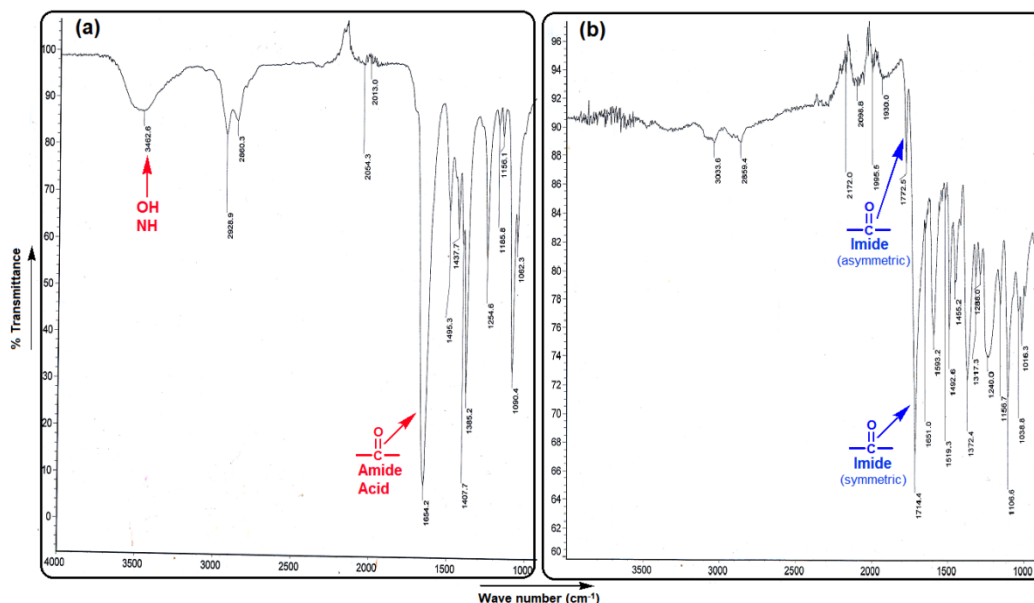
The diamine 3APX was first condensed with three commercially available dianhydrides (BTDA, ODPDA, 6FDA) for synthesis of simple polyimides labelled as B3A, O3A and F3A depending upon type of dianhydride used (these are referred as the polyimides because they were prepared using the single diamine). Then 3APX and the same dianhydrides were reacted with each other in the presence of 4,4'-methylenedianiline (MDA) as a co-diamine and three new copolyimides BM3A, OM3A and FM3A were prepared (they are referred as copolyimides because two diamines were used in their synthesis). The polymerization in both cases was carried out by two-step method: the first step involves the formation of polyamic acid solution while the second step consists of cyclodehydration of the resulting polyamic acid solution by thermal imidization.

The structures of the polyimides and copolyimides were evaluated by FTIR spectroscopic technique: both at polyamic acid stage (prepolymer) and after imidization. At polyamic acid stage, appearance of absorption bands around 1650 cm^{-1} corresponding to amide carbonyl

supported the condensation of diamines with dianhydrides. OH and NH groups of polyamic acid displayed broad absorption bands in their typical region of 3100-3600 cm^{-1} . FTIR spectra of polyimides and copolyimides showed characteristic absorption bands associated with the five membered imide ring around 1780 and 1715 cm^{-1} (asymmetric and symmetric C=O stretches respectively) along with C-N-C stretching absorptions around 1370 cm^{-1} . The completion of the imidization (i.e. conversion of polyamic acid to polyimide) was confirmed by the disappearance of OH and NH bands and shifting of carbonyl stretching vibrations towards higher frequency i.e. from 1650 to 1715 cm^{-1} . FTIR data for the polyimides and copolyimides is listed in [Table 4](#). Representative FTIR spectra of polyimide B3A at the polyamic acid stage and after imidization are shown in [Fig. 8](#).

