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Synthesis and characterization of thermally stable polyimides containing spacer methylene linkage and cardo moieties

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Abstract

A series of thermally stable and organo-soluble polyimides (PIs) were synthesized via a conventional two-step thermal imidization process involving the polycondensation of a newly developed diamine monomer, 1,1′-bis-[4-(4′-benzylamineoxy) phenyl] cyclohexane (BBAPC), with five commercially available aromatic dianhydrides. The novel diamine (BBAPC), which incorporates methylene linkages and cardo moieties, was successfully synthesized. The resulting polyimides demonstrated excellent thermal stability, good solubility in aprotic polar solvents, and inherent viscosities ranging from 0.40 to 0.58 dL/g. Wide-Angle X-ray Diffraction (WAXD) patterns revealed that all the synthesized polyimides are amorphous in nature. Differential Scanning Calorimetry (DSC) analysis showed glass-transition temperatures (Tg) between 157°C and 196°C, suggesting ease of processing. Thermogravimetric analysis (TGA) indicated 10% weight loss (T_{10}%) in the temperature range of 377-554°C, with char yields between 26% and 39% at 900°C under a nitrogen atmosphere, depending on the dianhydride used. Structure-property relationships were examined in detail, highlighting the potential of these materials for advanced high-performance applications.

Keywords: Polyimides, spacer methylene-cardo moiety, TGA, DSC, thermally stable, WAXD

Introduction

Polyimides are a vital class of polymers used in many high-performance applications. Many aromatic polyimides include imide bonds between two aromatic rings [1, 2]. This material possesses important properties such as thermal-oxidative stability, excellent electrical insulation, resistance to radiation and chemical solvents, and superior mechanical behaviour, which make it highly valuable for modern applications [3, 4]. These characteristics of aromatic polyimides arise from the presence of imide bonds linking two aromatic rings, which constitute the main structural backbone of the polymer chains [5, 6]. However, their outstanding performance is offset by the fact that rigid aromatic polyimides possess high melting points and glass transition temperatures (Tg), which hinder their processability and restrict their practical applications due to poor solubility in organic solvents. Many researchers have tackled these challenges by introducing various structural modifications, such as incorporating bulky pendant groups, flexible methylene units, and other packing-disruptive components into the polymer backbone. These structural modifications enhance the solubility and processability of polyimides while preserving their excellent thermal performance [7-16]. In this study, methylene spacer groups and cyclohexane moieties were inserted into the main of polymer structure. This change promotes the mechanical and chemical properties of rigid polyimides [17-20] without disrupting their thermal properties [21-24].

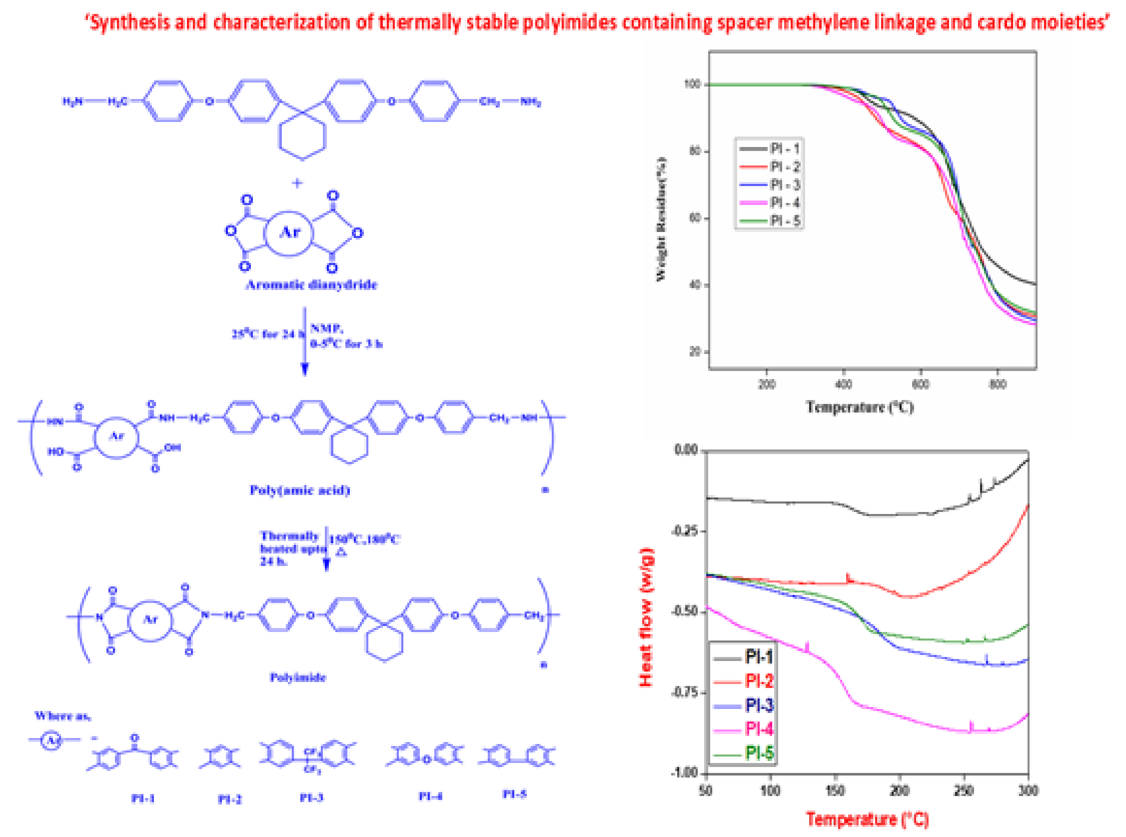
The thermal imidization of poly (amic acid) method employed in this study to synthesize and characterize a novel class of aromatic-aliphatic polyimides. 1, 1'-bis-[4-(4'-benzylamineoxy) phenyl] cyclohexane diamine monomer used as starting material which contain methylene linkage and cyclohexane moiety. Sequential reactions were carried out between the diamine monomer and various commercially available aromatic dianhydrides.

The resulting monomers and polymers were characterized using a number of spectroscopic methods, such as differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), inherent viscosity measurements, wide-angle X-ray diffraction (WAXD), FT-IR spectroscopy, ^{13}C-NMR, and ^{1}H-NMR.

2. Experimental

2.1. Materials: N-Methyl-2-Pyrolidinone and N,N'-Dimethylacetamide were used after purification, phenol, 10% palladium on charcoal, hydrazine hydrate, 3,3',4,4'-Benzophenone tetracarboxylic dianhydride, Pyromellitic dianhydride, 4,4'-Oxydiphthalic anhydrides, 3,3',4,4'-Biphenyl tetracarboxylic dianhydride, and Hexafluoroisopropylidene dianhydride were all used exactly as supplied.

Graphical Abstract



'Synthesis and characterization of thermally stable polyimides containing spacer methylene linkage and cardo moieties'

2.2 Measurements: Thermo Nicolet spectrometer -FT-IR spectra (650-4000 cm⁻¹). Bruker spectrometer - ¹H-NMR (400 MHz) and ¹³C-NMR (100 MHz). Ultima IV system (Japan) - XRD. Ubbelohde viscometer - Inherent viscosities. Mettler-Toledo - TGA and DSC.

2.3 Monomer Synthesis: The diamine monomer 1, 1' bis [4-(4'-benzylamine oxy) phenyl] cyclohexane (BBAPC) was prepared in four steps.

