Synthesis and Characterization of novel Poly(ether-imide)s derived from Thiazolediamine and aromatic dianhydrides

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Abstract

A novel ether linkage Thiazole diamine 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yloxy)phenyl)thiazol-2-amine(III) was synthesized in a simple procedure, which was then employed to prepare a series of polyimides with commercial aromatic dianhydrides, such as pyromellitic dianhydride (PMDA), 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane(6FDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-oxydiphthalic anhydride (ODPA). The polyimides inherent viscosities of these poly(ether-imide)s were in the range 0.37 to 0.71 dL/g, indicating formation of moderate molecular weights. These polymers exhibited good solubility in various polar aprotic solvent such as N-methyl-2-pyrrolidone (NMP) and H\textsubscript{2}SO\textsubscript{4} etc. X-Ray diffraction pattern of polymers showed amorphous nature. Thermal stability was assessed by 10\% weight loss temperature and the degradation temperature of the resultant polymers falls in the ranges from 395°C to 464°C in nitrogen. The glass transition temperature was in the range of 214-244°C.

Keywords: Inherent viscosity; Solubility; Thermal stability.

1. Introduction

The class of aromatic polyimide came into focus since 1950, after successful development of the two step polyimide synthesis by DuPont [2]. This class of polyimides possesses a 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 [3-5]. 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.[6,7]. However, high softening temperature and poor solubility in different organic solvents of these polymers preclude the processing in both melt and solution condition. Several approaches have been taken to circumvent the poor processability of this class of polymer. One successful approach, has been executed by General Electrical with an introduction of flexible ether linkage (–O–)[8,9] and isopropylidene [–C(CH\textsubscript{3})\textsubscript{2}–] moiety [10,11] into the polymer backbone resulting the Ultem 1000\textsuperscript{®} [12,13]. It exhibited excellent thermal stability and good mechanical properties. Other various approaches investigated to ease the polyimide processing include addition of bulky side groups or bulky units in the polymer backbone [14,15], or noncoplanar [16].
oralicyclic monomers [17] in the main chain.

The objective of the present work was to synthesis a new series of poly(ether-imide)s containing napthyl moiety and ether linkage along the backbone and to examine the effect of their integration on the polymer properties such as solubility and thermal behavior. Thus, a series of new aromatic poly(ether-imide)s containing napthyl moiety was prepared, first step involved conventional ring-opening polycondensation of (m-BABPC with the dianhydrides in NMP at low temperature to form linear open chain poly(amic acid). In the step second the conversion of poly(amic acid) to polyimides was performed by thermal process for the consequent cyclodehydration to form poly(ether-imide)s. The prepared poly(ether-imide)s were characterized by inherent viscosity measurements, solubility tests, FT-IR spectrum, thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) studies and X-ray diffraction studies.

2. Experimental

2.1. Materials

All the solvents/chemicals were purified before use by using standard procedures.

The reagents such as 2′-naphthol, 4-fluoroacetophenone, thiourea, iodine, terephthalaldehyde (TPA), isophthalaldehyde (IPA) were purchased from Sigma Aldrich (USA) and were used as received. N, N′-Dimethylacetamide was refluxed over barium oxide for 4h, the liquid was decanted in a Dimethylacetamide was refluxed over barium oxide for 4h, the liquid was decanted in a separate round bottom flask and distilled at reduced pressure over calcium hydride and stored over Linde type 4 Å Molecular sieves. The reagents such as 2′-naphthol, 4-fluoroacetophenone, thiourea, iodine, terephthalaldehyde (TPA), isophthalaldehyde (IPA) were purchased from Sigma Aldrich (USA) and were used as received. N, N′-Dimethylacetamide was refluxed over barium oxide for 4h, the liquid was decanted in a separate round bottom flask and distilled at reduced pressure over calcium hydride and stored over Linde type 4 Å Molecular sieves. Pyromelliticdianhydride / 3, 3′, 4, 4′ - (Hexafluoroisopropylidene) diphthalic anhydride (6FDA,) (Sigma Aldrich) was heated in vacuum at 250°C for 3 h prior to use.

