



## Soluble and Thermally Stable New Pyridine-based Poly(Ether Imide)s Synthesized Through Conventional and Ionic Liquid Methods

Elaheh Gharekhani<sup>1\*</sup>, Shahram Mehdipour-Ataei<sup>2</sup>, and Masoud Taghi-Ganji<sup>1</sup>

(1) Department of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran

(2) Iran Polymer and Petrochemical Institute, P.O. Box: 14965/115, Tehran, Iran

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### ABSTRACT

Novel types of polyimides with specific properties were prepared by two ways, namely the conventional two-step and ionic liquid methods (IL) to compare the final polymer characteristics. In this way, nucleophilic substitution reaction of 4,4'-oxydianiline with 6-chloronicotinoyl chloride yielded a dichlorodiamide compound (DCDA) which by reaction with 5-amino-1-naphthol afforded a new diamine with specific structural features. Polycondensation reaction of the diamine with different aromatic dianhydrides using a two-step method and in an ionic liquid of one step method resulted in formation of novel polyimides. All the precursors and polyimides were fully characterized using routine analytical methods and their physical and thermal properties including solution viscosity, thermal stability and behaviour, crystallinity and solubility were investigated. According to the obtained results polyimides showed high thermal stability and improved solubility. Using IL as a media in one step method for the preparation of polyimides led to improved properties in comparison to conventional two-step method of imidization. The inherent viscosity of the polymers was in the range of 0.40-0.88 dL/g for polyimides prepared via two-step method, and 0.52-0.93 dL/g for polyimides prepared via IL one-step method. The weight loss of 10% as an important criterion for evaluation of thermal stability occurred in the range 430-445°C for polyimides prepared by two-step method, while the same weight loss took place in the range 457-474°C for polyimides prepared by IL one-step method.

### Key Words:

polyimide;  
thermally stable;  
polycondensation;  
ionic liquid;  
solubility.

### INTRODUCTION

Aromatic polyimides are well established as high performance polymers and they are known as high temperature resistant materials [1]. High-performance polymers are a significant class of polymers and there are growing demands for them. Therefore, in recent years syntheses of high-performance polymers have attracted many researchers' attentions. In general, they show high thermal stability, good chemical resistance,

and excellent mechanical properties. Among different high-performance polymers, polyimide materials are noted for their high thermal stability, solvent resistance, excellent insulating integrity, good mechanical strength, excellent dimensional stability, low coefficient of friction, high dielectric strength, low dielectric constant, low out-gassing, and resistance to creep and wear [2].

In the last decades, thermally

(\*) To whom correspondence to be addressed.

E-mail: [e\\_gharekhani@iut-tub.ac.ir](mailto:e_gharekhani@iut-tub.ac.ir)

stable polymers have received extensive interest due to the increasing demands for high temperature polymers as replacements for metals or ceramics in automotive, aerospace, and microelectronic industries. Polyimides and polyamides are certainly two of the most successful classes of high temperature polymers [3-6]. Copolymerization of these polymers could offer unique collection of properties.

Poly(amide-imide)s deserve particular attention as they are probably the class of copolyimides that most closely resemble the thermal properties of aromatic polyimides. Furthermore, the inclusion of an amide group into the polyimide backbone increases its processability, solubility, and mouldability [7]. Poly(amide-imide)s can be synthesized by polycondensation based on various monomers containing anhydride, carboxylic acid, or aromatic amino groups [8-10].

Recently, considerable efforts have been made to modify the chemical structure of polyimides to change their properties with regard to a specific property [11-14]. In order to enhance their solubility and processability while maintaining thermal stability, the incorporation of bulky substituents or bulky pendant groups [15], flexible ether units [16], and polar structures into rigid polymer backbones [17,18] have been suggested.

The purpose for selection of heterocyclic rings in the main chain of the synthetic polymer is to impart certain properties to the polymer. Among different heterocyclic rings, the benefit of using a pyridine nucleus is supported by its high thermal stability derived from its molecular symmetry and aromaticity [19,20]. Also, the presence of nitrogen atom in the structure creates a polarized bond which improves the solubility of the polymers due to increased dipole-dipole interactions in the polymer-solvent system. Therefore, the main advantage of using pyridine in the backbone of polyimides is to increase their solubility while maintaining their thermal stability.