Synthesis of 1, 1' bis (4-hydroxyphenyl) cyclohexane (BHPC): A mixture of phenol (0.50 mol) and cyclohexanone (0.25 mol) in concentrated hydrochloric acid (100 mL) and glacial acetic acid (50 mL) was stirred vigorously in a 500 mL round-bottom flask at 45 °C for 5 hrs, followed by stirring at temperature (25 °C) for 16-18 hrs. The resulting pink crystalline product was collected by vacuum filtration, washed sequentially with hot distilled water and benzene and then dissolved in aqueous sodium hydroxide solution. The alkaline solution was filtered if necessary; the filtrate was acidified by slow addition of concentrated hydrochloric acid with stirring, precipitating the purified product. This product was collected by vacuum filtration, washed thoroughly with cold distilled water until the washings were neutral, and dried under reduced pressure at 50 °C for 6 hrs. The dried product was recrystallized from hot methanol to yield of the target compound. Yield: 21.83 gm (91%) M.P.:-188-190 °C

2.3.2 Synthesis of 1, 1' bis[4-(4'-benzaldehyde oxy) phenyl] cyclohexane (BBPC)

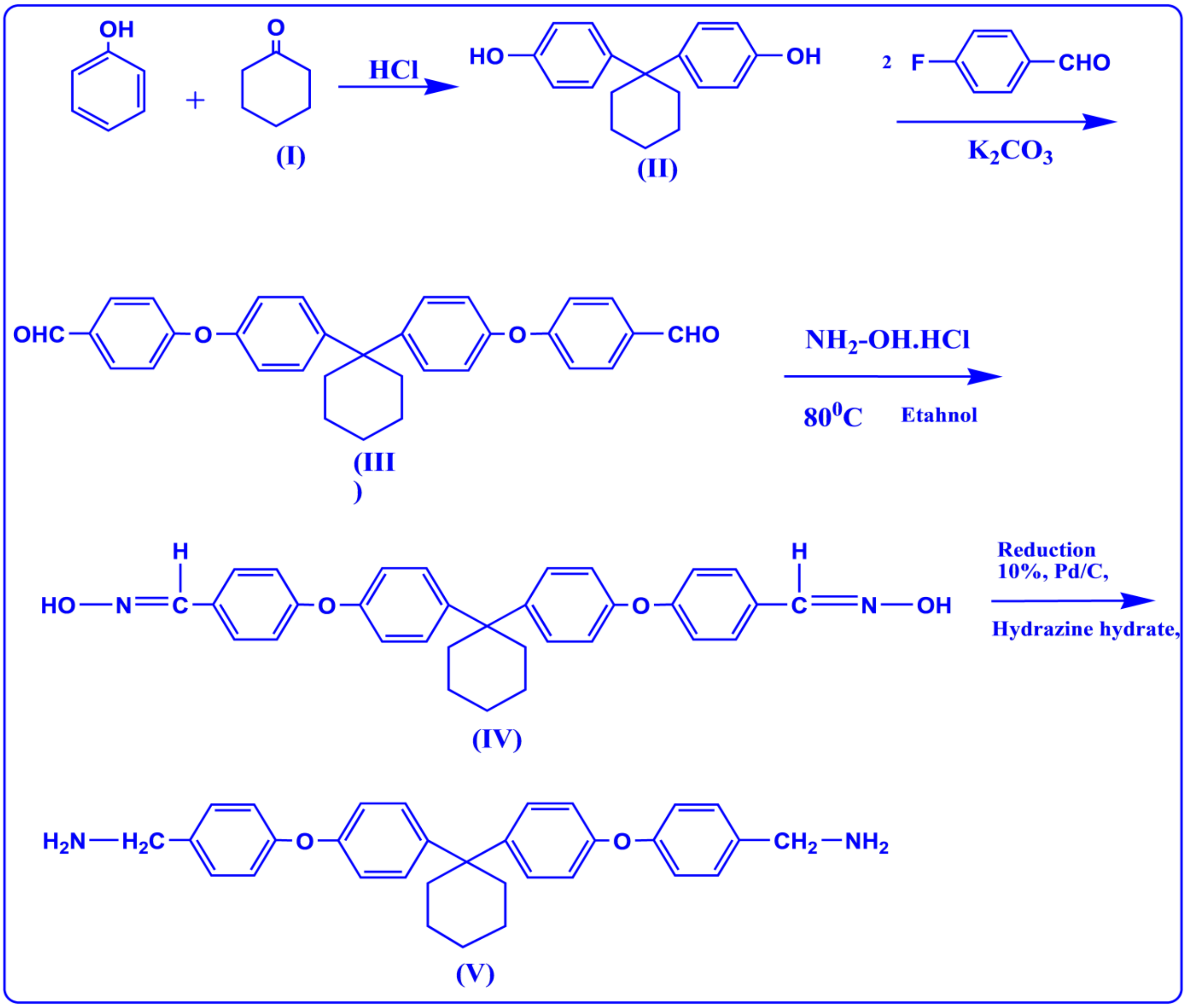
A 500 mL three-necked flask equipped with reflux condenser, $CaCl_2$ guard tube, thermowell, N_2 inlet, and stirrer was charged with 1,1-bis(4-hydroxyphenyl)cyclohexane (13.4 g, 0.05 mol) and 4-fluorobenzaldehyde (12.412 g, 0.10 mol) in anhydrous DMAc (125 mL). Anhydrous K_2CO_3 (13.821 g, 0.10 mol) was added under N_2. The reaction mixture was refluxed for 5 hours, then cooled to room temperature and quenched with water. The resulting solid was filtered, washed, dried, and recrystallized. Yield: 21.803 g (91%); Melting Point: 110-112 °C.

2.3.3 Synthesis of 1, 1' bis [4- (4'-benzaldoxime oxy) phenyl] cyclohexane (BBOPC): In 100 mL three necked flask 2.38 gm (0.005mol) BBPC has placed 5 mL distilled ethanol poured in flask. A solution of 0.7 gm Sodium hydroxide pellets (AR Gr) and 2 mL distilled water was prepared and poured in the flask 0.75 gm (0.11 mol) hydroxylamine hydrochloride (AR Gr) has weighed and solution prepared by addition of 2 mL distilled water. This solution poured in three necked reaction flask. This solution flask stirred at room temperature. Then reflux this solution at 80 °C temperature for 2 hrs. Finally distilled out 5 mL ethanol from solution, allowed to cool at room temperature acidified this solution by addition of sufficient quantity (1 or 2 drops) of glacial acetic acid with 4 mL distilled water added in it. The Dioxime separated, filtered it, residue washed with water till free from acid compound dried and weighed. Recrystallization of dioxime was carried out in ethanol.