2.2. Measurement

2.3. Monomer Synthesis

2.3.1. Synthesis of 2, 2′-Dihydroxy-1, 1-binaphthyl (I)

In a three necked flask equipped with a dropping funnel and reflux condenser. 14.4g (0.1 mol) of 2-naphthol and 600 mL of water were placed and heated to boil. To the boiling liquid containing 2-naphthol in suspension; a solution of 28 g (0.1 mol) crystallized iron (III) chloride in 60 mL water was added. While addition of iron (III) chloride solution, oily drops of 2-naphthol was observed. Further reaction mixture was boiled till oily drops were disappeared and the 2, 2′-Dihydroxy-1, 1-binaphthyl (I) separates out in flasks boiled for 10 minutes. The hot suspension was filtered through the previously warmed Buckner funnel; the crude product was washed with boiled water and dried well. The 2, 2′-dihydroxy-1,1-binaphthyl was recrystallized from toluene (about 150 mL) to get colorless crystals.

Yield: 13.12 g (92.25 %)

M. P.: 217°C.

2.3.2. Synthesis of 2, 2′-Bis (4-acetophenone)-1, 1-binaphthyl (II)

In a 500 mL three neck round bottom flask equipped with calcium chloride guard tube, thermo well, N₂ gas inlet were placed 14.3g 2,2′-dihydroxy-1,1binaphthyl(0.05 mol) and 13.814 g 4-fluoroacetophenone (0.1 mol ) in 125 mL N,N-dimethyl acetamide (DMAc), then 13.821 g of anhydrous K₂CO₃ was added. The resulting reaction mixture was refluxed for 5 h. The progress of reaction was studied by TLC method. After completion, reaction mixture was cooled to room temperature and water was added in it for precipitating the product from solution. Finally the product was isolated by filtration, washed with water and finally dried under vacuum.
Yield: 21.61 g (82.75 %)
M.P.: 130°C
IR: 3033, 2974, 1696, 1594, 1403, 1222, 1071, 1062, 815, 774 cm⁻¹.

2.3.3. Synthesis of 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yloxy)phenyl)thiazol-2-amine(III)

synthesized as per the procedure reported in Chapter 2C.2.2.3

In a 100 mL three neck round bottom flask added compound I (0.4 g (0.001 mol) and iodine 0.252 g (0.003mol), Thiourea 1.2 g (0.006mol) and the mixture was stirred in THF at reflux for 48 h. Then poured the solution with stirring in water, the yellow solid was obtained. Product was recrystallized in ethanol.

Yield: 11.80 g (81.49 %)
M.P.: 165°C.
IR: 3300, 3275, 3091, 3010, 1607, 1509, 1376, 1219, 1157, 1014, 827, 781 cm⁻¹. ¹H NMR (d₆-DMSO): δ = 8.14 (d, 4H), 7.92 (d, 2H), 7.49 (t, 2H), 7.32 (t, 4H), 7.29 (d, 4H), 6.81(d, 4H), 6.09 (d, 2H), 3.93 (s, 4H). ¹³C NMR (d₆- CDCl₃): δ = 168.95, 151.48, 147.68, 129.32, 125.51, 124.81, 124.21, 123.26, 121.8, 121.77, 120.83, 119.84, 117.17, 114.46, 113.93, 113.80, 103.80. Mass Spectra m/e (m+1) = 635.

2.4. Synthesis of poly(ether-imide)s from 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yloxy)phenyl)thiazol-2-amine(III)

The synthesis of the poly(ether-imide) PI-I is given. In a 100 mL three-neck round-bottom flask equipped with a magnetic needle, nitrogen gas inlet and calcium chloride guard tube were placed o.634 g (0.001mol) 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yloxy)phenyl)thiazol-2-amine(III), (m-BABPC) in 3.6 mL of N-methylpyrrolidone (NMP) and the resulting solution was cooled to 0°C in ice bath. To this cold solution, 0.218 g (0.001 mol) of solid Pyromelliticdianhydride (PMDA) was added in lots over 1 hour and stirred at 0°C for 3 h and for 24 h at room temperature under a nitrogen atmosphere, during which viscosity of the reaction mixture increased. The viscous polymer solution was poured into methanol to precipitate poly(amic-acid), filtered and washed with methanol. The poly(amic-acid) was dried under vacuum at 50°C. The Inherent viscosity (ηinh.) of resultant poly(amic acid) -I was 0.30 dL/g measured in NMP at a concentration of 0.5 g/dL at 30°C.