Table 4 FTIR data (cm^{-1}) of polyimides and copolyimides

Polymer	OH, NH	C=O	OH, NH	C=O	C-N
	Before imidization		After imidization		(imide)
B3A	3463	1654	-	1714,1773	1372
O3A	3424	1647	-	1712,1773	1375
F3A	3478	1658	-	1717,1781	1368
BM3A	3437	1645	-	1718,1772	1371
OM3A	3525	1650	-	1715,1776	1372
FM3A	3462	1652	-	1714,1782	1372

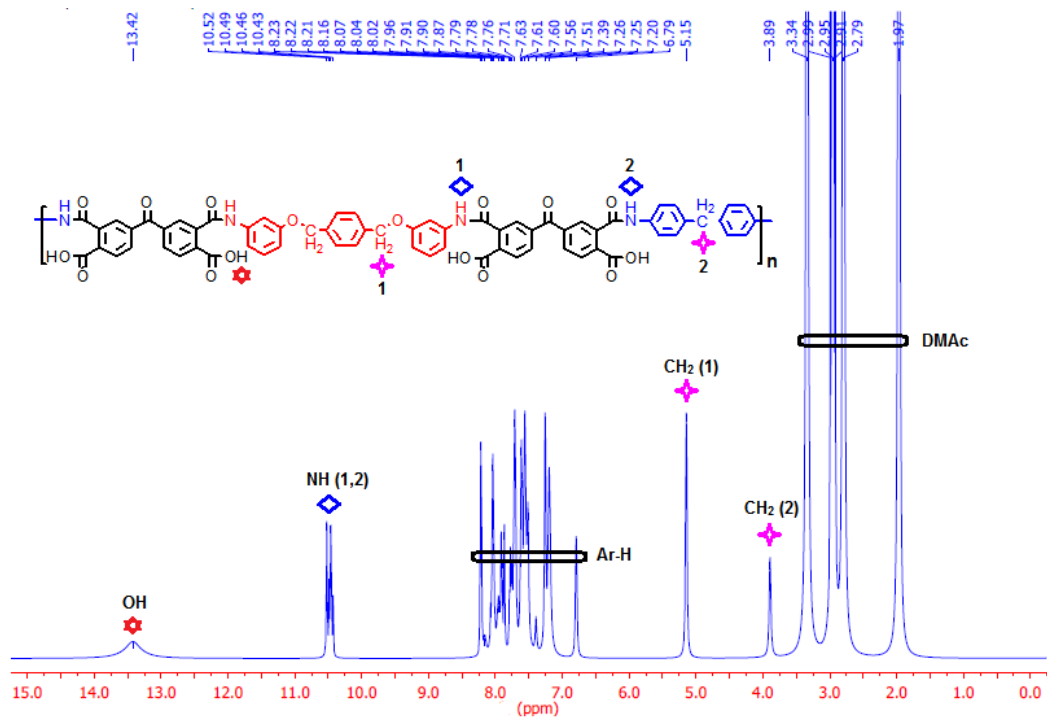
Fig. 8 FTIR spectra of B3A at polyamic acid stage (a) and after imidization (b)

¹H NMR spectra of all the polymers and copolymers were recorded at the polyamic acid stage since the final polymers (polyimides and copolyimides) were insoluble. This technique complemented the FTIR spectroscopy in terms of amide acid formation as signals for amide and carboxylic acid protons were observed around 10 and 13 ppm respectively [30]. Moreover, absence of any signal due to amine protons at 4.99 ppm (present in spectrum of 3APX) confirmed the consumption of amino groups due to its reaction with dianhydride moieties. Protons of aromatic rings resonated in their characteristic region 8.23-6.74 ppm depending upon their position in the backbone and nature of substituents attached. Two-proton singlet signals around 5.10 ppm observed in the spectra of polyamic acids are attributed to methylene groups present in the structure inherited from diamine 3APX. As expected, ¹H NMR spectra of copolyamic acids displayed two such signals around 5.10 and 3.89 ppm which are confirming the presence of two different types of CH₂ moieties in the polymer chains acquired from two different diamines i.e. 3APX and MDA, hence it is confirming the preparation of copolyimide. Among these signals, methylene protons of 3APX resonated downfield as compared to MDA.

Data obtained by ^1H NMR spectroscopic study of polymers and copolymers at polyamic acid stage is summarized in Table 5. The representative ^1H NMR spectrum of copolymer BM3A with the assignment of protons is shown in Fig. 9 which is in complete agreement with the proposed structure.