Yield = 2.965 gm M. P. = 140 °C

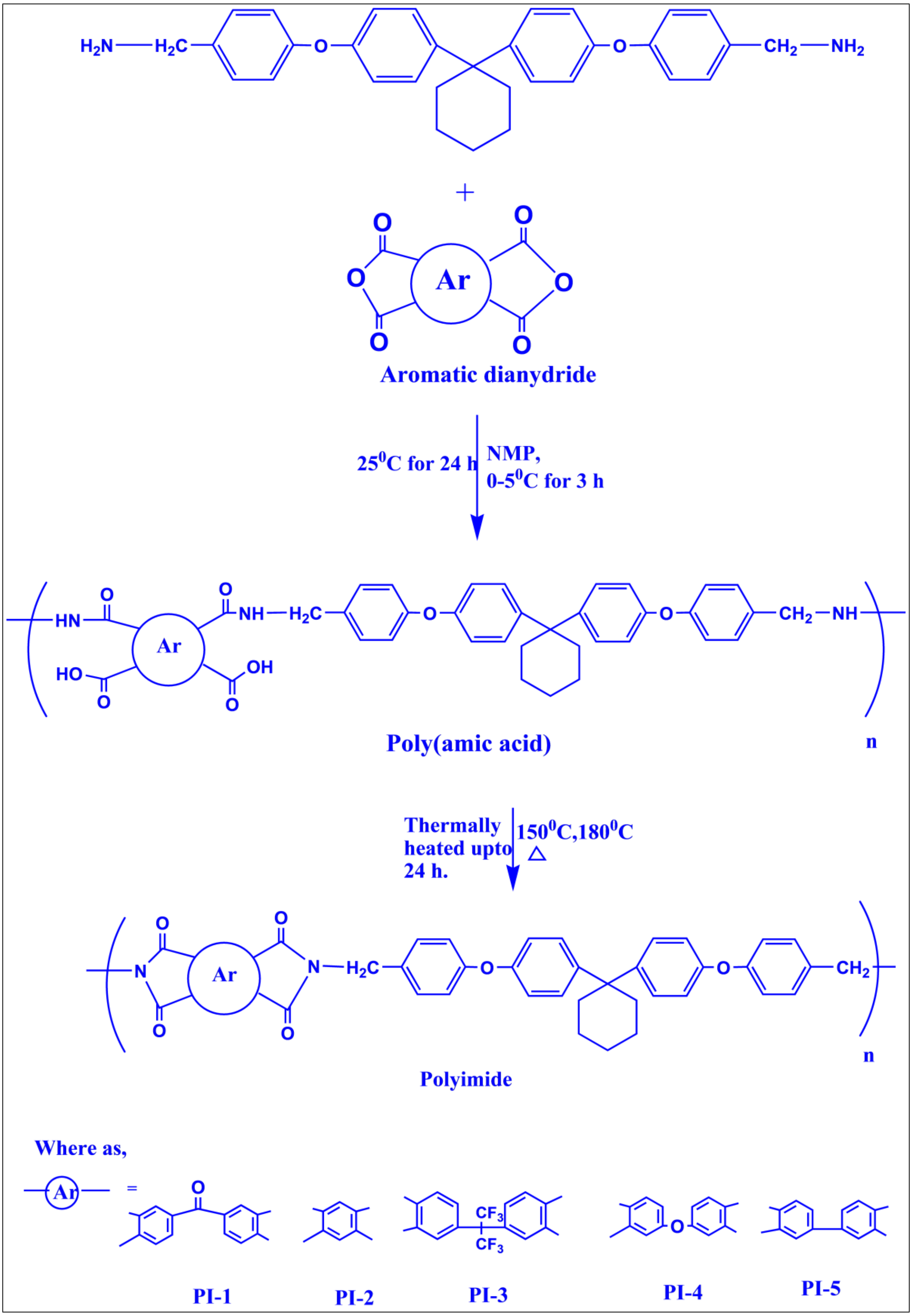
2.3.4 Synthesis of 1, 1' bis [4- (4'-benzylamine oxy) phenyl] cyclohexane (BBAPC): BBOPC (0.506 g, 1 mmol), 10% Pd/C (0.0297 g), and ethanol (20 mL) were refluxed at 80 °C. Hydrazine hydrate (90%, 5 mL) was added dropwise over 45 minutes, and the mixture was stirred for 12 hours. After hot filtration to remove the catalyst, the filtrate was concentrated and poured into water (200 mL) to precipitate the product. The solid was filtered, washed with water, recrystallized from ethanol, and dried under vacuum at 80 °C.

Yield: 0.297 g M.P.: 210-212 °C



Scheme 1: Synthesis of 1, 1-bis [4-(4'-benzylamine oxy) phenyl] cyclohexane (BBAPC

2.4 Polymer Synthesis: Novel polyimides were synthesized via a conventional two-step thermal imidization process from poly(amic acid) precursors, which were prepared by the polycondensation of the aromatic diamine 1,1-bis[4-(4'-benzylaminooxy)phenyl]cyclohexane with five commercially available aromatic dianhydrides: 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA), 4,4'-oxydiphthalic anhydride (ODPA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) [25].



Scheme 2: Synthesis of polyimides from BBAPC and different dianhydrides

3. Results and Discussion

3.1 Synthesis and Structural characterization of BBAPC monomer: The novel aromatic diamine, 1,1’-bis[4-(4’-benzylaminooxy) phenyl] cyclohexane (BBAPC), was synthesized through a multi-step procedure starting from bisphenol derivatives, as outlined in Schemes 1 and 2. The chemical structures of the synthesized BBAPC monomer and its intermediate compounds were confirmed by ^1H-NMR and ^13C-NMR spectroscopy, as illustrated in Figures 1-6.