The poly(amic-acid) was consequently cyclized by thermal imidization; where the polymer was taken in flask and heated step wise under nitrogen flow for 1 hour at 100°C, then 1 hour at 150°C and finally for another 1 hour at 200°C. This process ensured the complete imidization. The overall yield is 99%. The series of poly (ether-imide)s (PI-II to PI-V) was synthesized by utilizing above procedure, where in (m-BABPC) polycondensed with different dianhydrides.

3. Results and Discussion

3.1. Monomer Synthesis

Synthesis of 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yloxy)phenyl)thiazol-2-amine(III)

New diamine 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yloxy)phenyl)thiazol-2-amine(III) were successfully synthesized in several steps starting from naphthol(Scheme-1).

The 2, 2'-dihydroxy-1, 1-binanphthyl (I) was synthesized by reacting 2-naphthol in presence of crystallized iron (III) chloride as catalyst. The 2, 2'-Bis(4-acetophenone)-1, 1-binapthyl (II) was obtained by reacting 2, 2'-dihydroxy-1, 1-binanphthyl with 4-Fluorocacetophenone and potassium carbonate as catalyst in DMAc. The structure of (II) was characterized by infrared spectroscopy.

The infrared spectra of (II) (Fig.1.) showed strong absorption bands at 3033 and 2974 cm⁻¹ corresponding to aromatic and aliphatic C-H stretching vibrations. Spectrum also showed absorption near 1403 cm⁻¹ due to C-H bending vibration. Absorption at 1696 cm⁻¹ of carbonyl(C=O) stretching absorption was corresponding to acetyl carbonyl moiety.
The absorption bands in the region 1222 cm\(^{-1}\) and 1071 cm\(^{-1}\) showed aromatic and aliphatic C-O-C stretch. The new thiazole amine monomer 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yloxy)phenyl)thiazol-2-amine(III) was confirmed by IR, NMR (\(^1\)H and \(^{13}\)C) and mass spectroscopy. FT-IR spectrum of 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yloxy)phenyl)thiazol-2-amine(III) (Fig.2.) exhibited N-H stretching absorption bands at 3275 cm\(^{-1}\) (asymmetric N-H stretching) and 3091 cm\(^{-1}\) (symmetric N-H stretching) and C-O-C stretching at 1219 cm\(^{-1}\) and 1157 cm\(^{-1}\). Band at 3010 cm\(^{-1}\) is due to aromatic C-H stretching of naphthyl moiety and very broad absorption bands near 3300 cm\(^{-1}\) was corresponding to N-H stretch of \(–\text{NH}_2\) group.

Scheme 1. Synthesis of 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yloxy)phenyl)thiazol-2-amine(III)

Fig.1. FT-IR spectrum of 2, 2’-Bis (4-acetophenone) - 1, 1binaphthyl (II)
Fig. 2. FT-IR spectrum of 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yl)oxy)phenyl)thiazol-2-amine (III)

The proton NMR spectrum (Fig. 2C, 3.) of (III) showed the NMR singlet at 3.93 δ corresponding to amine (–NH₂) proton. The signals in the range of 7.29 and 6.81 δ of (8H) are attributed to the aromatic protons of phenylene rings whereas signal at 8.14, 7.92, 7.49 and 7.32 δ (12H) are assigned to naphthalene proton. The NMR signal appears at 6.09 δ singlet attributed to methylene of –CH attached to ring.

Fig. 3. ¹H-NMR of 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yl)oxy)phenyl)thiazol-2-amine (III)

The ¹³C NMR spectrum (Fig. 4.) of 4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yl)oxy)phenyl)thiazol-2-amine (III) Seventeen NMR signals corresponding to 17 different types of carbons. The amine attached carbon appeared at 168.95 δ for (C-NH₂); whereas quaternary carbons showed signals at 151.48, 147.68, 129.32, 125.51, 123.26, 119.84 δ. The CH carbons appeared at 124.82, 124.21, 123.27, 121.78, 120.83, 119.85, 114.46, and 113.93 δ whereas CH carbon bind with sulphur showed NMR signals at 103.80 δ.
Fig. 4. $^{13}$C-NMR of 4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yloxy)phenyl)thiazol-2-amine(III)

The mass spectrum of 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yloxy)phenyl)thiazol-2-amine (III) (Fig. 5.) showed molecular ion peak at m/e (m+1) at 635 corresponding to molecular weight of 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yloxy)phenyl)thiazol-2-amine (III).