It is noteworthy that further applications of ionic liquids as green and polar media for different reactions have been reported. They are organic salts that are liquid at ambient temperatures. They are highly polar solvents that dissolve several organic and inorganic compounds and are non-volatile. Application of ILs as solvents for organic synthesis

and polymerization facilitates the separation of polymer and catalyst as they may reduce the extent of side-reactions [21,22].

Here we wish to express the preparation of novel poly(ether imide)s from polycondensation of a new diamine monomer with different dianhydrides using two different methods [23]. The diamine was prepared via reaction of 4,4'-oxyaniline (ODA) with 6-chloronicotinoyl chloride and subsequent reaction of this dichloro compound with 5-amino-1-naphthol. According to this strategy, the fully aromatic diamine contained pyridine units, naphthalene moieties, ether groups, and amide structures. Polycondensation reactions of the prepared diamine with different dianhydrides using conventional and ionic liquid methods afforded different poly(ether imide)s containing preformed amide units with high thermal stability and improved solubility. Structure-property relations of these newly formed polyimides were investigated and the effect of polymerization methods on the properties of the final polymers was studied.

## EXPERIMENTAL

### Materials

Pyromellitic dianhydride (PMDA), 3,3',4,4'-bezophenonetetracarboxylic dianhydride (BTDA), *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethylsulphoxide (DMSO), *m*-cresol, toluene,  $K_2CO_3$ , methanol, pyridine, 4,4'-oxydianiline (ODA), and acetic anhydride were obtained from Merck, Germany. 4-Aminophenol, 5-amino-1-naphthol, 6-chloronicotinoyl chloride, 1-ethyl-3-methylimidazolium bromide, and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) were purchased from Aldrich, USA. PMDA, BTDA, and 6FDA were dried in vacuum oven at 110°C for 5 h. NMP, DMAc, DMF and toluene were purified by vacuum distillation over calcium hydride.

### Instruments

Infrared measurements were performed on a Bruker-IFS48 FTIR spectrometer (Ettlingen, Germany). The  $^1H$  NMR spectra were recorded in DMSO- $d_6$  solution using a Bruker Avance 300 MHz (GmbH, Germany).

Elemental analyses were performed by a CHN-O-Rapid Heraeus elemental analyzer (Wellesley, MA). Differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA) were recorded in air at a heating rate of 10°C/min on a Stanton Redcraft STA-780 (London, UK). Inherent viscosities were measured by using an Ostwald viscometer at a concentration of 0.5 g dL<sup>-1</sup> in NMP at 30°C. Wide angle X-ray diffraction patterns were performed at room temperature on an X-ray diffractometer (Siemens model D 5000, Germany) using Ni-filtered CuK<sub>α</sub> radiation (40 kV, 25 mA) with scanning rate of 3°/min.

### Monomer Synthesis

#### *Synthesis of Dichlorodiamide Compound (DCDA)*

Into a 100-mL, two-necked, round-bottomed flask equipped with drying tube (CaCl<sub>2</sub>), a nitrogen inlet tube, an ice bath, and a magnetic stirrer was placed 2.00 g (10.0 mmol) of ODA. Then 60 mL of NMP was added to the flask and it was maintained at 0°C for 30 min with continuous stirring under inert nitrogen gas. Then, 17 mL of propylene oxide was added to the mixture and stirred at the same temperature for 3 min; followed by addition of 3.97 g (22.2 mmol) of 6-chloronicotinoyl chloride to the mixture while the temperature of mixture was raised to ambient temperature and kept for 6 h. The flask content was then poured into 200 mL of distilled water with stirring. The precipitated product was washed with hot water and methanol, repeatedly. The product was dried in an oven at 60°C for about 8 h. The yield of the reaction was about 88 % (4.20 g). mp > 300°C. [IR (KBr) ν (cm<sup>-1</sup>): 3237-3400 (N-H), 1645 (C=O), 1450-1600 (C=C), 1226 (-O-); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ (ppm): 7.03 dd (4H, benzene), 7.70 d (2H, py), 7.77 dd (4H, benzene), 8.36 dd (2H, py), 8.94 d (2H, py), 10.50 s (2H, amide); elemental analysis calculated for C<sub>24</sub>H<sub>16</sub>N<sub>4</sub>O<sub>3</sub>C<sub>12</sub>: C, 60.12 %; H, 3.34 %; N, 11.69 %; found: C, 60.21 %; H, 3.45 %; N, 11.60 %].