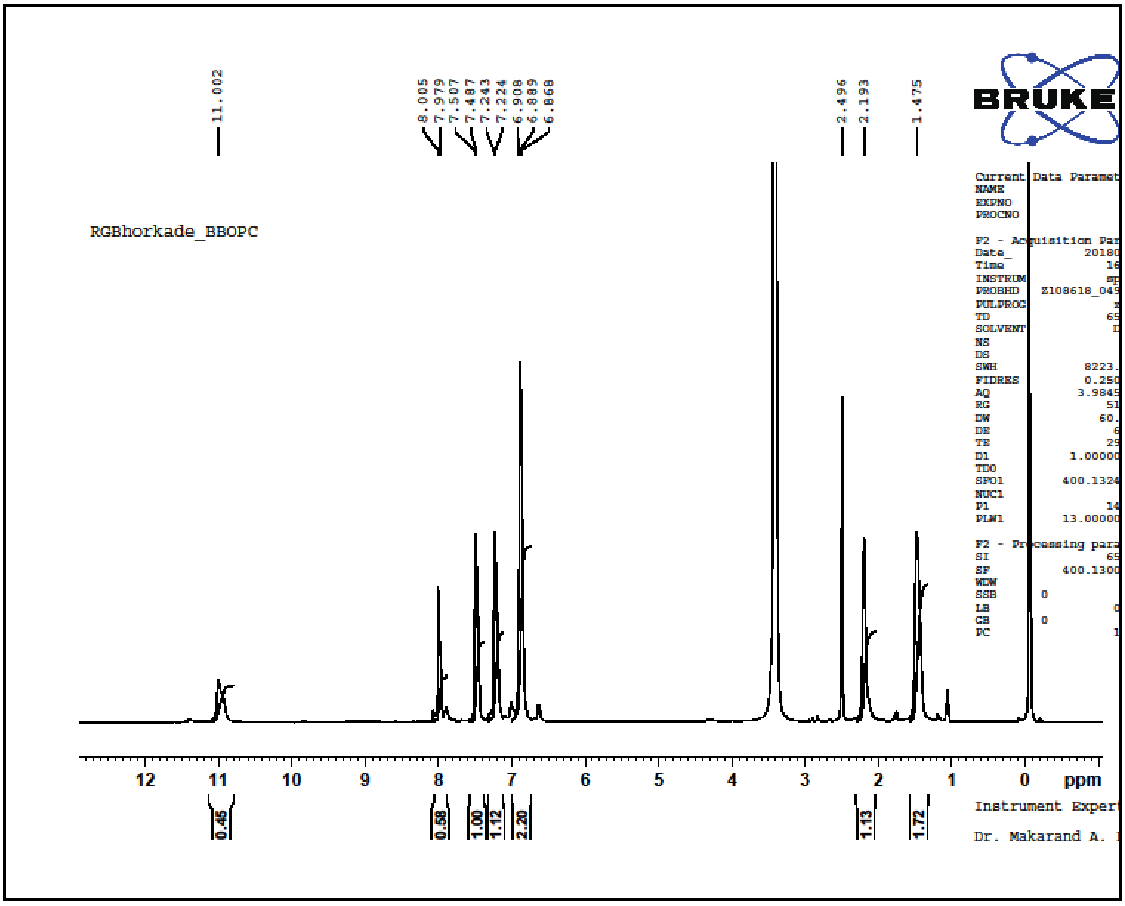


Fig 1: ^{1}H-NMR Spectrum of BBOPC

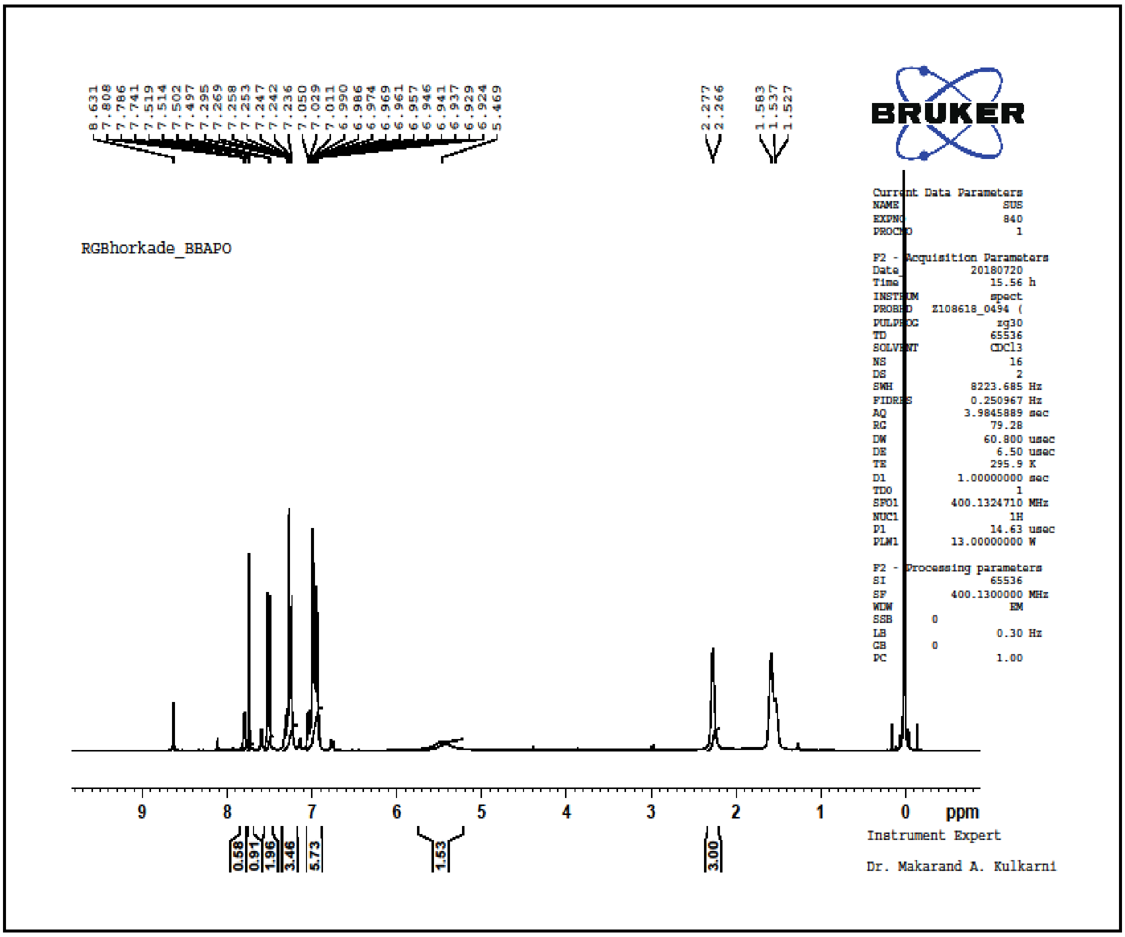


Fig 2: ^{1}H-NMR Spectrum of BBAPC

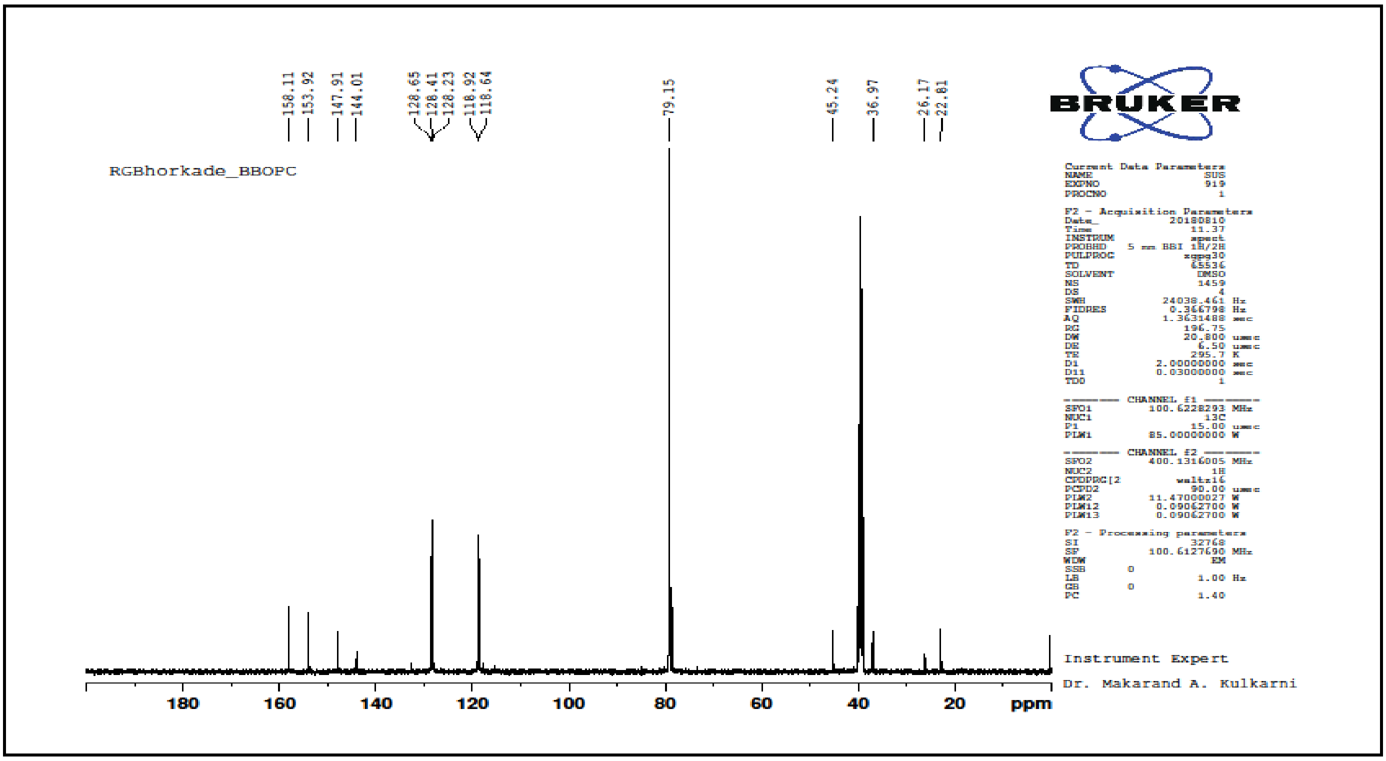


Fig 3: ^{13}C-NMR Spectrum of BBOPC

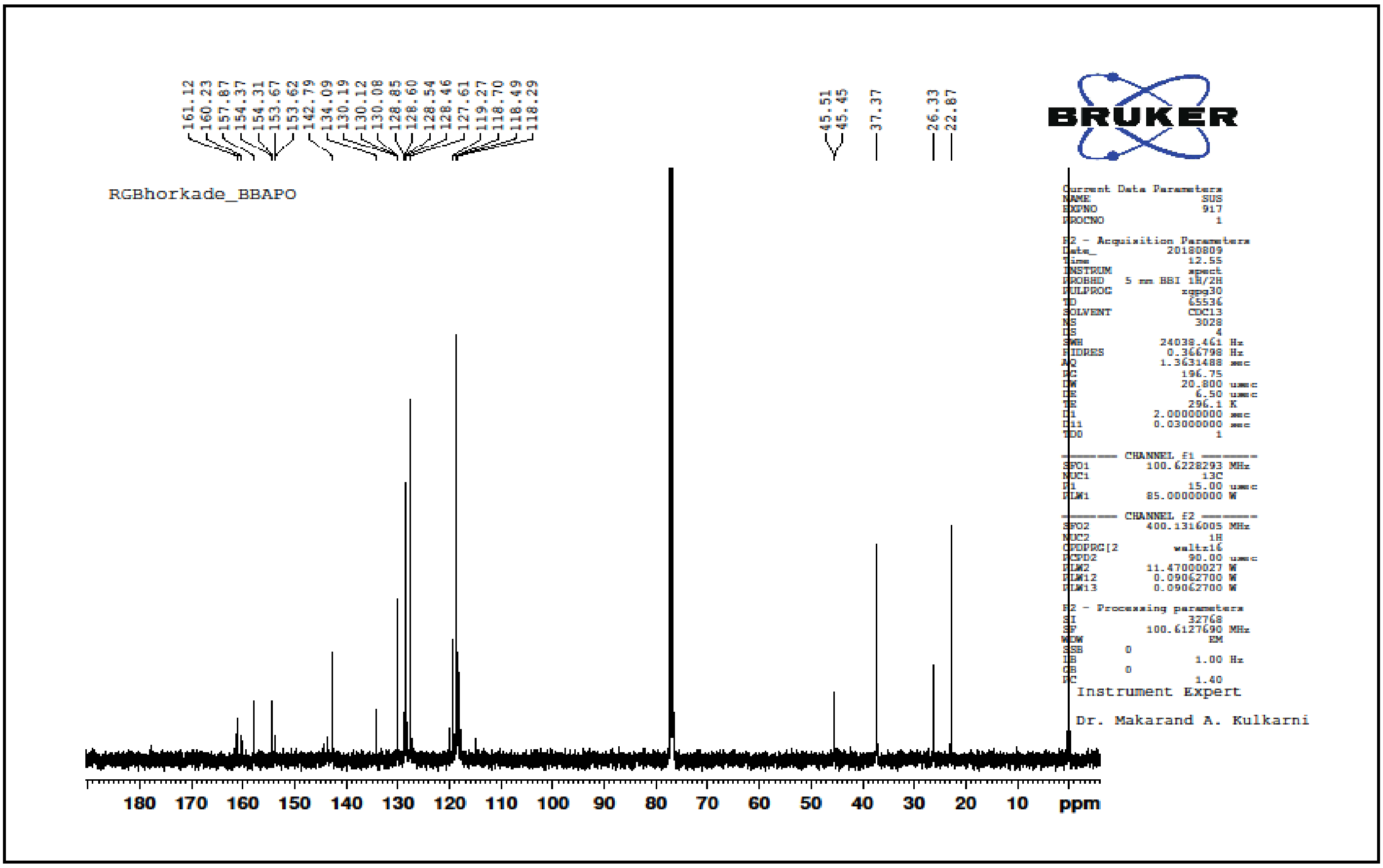


Fig 4: ^{13}C-NMR Spectrum of BBAPC

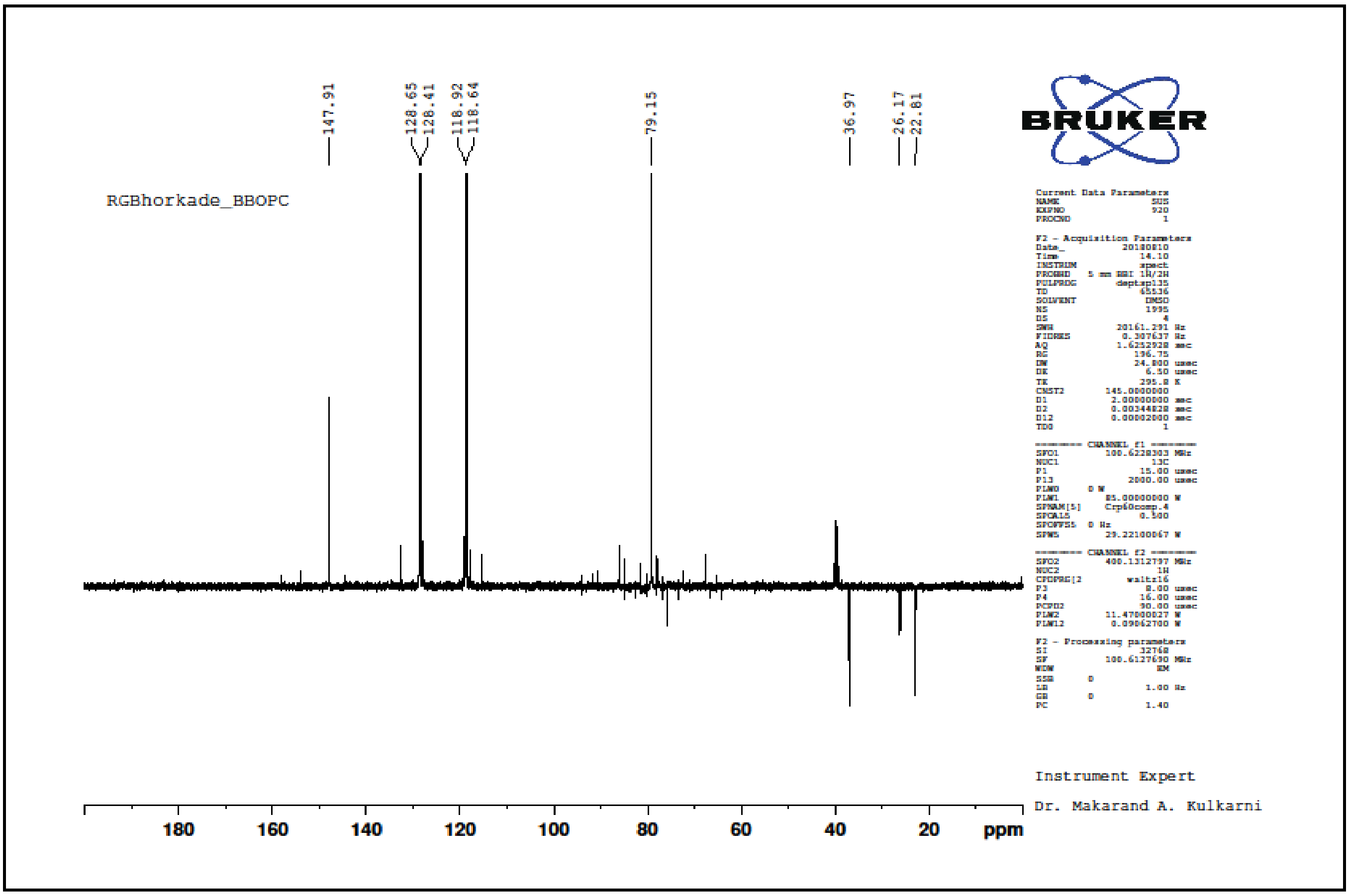


Fig 5: DEPT ^{13}C-NMR Spectrum of BBOPC

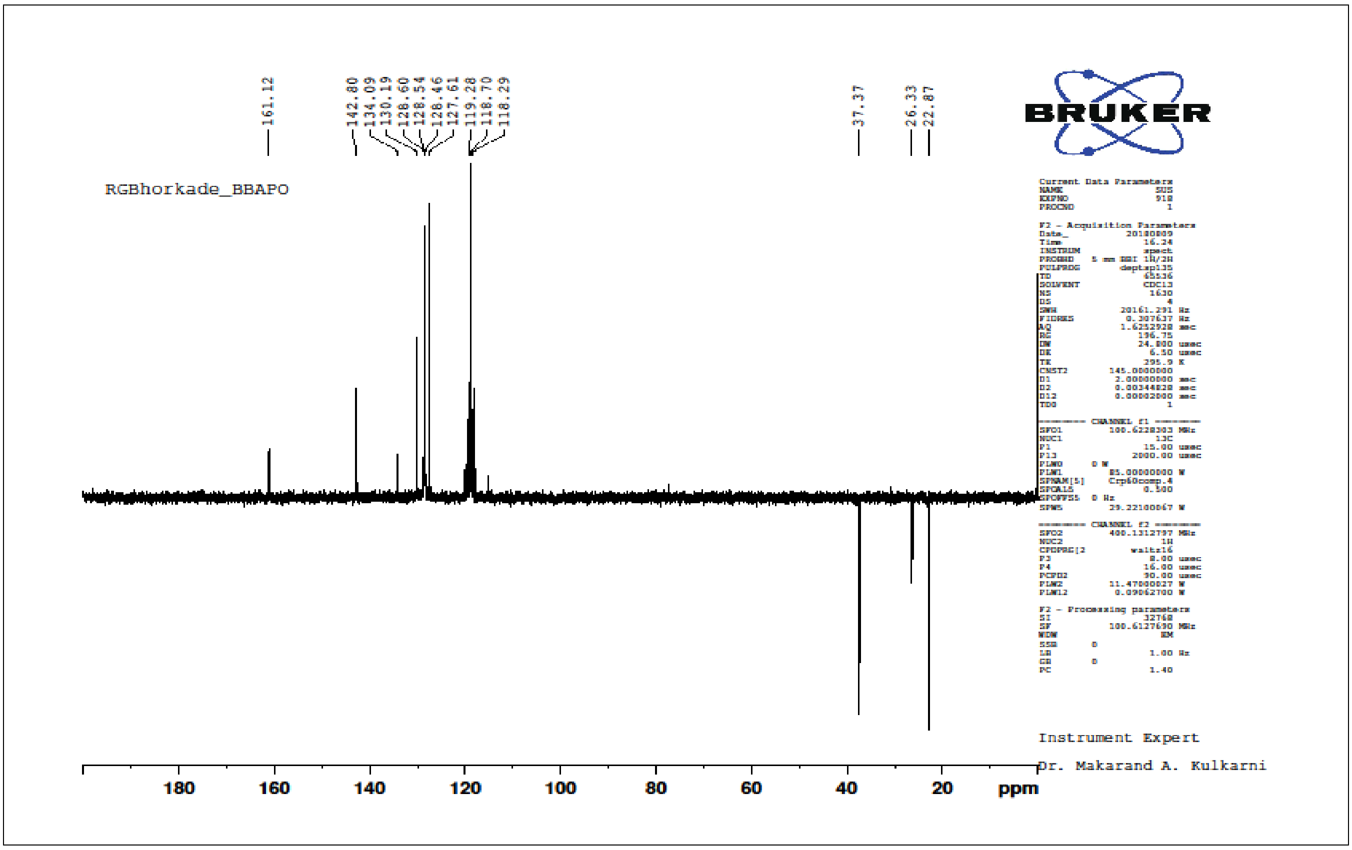


Fig 6: DEPT ^{13}C-NMR Spectrum of BBAPC

3.2 Synthesis and Structural characterization of Polymers: Five novel polyimides incorporating preformed imide units, flexible ether linkages, and aliphatic methylene spacers were fabricated via stoichiometric polycondensation. The aromatic diamine 1, 1-bis[4-(4'-benzylaminooxy) phenyl] cyclohexane (BBAPC) was reacted with five commercial aromatic dianhydrides-BTDA, PMDA, 6FDA, ODPA, and