Fig. 5. Mass spectrum of 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yloxy)phenyl)thiazol-2-amine(III)

3.2. Polymer Synthesis

From all above spectral characterization data, it confirmed that, 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yloxy)phenyl)thiazol-2-amine(III) diamine monomer was formed.

3.2. Polymer Synthesis

Synthesis of poly(ether-imide)s from 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yloxy)phenyl)thiazol-2-amine(III)
New series of polyimides containing naphthyl group, ether linkage were synthesized by the reaction of stoichiometric quantities of diamines and five different aromatic dianhydrides as shown in Scheme 2.; wherein step first involved conventional ring-opening polycondensation of 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yl)oxy)phenyl)thiazol-2-amine (III) with the dianhydrides in NMP at low temperature to form linear open chain poly (amic acid). In the step second the conversion of poly (amic acid) to polyimides was performed by thermal process for the subsequent cyclodehydration to form poly (ether-imide)s. During the imidization the colour of poly (amic acid) changed from pale yellow to deep brown as the imidization proceeded.

Scheme 2. Synthesis of poly(ether-imide)s from novel diamine with different dianhydrides.
The yield and viscosity results of polyamic acid synthesis are summarized in Table 1. The reaction mixture was homogenous throughout the progress of reaction and gave viscous poly(amic acid)s, which were further transformed to polyimides by thermal imidization as described in procedure 2.3. All the polymers were obtained in the quantitative yields. The inherent viscosities of these poly (amic acid)s were in the range of 0.32 to 0.71 dL/g; this indicates the formation of moderate to high molecular weight of polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monomers</th>
<th>Yield %</th>
<th>Inherent Viscosity dL/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI-I</td>
<td>TDA</td>
<td>99</td>
<td>0.30</td>
</tr>
<tr>
<td>PI-II</td>
<td>TDA</td>
<td>99</td>
<td>0.38</td>
</tr>
<tr>
<td>PI-III</td>
<td>TDA</td>
<td>99</td>
<td>0.32</td>
</tr>
<tr>
<td>PI-IV</td>
<td>TDA</td>
<td>98</td>
<td>0.37</td>
</tr>
<tr>
<td>PI-V</td>
<td>TDA</td>
<td>98</td>
<td>0.71</td>
</tr>
</tbody>
</table>

*Inherent viscosity was measured at a concentration of 0.5 g/dL ml in NMP at 30°C

**Structural characterization**

The formations of PIs were confirmed by FTIR spectroscopy. Figure (Fig 6.) shows the FT-IR spectra of PIs. The complete conversion of the amic acid to imide ring was proved by the corresponding C=O stretching of carboxylic acid and 1666 cm⁻¹ corresponding to C=O imide stretching, together by the appearance of absorption bands at about 1784 cm⁻¹ (asymmetrical C=O stretching), 1721 cm⁻¹ (symmetrical C=O stretching), 1361 cm⁻¹ (C-N stretching), and 749 cm⁻¹ (C=O bending) corresponding to the characteristic of imide bands. Obviously, in addition, absorption band at 1263 cm⁻¹ attributed to aromatic ether (Ar-O-Ar) stretching was also observed.

![Fig.6. FT-IR Spectrum of PI-I to PI-V](image-url)
The structural features of the poly(ether-imide)s were characterized by FT-IR spectroscopy of poly(ether-imide) PI-I is shown in (Fig 6.) The characteristic absorption bands of the imide rings appeared at around 1776 and 1723 cm\(^{-1}\) (typical of imide carbonyl asymmetrical and symmetrical stretching), 1361 cm\(^{-1}\) (C–N stretching), and 742 cm\(^{-1}\) (C–N bending). The absorption band at 1016 cm\(^{-1}\) is due to the imide ring deformation. In addition, absorption band at 1233 cm\(^{-1}\) attributed to aromatic ether (Ar-O-Ar) stretching was also observed.