Table 5 ^1H NMR data (ppm) of polymers and copolymers at polyamic acid stage.

Polymer	OH	Amide	Ar-H	CH ₂	CH ₂
				(3APX)	(MDA)
B3A	13.40	10.48-10.45	8.20-6.74	5.07	-
O3A	13.42	10.46-10.38	8.03-6.74	5.09	-
F3A	13.53	10.52-10.46	8.09-6.76	5.09	-
BM3A	13.42	10.52-10.43	8.23-6.79	5.15	3.89
OM3A	13.32	10.36-10.31	7.99-6.74	5.09	3.87
FM3A	13.46	10.50-10.46	8.04-6.78	5.12	3.89

Fig. 9 ^1H NMR spectrum of BM3A at polyamic acid stage

3.3. Thermal stability

Thermal behavior of synthesized polyimides and their corresponding copolyimides was evaluated by three different types of thermogravimetric analysis: i) temperature scan (dynamic) under nitrogen, ii) temperature scan (dynamic) under air and iii) isothermal under air. The ambition of the study was to evaluate the performance of polyimides and copolyimides in high temperature resistant applications; because most often polymer system undergoes failure due to extended exposure at a particular temperature at which short time exposure does not induce severe degradation.

3.3.1. Dynamic thermal analysis under nitrogen

In this study the weight loss was measured by increasing the temperature of system from 50-800 °C at a rate of 20 °C/minute under nitrogen atmosphere. The data was analyzed in terms of weight loss (%) for thermogravimetric analysis (TGA) and the derivative of the weight loss

(%/°C) for differential thermogravimetric analysis (DTG) as a function of temperature. The representative comparative TGA and DTG thermograms are shown in Fig. 10 and temperatures (°C) at three weigh losses i.e. 2, 5 and 10% symbolized as T_2 , T_5 and T_{10} respectively are summarized in Table 6. The T_2 is most indicative of the onset of the thermal degradation, whereas T_5 and T_{10} provide information about stability after the degradation has already started. It is evident from graphics in Fig. 10 and values of T_2 in the tabulated data that polyimides and copolyimides displayed relatively high thermal stability as their thermal decomposition started around 400 °C. The temperature at 5% weight loss (T_5) for polyimides was observed in the range of 425-460 °C while T_{10} was found between 466-498 °C. Residual weight at 800 °C (R_{800}) was also measured and found between 48-62%. The comparison of T_2 , T_5 , T_{10} and R_{800} revealed that polyimides derived from BTDA (B3A) are thermally more stable than ODPDA (O3A) and 6FDA (F3A) counterparts (Fig. 10a).

Thermogravimetric analysis of copolyimides disclosed that incorporation of 4,4'-methylenedianiline (MDA) in the backbone of polyimides resulted in enhancement of their temperature resistance as T_5 and T_{10} followed an increasing trend towards higher temperatures as compared to their respective polyimides (Fig. 10b). In case of polyimide B3A and its respective copolyimide BM3A: T_5 & T_{10} were increased from 460 to 498, 498-546 °C respectively. Overall for copolyimides, T_5 ranged between 454-498 °C, T_{10} from 498-546 °C and R_{800} was found to be 49-63% with same order of thermal stability i.e. BM3A > OM3A > FM3A. Shape of TGA curves suggested multistep degradation mechanisms for polyimides and copolyimides, this supposition was supported by different peaks in DTG curves as shown in Fig. 10.

3.3.2. Dynamic thermal analysis under air

Thermal behavior of polyimides and copolyimides was also evaluated by changing the atmosphere from nitrogen to air while keeping the same heating rate and temperature range of dynamic TGA under nitrogen (20 °C/minute and 50-800 °C). It was observed that air slowed the decomposition between 400-550 °C in comparison of nitrogen atmosphere as demonstrated by representative TGA and DTG curves of O3A in Fig. 10c along with slight shift of T_{10} value towards higher temperature i.e. from 467 to 481 respectively (Table 6). However, the degradation of polymers was accelerated after 550 °C as a result R_{800} were reduced (from 52 to 14% for O3A). 6FDA based polymers (F3A & FM3A) were decomposed completely in air as no residue was left at 800 °C. Like the findings of dynamic thermal analysis under nitrogen, these studies (temperature scan under air) also showed that thermal stability of polyimides was improved by incorporation of MDA in their backbone: T_5 of polyimide B3A was increased from 466 to 503 °C for its corresponding copolyimide BM3A (Fig. 10d).