BPDA-using the standard two-step thermal imidization method (Scheme 3). Step I: BBAPC underwent ring-opening polymerization with the dianhydrides in N-methyl-2-pyrrolidone (NMP) at ambient temperature, generating linear poly (amic acid) precursors. Step II: Thermal cyclodehydration of these precursors converted the poly (amic acid)s into the target polyimides.

All synthesized polyimides were obtained in excellent yields ranging from 96% to 98%. The inherent viscosities of their corresponding poly(amic acid) (PAA) precursors, measured in N-methyl-2-pyrrolidone (NMP) at 0.5 g/dL and 25 °C, were in the range of 0.40-0.58 dL/g, indicating moderate to high molecular weights. The successful formation of polyimides was confirmed by FT-IR spectroscopy (Figures 7 and 8). For example, the FT-IR spectrum of PAA-5 (BPDA-based poly(amic acid), Figure 10) exhibited broad absorption bands in the 3400-3000 cm^{-1} region corresponding to O-H and N-H stretching vibrations, along with peaks at 1650 cm^{-1} and 1594 cm^{-1} attributed to amide C=O stretching. Additional peaks were observed at 3060 cm^{-1} (aromatic C-H), 2935 cm^{-1}, and 2860 cm^{-1} (aliphatic C-H stretching). After thermal imidization, the spectrum of PI-5 (Figure 11) showed characteristic imide absorption bands at 1777 cm^{-1} (asymmetric C=O stretching), 1418 cm^{-1} (C-N stretching), 1105 cm^{-1} (C-N-C stretching), and 729 cm^{-1} (imide ring deformation), confirming successful cyclodehydration. The complete conversion of PAA to polyimide was further supported by the disappearance of amide bands (3500-3100 cm^{-1} and 1732 cm^{-1}) in the PI spectra, while the aliphatic (2942 cm^{-1}) and aromatic (3060 cm^{-1}) C-H stretching bands remained intact.