FT-IR spectrum poly(ester-imide) PI-III is shown in (Fig 6.) They displayed similar pattern of all absorption bands characteristic of poly ether imide. The disappearance of the amic-acid bands indicates an almost complete conversion of the poly (amic acid) precursor into the polyimide. The characteristic absorption bands of the imide rings appeared at 1777 and 1723 cm\(^{-1}\) (typical of imide carbonyl asymmetrical and symmetrical stretching), 1358 cm\(^{-1}\) (C–N stretching), and 756 cm\(^{-1}\) (C–N bending). The absorption band at 1061 cm\(^{-1}\) is due to the imide ring deformation. In addition, absorption band at 1231 cm\(^{-1}\) attributed to aromatic ether (Ar-O-Ar) stretching was also observed.

FT-IR spectrum poly (ether - imide) PI-V is shown in (Fig 6.) They showed similar pattern of all absorption bands characteristic of poly ether imide. The characteristic absorption bands of the imide rings appeared at 1721 cm\(^{-1}\) (typical of imide carbonyl symmetrical stretching), and 749 cm\(^{-1}\) (C–N bending). In addition, absorption band at 1229 cm\(^{-1}\) attributed to aromatic ether (Ar-O-Ar) stretching was also observed.

All of the poly(ether-imide)s also exhibited strong characteristic absorption bands at 2970 and 3070 cm\(^{-1}\) is exhibited due to (C-H stretching) of aliphatic and aromatic respectively.

### Properties of poly(ether-imide)s

#### Solubility of poly(ether-imide)s

The solubility of poly(ether-imide)s were carried out at 3% w/v in organic solvents at room temperature. The solubility data is shown in Table 2. The literature reveals that polyimides generally show poor solubility in common organic solvents. Interestingly, poly(ether-imide)s PI-2 showed excellent solubility in solvents such as DMF, DMAc, NMP, DMSO and H\(_2\)SO\(_4\) at room temperature. The poly(ether-imide)s PI-3 shows poor solubility in DMAc, DMSO and DMF; this is attributed due to compact packing of (ODPA). All the poly(ether-imide)s were insoluble in THF, DCM and chloroform and partly soluble in pyridine. All the polyimides show good solubility in NMP. The improved solubility of these poly(ether-imide)s could be attributed to the combined effect of presence of multipleisomerisms. The features are responsible for decrease in packing density and intermolecular interactions between polymer chains are ether linkages, Naphthyl ring.

### Table 2. Solubility Behavior of Poly(ether-imide)s

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvents</th>
<th>DMF</th>
<th>DMAc</th>
<th>DMSO</th>
<th>NMP</th>
<th>Pyridine</th>
<th>THF</th>
<th>CHCl(_3)</th>
<th>DCM</th>
<th>H(_2)SO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI-1</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>++</td>
</tr>
<tr>
<td>PI-2</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>++</td>
</tr>
<tr>
<td>PI-3</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>++</td>
</tr>
<tr>
<td>PI-4</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>++</td>
</tr>
<tr>
<td>PI-5</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>++</td>
</tr>
</tbody>
</table>

(+ +) Soluble at room temperature, (+) soluble after heating, (++) partially soluble, (--) insoluble.

### Thermal properties

Thermal behaviour of poly(ether-imide)s was estimated by means of thermogravimetry and differential scanning calorimetry. The thermal stability of the poly(ether-imide)s was studied by...
thermogravimetric analysis at a heating rate of 10°C /min in nitrogen atmosphere. Table 3 incorporate the thermal data such as glass transition temperature (Tg), initial decomposition temperature (Td), temperature at which 10% weight loss occurred (T10) and residual weight at 900°C.