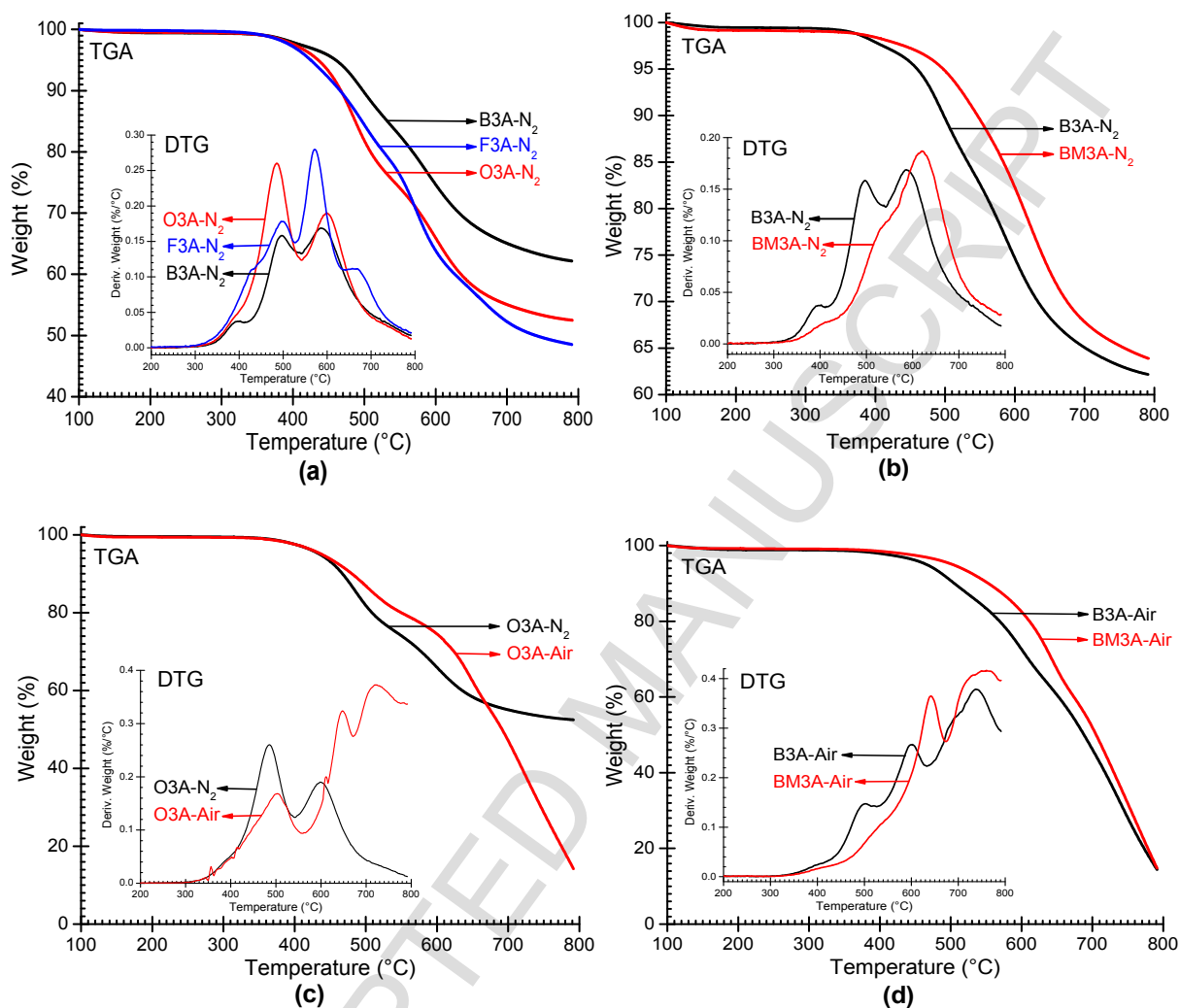
Table 6 Dynamic thermogravimetric analysis (TGA) data of polyimides and copolyimides