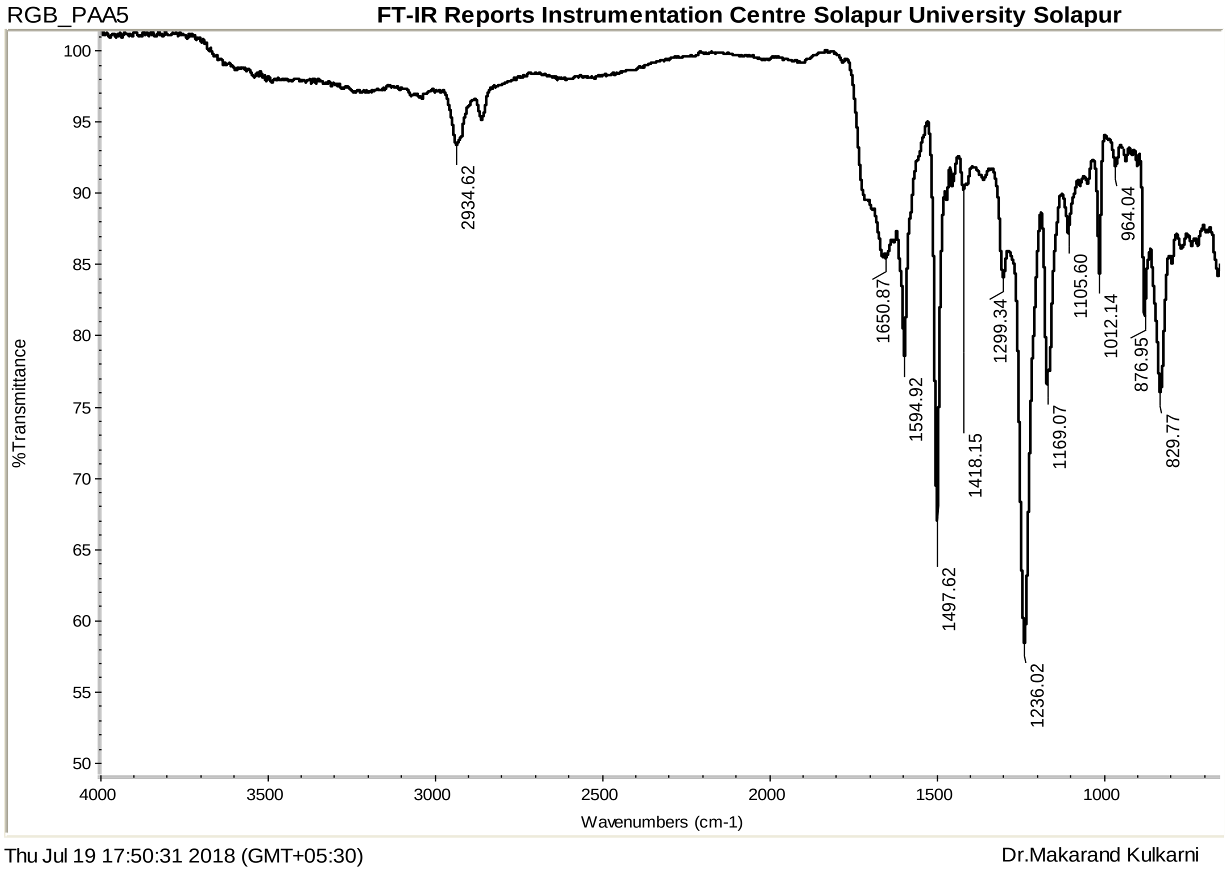


Fig 7: FT-IR Spectrum of PAA-5

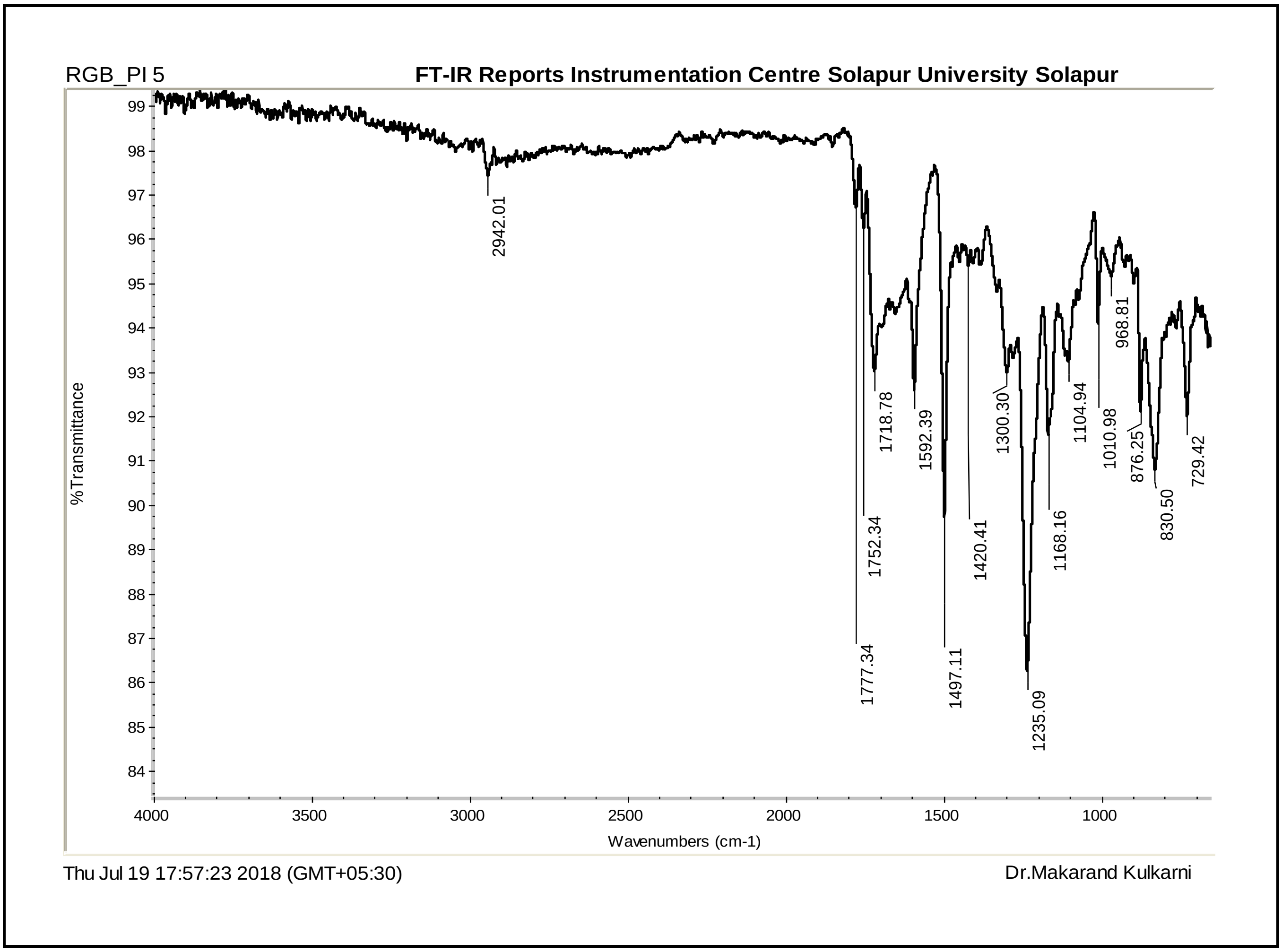


Fig 8: FT-IR Spectrum of PI-5

3.3 Solubility and Inherent viscosity

The solubility of the synthesized polyimides was evaluated qualitatively in various organic solvents, with solubility defined as the formation of a stable 3% (w/v) solution. All polyimides dissolved in aprotic solvents including DMAc, NMP, DMSO, and DMF. However, solutions in pure solvents (without LiCl) exhibited significantly lower solubility, likely attributable to rigid polymer backbones and strong interchain interactions. Notably, PI-3 (derived from 6FDA) demonstrated enhanced solubility in DMSO and DMF compared to polyimides from other dianhydrides. This improvement is ascribed to the bulky $-CF_3$ groups in 6FDA, which disrupt chain regularity and packing density, thereby reducing interchain cohesion. Inherent viscosities (η_{inh}) of the poly (amic acid) precursors (PAA-1 to PAA-5) were measured at 30°C in NMP (0.5 g/dL) to estimate relative molecular dimensions. All PAAs exhibited excellent solubility in aprotic solvents at room temperature. The recorded η_{inh} values ranged from 0.40 to 0.58 dL/g (Table X), consistent with the formation of moderate-to-high molecular weight polymers.