### Synthesis of Diamine

The reaction components including, 3.83 g (8.00 mmol) of DCDA, 2.93 g (18.4 mmol) of 5-amino-1-naphthol, 40 mL of NMP and 28 mL of dry toluene were placed into a 100-mL three-necked round-

bottomed flask equipped with a Dean-Stark trap, a condenser, a nitrogen inlet tube, a thermometer, an oil bath, and a magnetic stirrer. Then, 3.73 g (27.0 mmol) of K<sub>2</sub>CO<sub>3</sub> was added to the mixture and the reaction mixture was heated to 140°C for 6 h with continuous stirring. The generated water was removed from the reaction mixture by azeotropic distillation. The reaction temperature was raised to 165°C and kept at the same temperature for 21 h. Then, the resulting reaction mixture was cooled and poured into water. A volume of 100 mL of 5% NaOH was added to the mixture and the mixture was filtered and washed with hot water. The crude mixture was washed repeatedly with a 5% NaOH solution, water, and finally hot methanol. The obtained product was dried in an oven at 80°C. Yield of the reaction was about 90% (5.20 g). mp 198-200°C. [IR (KBr) ν (cm<sup>-1</sup>): 3358-3450 (N-H), 1656 (C=O), 1460-1600 (C=C) and 1249 and 1216 (-O-); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ (ppm): 5.87 s (4H, amine), 6.71 d (2H, naphthyl), 6.96 d (2H, naphthyl), 7.02 d (4H, benzene), 7.19 dd (2H, naphthyl), 7.25 dd (2H, naphthyl), 7.38 d (2H, naphthyl), 7.40 d (2H, py), 7.73 d (4H, benzene), 8.03 d (2H, naphthyl), 8.35 d (2H, py), 8.60 s (2H, py), 10.32 s (2H, amide); elemental analysis calculated for C<sub>44</sub>H<sub>32</sub>N<sub>6</sub>O<sub>5</sub>: C, 72.93 %; H, 4.42%; N, 11.60 %; found: C, 72.29 %; H, 4.31 %; N, 11.82 %].

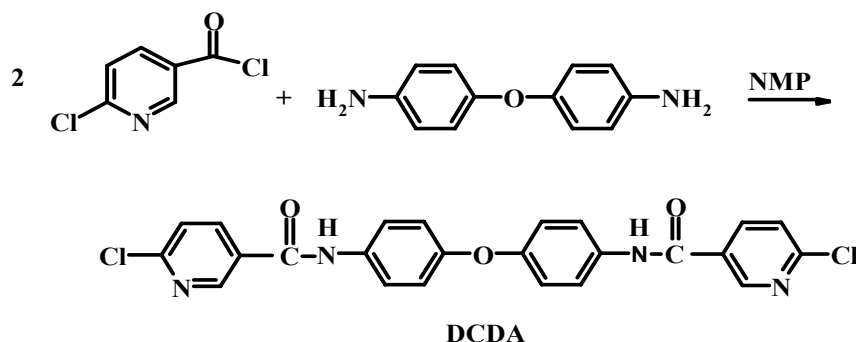
### Polymer Synthesis

#### *Two-step Method of Imidization to Synthesize Poly(amic acid)*

Into a round-bottomed flask equipped with a drying tube, a nitrogen inlet tube, a magnetic stirrer and an ice bath, 2.00 mmol of diamine and, 15 mL of NMP were added and stirred for 30 min at 0°C. Then, 2.00 mmol of dianhydride was added and the mixture was stirred at the same reaction temperature for 1 h. The reaction temperature was kept at ambient temperature for 24 h. The mixture was poured into 200 mL of water/ methanol 1/3 volume ratios. Then it was filtered, washed with hot water, and dried under vacuum oven for 12 h at 40°C.

### Polymerization

Into a 100-mL two-necked round-bottomed flask equipped with a magnetic stirrer, a nitrogen gas inlet tube, and a reflux condenser were placed 1.00 g of



Scheme I. Preparation of DCDA.

poly(amic acid) and 5 mL of dry NMP. The mixture was stirred and then 5 mL of acetic anhydride and 2.5 mL of pyridine were added. The mixture was stirred for 30 min and then slowly heated to 140°C and held for 6 h at the same temperature. The mixture was then cooled and poured into water and filtered, washed with hot water and methanol, and finally dried overnight under vacuum at 120°C.