Polymer	T_2 (°C)		T_5 (°C)		T_{10} (°C)		R_{800} (%)	
	N ₂	Air	N ₂	Air	N ₂	Air	N ₂	Air
B3A	397	396	460	466	498	506	62	14
O3A	391	391	436	438	467	481	52	14
F3A	387	387	425	431	466	478	48	0
BM3A	420	427	498	503	546	553	63	15
OM3A	411	411	463	478	501	529	58	15
FM3A	400	400	454	473	498	524	49	0

T_2 = Temperature at 2% weight loss T_5 = Temperature at 5% weight loss

T_{10} = Temperature at 10% weight loss R_{800} = Residual weight (%) at 800 °C

Fig. 10 Comparative dynamic TGA and DTG graphics (Nitrogen/Air, 20 °C/min): B3A-N₂, O3A-N₂, F3A-N₂ (a), B3A-N₂, BM3A-N₂ (b), O3A-N₂, O3A-Air (c), B3A-Air, BM3A-Air (d)



3.3.3. Isothermal TGA

Dynamic thermal analysis revealed that polyimides and copolyimides retained their structural integrity at elevated temperatures (350-400 °C) thus have the potential to be used as high temperature resistant materials. However life time at particular temperature is another important criterion behind the selection of polymers for specific applications. In order to evaluate the properties of synthesized polyimides and copolyimides in this respect, isothermal thermogravimetric analysis (TGA) were performed. During these experiments, temperature of

the system was increased at 50 °C/min up to the selected isothermal point; material was retained at that temperature for 30 minutes in air and change in weight % was recorded as function of time. The selection of temperature for this study was done by analyzing polyimide B3A isothermally at three different temperatures of 350, 400 and 450 °C based on the previous investigation (Dynamic TGA). Fig. 11a shows that no weight loss was observed during isothermal treatment at 350 °C. However, weight loss was recorded at 400 °C which was more significant at 450 °C than at 400 °C. Therefore 400 °C was selected as a suitable temperature for comparing samples. Data is summarized in Table 7 and representative isothermograms are shown in Fig. 11b,c. These results complemented the dynamic TGA findings: 1) degradation of polymers started around 400 °C, 2) BTDA derivatives (B3A and BM3A) are thermally more stable (Fig. 11b) and 3) thermal stability of polyimides was improved by copolymerization with MDA as copolyimides displayed less weight loss after 30 minutes of isothermal treatment (Fig. 11c). The weight loss at the start of experiment i.e. till 4 minutes or 200 °C is attributed to trapped moisture in chains. This was verified by subjecting the polyimide B3A to a second run after 12 hrs of first run; results are shown in Fig. 11d.

Moreover, the shape of curves in Fig. 11b suggested that decomposition rates of polymers were higher at the start of experiments i.e. between 5-15 minutes, however it followed decreasing trend with the passage of time which was more significant for 6FDA based polymers (F3A, FM3A). This is attributed to the degradation of terminal groups of polymer chains at the start of experiment: resulting in the evolution of CO, CO₂, H₂O, CH₄ along with formation of thermally stable products like aromatic hydrocarbons, amines and/or nitriles. These have been observed by other authors using TGA/FTIR/MS techniques to investigate the mechanism of polyimide degradation [31]. Once these groups are broken down then cleavage of internal portion of

polymer chain becomes difficult or slower at 400 °C. These justifications were also found supported from the results of Fig. 11d where the rate of decomposition (slope) is slower in the second run as compared to first one since end groups were consumed during first run. Such observations suggest that thermal stability could possibly be further improved by additional studies on the cyclodehydration of the polyamic acid.