3.4 Thermal Analysis

The thermal behavior of the synthesized polyimides (PI-1 to PI-5) was evaluated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The key thermal parameters examined included the glass transition temperature, initial decomposition temperature, 10% weight-loss temperature, temperature at maximum decomposition rate, and residual char yield at 900 °C. DSC analysis (Figure 10) revealed that the polyimides exhibited values in the range of 157-196 °C, indicating moderate to high chain rigidity. TGA thermograms (Figure 9) demonstrated excellent thermal stability, with minimal weight loss observed below 300 °C. The decomposition profiles showed initial decomposition temperatures between 301°C and 325 °C, 10% mass-loss temperatures ranging from 483°C to 568°C, and maximum decomposition rate temperatures between 729 °C and 764 °C. Furthermore, the char yields at 900 °C were found to be between 28% and 40%, confirming the high thermal resistance and char-forming ability of these polyimide materials.

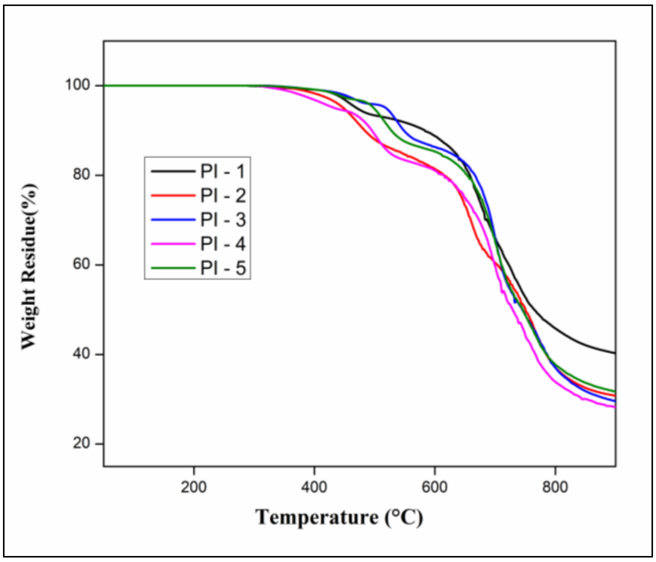


Fig 9: TGA Curves of PI-1 to PI-5

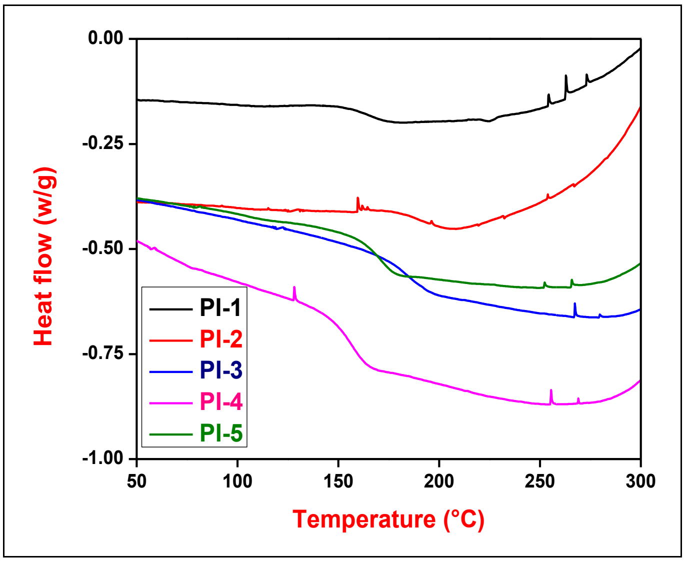


Fig 10: DSC Curves of PI-1 to PI-5

3.5 WAXD Analysis: The crystallinity of polyimides PI-1 to PI-5 was characterized by wide-angle X-ray diffraction at room temperature (2θ range: 10-35°). All samples exhibited broad halo patterns in their diffractograms (Fig. 11), confirming amorphous morphology. The nonappearance of sharp peaks in the WAXD patterns shows the amorphous nature of the polyimides, signifying a lack of ordered packing in the polymer chains.

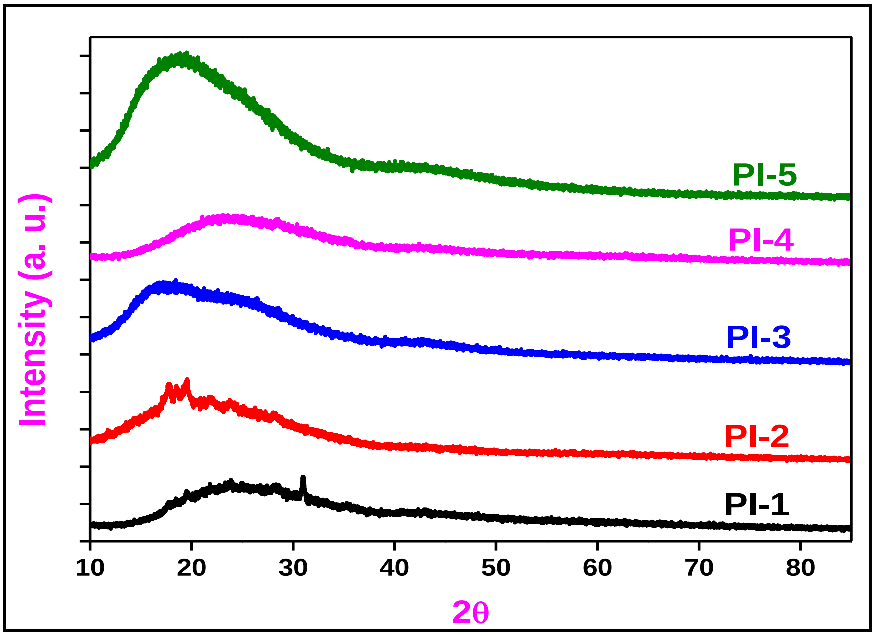


Fig 11: WAXD Curves of PI-1 to PI-5

4. Conclusions: A novel aromatic diamine, 1, 1′-bis[4-(4′-benzylaminooxy) phenyl] cyclohexane (BBAPC), containing ether and methylene linkages, was successfully synthesized and confirmed by FT-IR, ^1H NMR, and ^13C NMR spectroscopy. Aromatic-aliphatic polyimides were prepared by polycondensation of BBAPC with five aromatic dianhydrides (BTDA, PMDA, 6FDA, ODPA, BPDA) using a two-step method involving thermal imidization of poly (amic acid) precursors. The synthesized polyimides showed inherent viscosities between 0.40 and 0.58 dL/g in NMP, reflecting moderate to high molecular weights. These materials exhibited good solubility in aprotic polar solvents with DMAc, NMP, DMSO, DMF, and m-cresol. The glass transition temperatures (Tg) of the polyimides ranged from 157 to 196 °C and were influenced by the rigidity and symmetry of the dianhydride units. Wide-angle X-ray diffraction (WAXD) analysis revealed an amorphous morphology due to the disruption of chain packing by the cyclohexane spacer and flexible linkages. Thermogravimetric analysis (N_2) showed the polyimides have excellent thermal stability with minimal weight loss below 300 °C, T_{10}% between 483-568 °C, and 28-40% char yield at 900 °C. Flexible ether and methylene spacers enhanced solubility and processability without without reducing thermal stability.

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- **Conflict of Interest:** On behalf of all authors, the corresponding author states that there is no conflict of interest.
- **Ethical Approval:** Not applicable.
- **Informed Consent:** Not applicable.

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