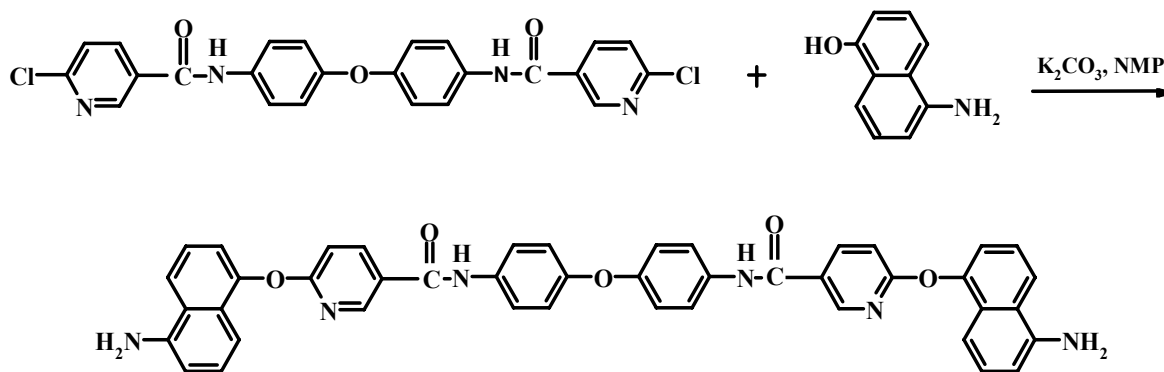
#### One-step Method of Imidization in Ionic Liquid

Into a 100-mL two-necked round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and a reflux condenser were placed 0.886 g (1.20 mmol) of diamine, 0.394 g (1.20 mmol) of dianhydride, and 2.62 g of 1-ethyl-3-methylimidazolium bromide. The mixture was stirred at room temperature for 10 min. Then, it was gradually heated to 180°C and held at this temperature for 10 h. An amount of 0.524 g of 1-ethyl-3-methylimidazolium bromide was added to the mixture and stirred for 5 min. After cooling, the mixture was poured into

350 mL of acetone. Then, it was filtered, washed with hot water and methanol and dried overnight under vacuum at 120°C.

## RESULTS AND DISCUSSION

To obtain soluble, thermally stable poly(ether imide)s some structural features were included in the preparation of a new diamine as a building block for preparation of the polyimide. Incorporation of ether linkage, bulky naphthyl pendant group, introduction of pyridine as a polar heterocyclic ring segment [24,25], and also inclusion of amide units and phenylation of backbone were considered to prepare the diamine. In this way, the diamine was prepared by two consecutive reactions. Reaction of 4,4'-oxydianiline with two moles of 6-chloronicotinoyl chloride in the presence of propylene oxide as an acid scavenger resulted in preparation of a dichlorodiamide (DCDA) (Scheme I). This compound was reacted with 5-



Scheme II. Preparation of diamine.

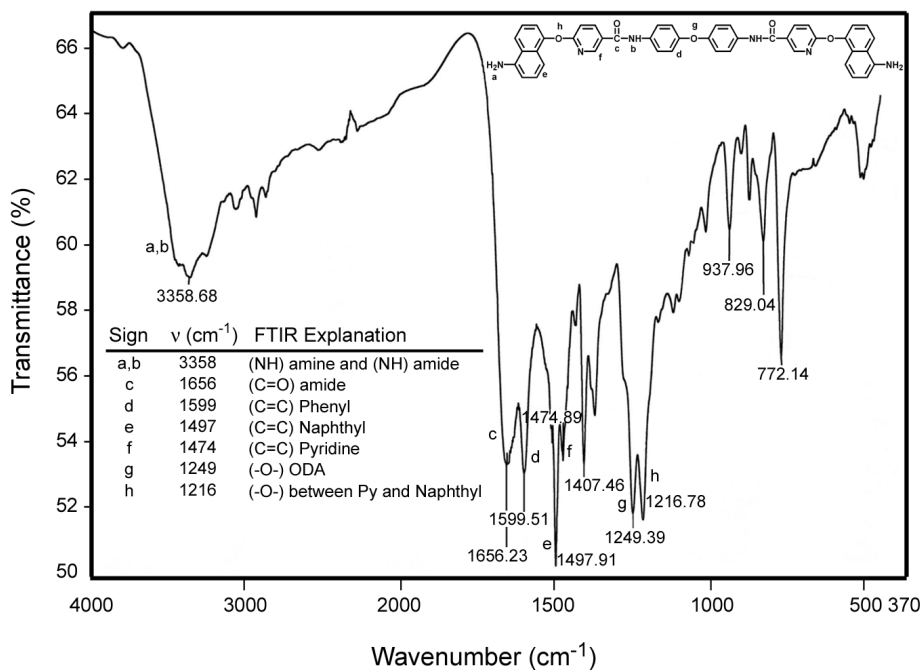


Figure 1. FTIR Spectrum of diamine.