Table 7 Isothermal thermogravimetric analysis (TGA) data of polyimides and copolyimides

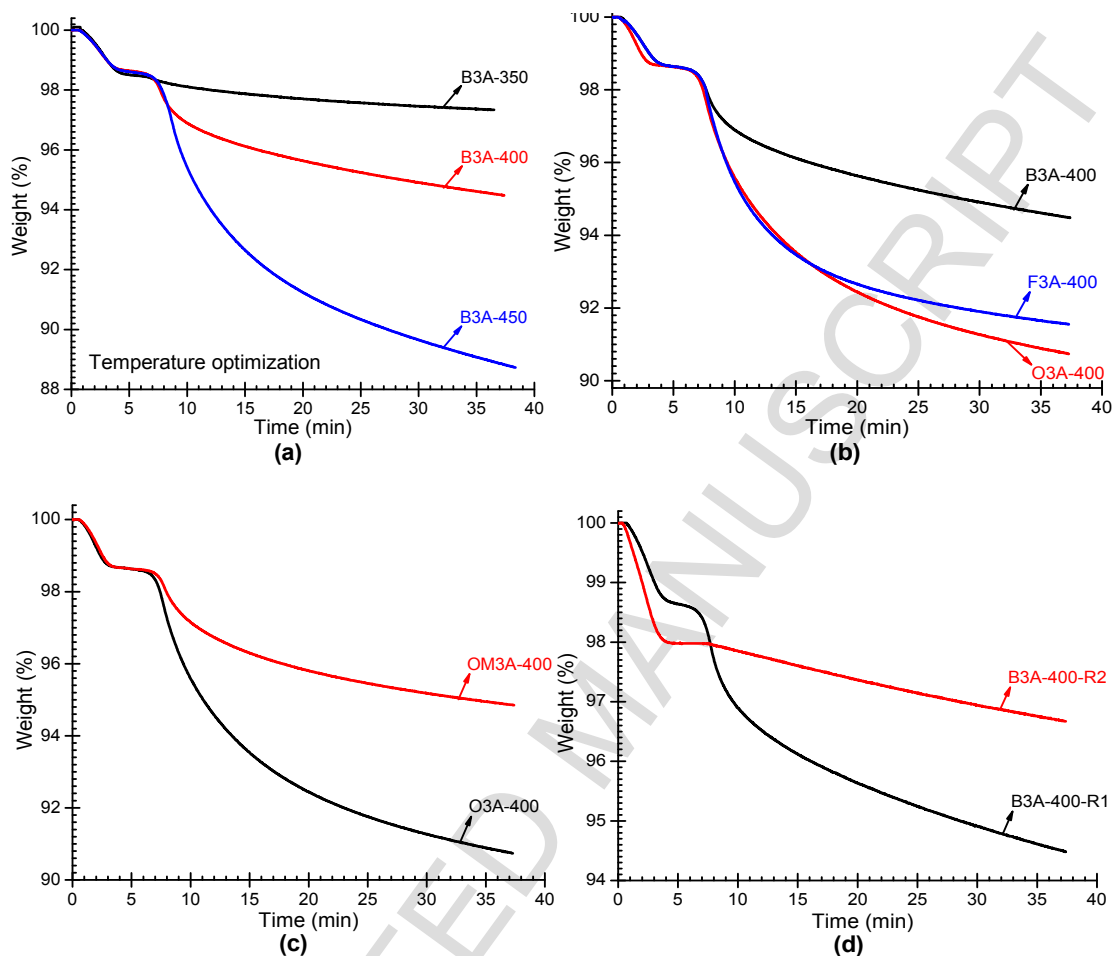
Polymer	W ₁₅ (%)	W ₂₅ (%)	W ₃₅ (%)
B3A (B3A-R1)	3.88	4.76	5.39
O3A	6.46	8.25	9.12
F3A	6.53	7.79	8.35
BM3A	2.92	3.45	4.67
OM3A	3.70	4.55	5.05
FM3A	3.17	3.73	4.84
B3A-R2	2.39	2.85	3.24

W₁₅ = Weight loss (%) after 15 minutes of isothermal treatment at 400 °C

W₂₅ = Weight loss (%) after 25 minutes of isothermal treatment at 400 °C

W₃₅ = Weight loss (%) after 35 minutes of isothermal treatment at 400 °C

Fig. 11 Isothermal TGA graphics (Air): B3A-350, B3A-400, B3A-450 (a), B3A-400, O3A-400, F3A-400 (b), O3A-400, OM3A-400 (c), B3A-400-R1, B3A-400-R2 (d).