Table 3. Physical properties of Poly(ether-imide)s

<table>
<thead>
<tr>
<th>Polymer</th>
<th>T_I° C in N_2</th>
<th>T_d° C in N_2</th>
<th>T_g°C</th>
<th>Residual Wt % at 900°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI-I</td>
<td>315</td>
<td>395</td>
<td>244</td>
<td>51</td>
</tr>
<tr>
<td>PI-II</td>
<td>326</td>
<td>411</td>
<td>236</td>
<td>54</td>
</tr>
<tr>
<td>PI-III</td>
<td>348</td>
<td>439</td>
<td>214</td>
<td>55</td>
</tr>
<tr>
<td>PI-IV</td>
<td>321</td>
<td>409</td>
<td>226</td>
<td>48</td>
</tr>
<tr>
<td>PI-V</td>
<td>374</td>
<td>464</td>
<td>239</td>
<td>57</td>
</tr>
</tbody>
</table>

b Temperature at which onset of decomposition was recorded by TG at a heating rate of 10°C /min.

Tg - Glass transition temperature determined by DSC at a heating rate of 10°C/min

Td – Temperature of 10% decomposition

T10 – Initial decomposition temperature.

Thermal stability of poly(ester-imide)s was investigated by thermogravimetric analysis (TGA) at a heating rate of 10°C/minute in nitrogen atmosphere (Fig. 7).

Fig 7. TGA curve of Poly(ether-imide)s PI-I to PI-V
The initial decomposition temperature, decomposition temperature at 10% weight loss (T10) and char yields at 900°C were calculated from original thermograms and the data is presented in Table 3. The initial decomposition temperatures are in the range 315°C-374°C. The Td value of polymer is an important criterion for evaluation of thermal stability and the values are in the range 395°C-464°C indicating their good thermal stability. The char yields/weight residues left at 900°C were in the range 48-57 %.

Glass transition temperatures (Tg) of poly(ether-imide)s were evaluated by means of differential scanning calorimetry (DSC) at a heating rate of 10°C/min in nitrogen atmosphere and Tg values are listed in Table 3. DSC curves of poly(ester-imide)s obtained from second heating scans are represented in (Fig. 8.)

![Fig.8. DSC curve of Poly(ether-imide)s PI-I to PI-V](image-url)

The thermal behavior data of the PIs, collected from DSC are summarized in Table 3. DSC revealed that rapid cooling from 400°C to room temperature produced predominantly amorphous samples, so that Tg of the polymer could be easily read in the second heating trace of DSC. As shown in (Fig. 8.), the Tg values of PIs were in the range of 216–244°C. The increasing order of Tg generally correlated with the structure of the dianhydride component. As expected, PI-I originated from PMDA showed the highest Tg value 244°C due to the incorporation of rigid pyromellitic units. However, PI-III derived from ODPA presented the lowest Tg value 214°C, which attributed to the presence of flexible ether linkages moieties in the polymer backbone.
X-Ray diffraction

The crystallinity of poly(ether-imide)s was determined by wide-angle X-ray diffraction (WAXD) studies. X-Ray diffractograms of poly(ether-imide)s derived from ATDA and commercial aromatic dianhydrides are reproduced in (Fig. 9.)

![XRD curve of Poly(ester-imide)s PI-I to PI-V](image)

Fig. 9. XRD curve of Poly(ester-imide)s PI-I to PI-V

The WAXD patterns of PI-I to PI-V polymers showed broad peak, which indicated that they were amorphous pattern, and it can be mainly explained by the introduction of bulky naphthyl groups and then greatly decrease the crystallinity of polymers.

4. Summary and Conclusions

A series of new poly(ether-imide)s containing naphthyl moiety, and ether linkages was synthesized from 4-(4-(1-(2-(4-(2-aminothiazol-4-yl)phenoxy)naphthalen-1-yl)naphthalen-2-yl)oxy)phenyl)thiazol-2-amine (III) and commercially available aromatic dianhydrides. Inherent viscosities of these poly(ether-imide)s were in the range 0.37 to 0.71 dL/g, indicating formation of moderate molecular weights. These polymers exhibited good solubility in various polar aprotic solvent such as Nmethyl-2-pyrrolidone (NMP) and H$_2$SO$_4$ etc. X-Ray diffraction pattern of polymers showed amorphous nature. Thermal stability was assessed by 10% weight loss temperature and the degradation temperature of the resultant polymers falls in the ranges from 395°C to 464°C in nitrogen. The glass transition temperature was in the range of 214-244°C.

5. References