amino-1-naphthol (1/2 molar ratios) in the presence of K<sub>2</sub>CO<sub>3</sub> to obtain a new diamine with unique structural features (Scheme II). The structure of dichloro compound and diamine were confirmed

using different spectroscopic methods and elemental analysis technique. FTIR and <sup>1</sup>H NMR spectra of diamine are shown in Figures 1 and 2, respectively. The novel diamine was prepared in such a way that to

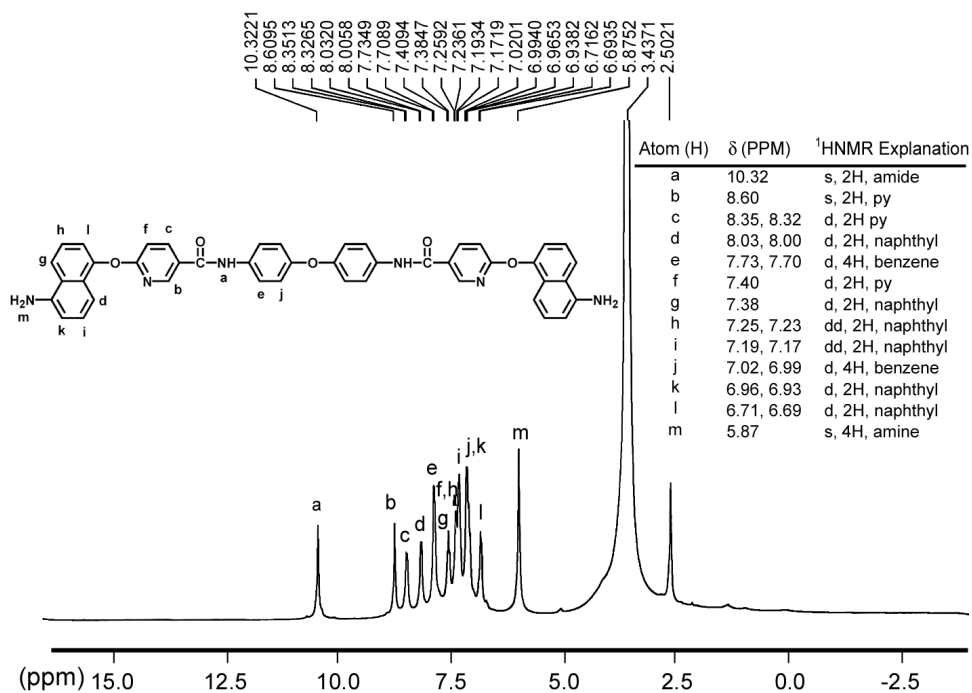
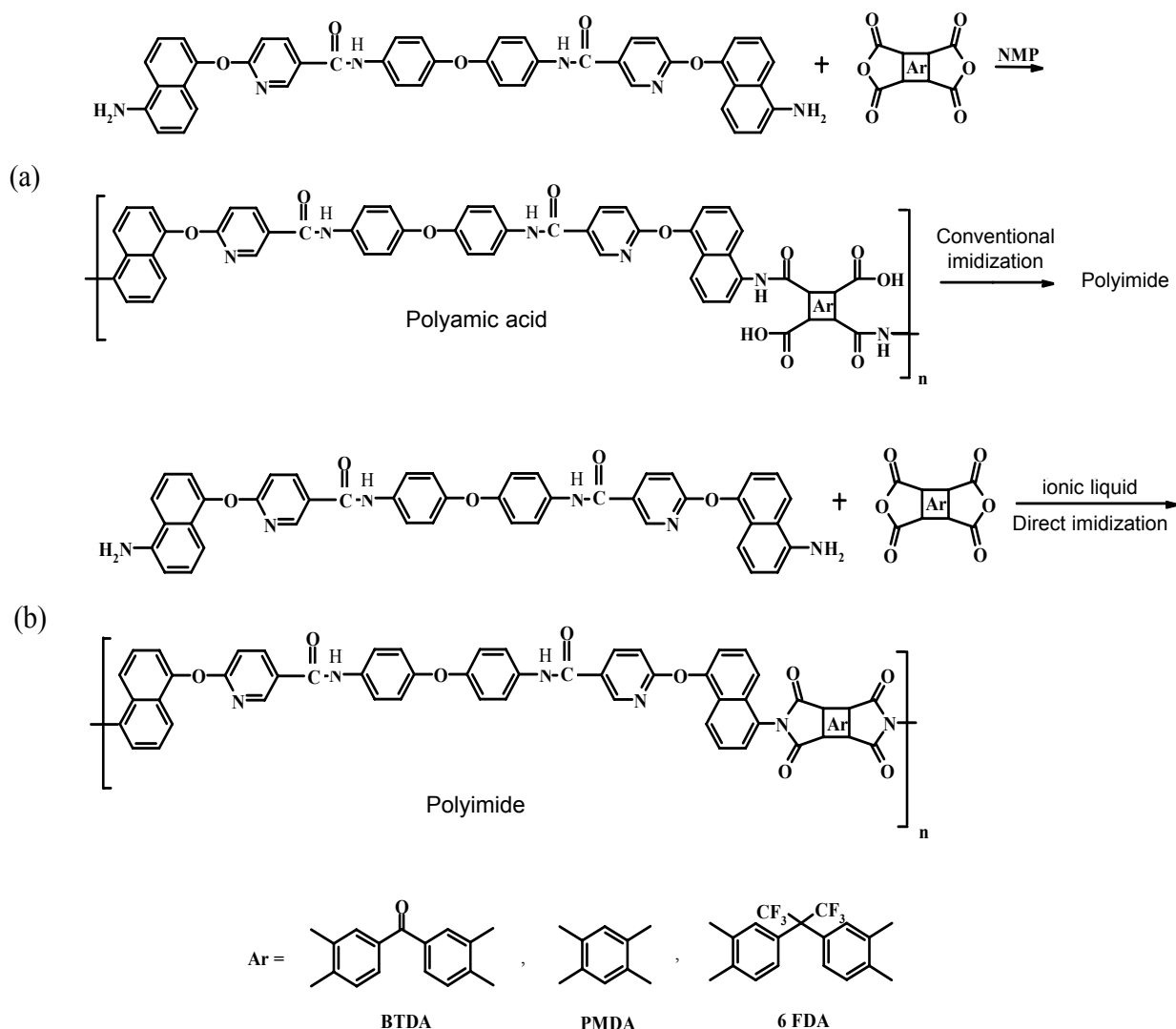