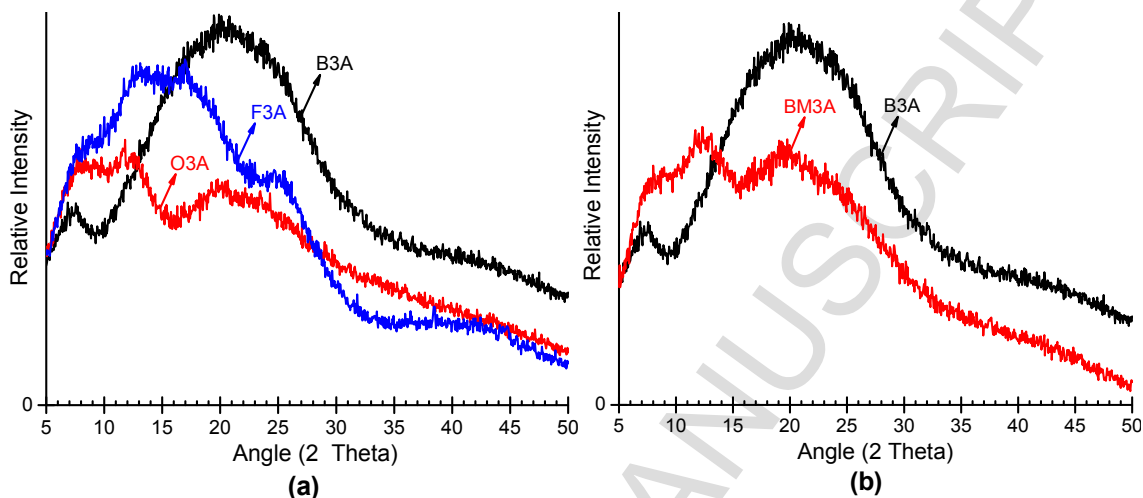


3.4. Wide angle X-ray diffraction analysis

All the polymers were characterized by wide angle X-ray diffraction analysis (WAXRD) in the region of $2\theta = 5-50^\circ$ at room temperature in order to gain insight into the molecular packing preferences. WAXRD diffractograms shown in Fig. 12a are illustrating the amorphous nature of polyimides although ancestor diamine monomer (3APX) was crystalline. This is attributed to kink in the structure introduced due to meta catenation of amino groups on phenyl rings with respect to ether linkage in the 3APX. Once these groups were involved in polymerization, they

disrupted the efficient packing of polymer chains. Moreover, the copolymerization with MDA does not significantly affected the morphology of parent polyimides as shown in Fig. 12b.

Fig. 12 Wide angle X-ray diffractograms: polyimides B3A, O3A, F3A (a), polyimide B3A and copolyimide BM3A (b).



4. Conclusions

A meta-catenated diamine monomer, corresponding polyimides and copolyimides were synthesized successfully. The structures were verified by FTIR and NMR spectroscopic techniques along with elemental and single crystal X-ray diffraction analyses. The objective of the research was to evaluate the thermal behavior of polyimides prepared from meta-catenated ether-based diamine along with measuring the effects of variation in dianhydride structure and copolymerization on thermal stability and morphology of polyimides. Comparison of data obtained from the dynamic TGA revealed that polyimides and copolyimides displayed substantially high thermal stability as decomposition started around 400 °C. Execution of copolymerization strategy with MDA further enhanced the temperature resistance of polyimides. Decomposition in air was slower between 400-550 °C however it was accelerated above 550 °C as compared to nitrogen. Isothermal TGA disclosed that synthesized polymers are capable to

withstand elevated temperatures (350-400 °C) for relatively long periods of time. WAXRD pattern indicated the amorphous nature of polymers.

Properties of polyimides can be tailored to desired ones either by modifying structures of monomers or via executing copolymerization strategy. The synthesized polymers have potential to be used as high temperature resistant materials for applications under severe conditions where excellent thermal stability is desired for extended period.

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Supplementary data

CCDC 1048113 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- Synthesis of meta-catenated diamine, polyimides and copolyimides.
- Structural elucidations by FTIR, NMR and elemental analysis.
- Spatial orientations of diamine monomer by single crystal XRD.
- Simulated and experimental powder XRD for structure verification.
- Dynamic and isothermal TGA for evaluation of thermal stability.

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