Figure 2. <sup>1</sup>H NMR Spectrum of diamine.



**Scheme III.** Preparation of: (a) polyamic-acid and polyimide via the conventional two-step imidization method and (b) polyimides via one-step ionic liquid method.

induce high thermal stability and improved solubility to the final polyimides. This was achieved by incorporation of pyridine heterocyclic aromatic polar rings, amide polar groups, ether flexible linkages, and bulky naphthyl units into the fully aromatic structure of diamine. Polycondensation reaction of the diamine with various aromatic dianhydrides including PMDA, BTDA, and 6FDA via a common two-step method (polyamic acid formation followed by chemical imidization) and using ionic liquid (IL) in one step method resulted in preparation of different poly(ether imide)s (Scheme III). All poly(ether imide)s were obtained in high yields and were fully characterized using conventional methods including FTIR,

$^1\text{H}$  NMR, and elemental analysis. The characterization results are collected in Table 1 and the representative spectra are shown in Figures 3 and 4.

The polymers show good solubility (about 1.5-1.8 g/dL) in polar aprotic solvents including NMP, DMAc, DMF, DMSO, and *m*-cresol. Presence of flexible ether groups, pyridine polar parts, and packing-hindrance bulky naphthyl units are the main factors for the enhanced solubility of the polyimides. In addition, BTDA and 6FDA-derived polyimides revealed higher solubility in the above polar aprotic solvents which was related to their higher flexibility with respect to rigid PMDA-derived polyimide (Table 2).

**Table 1.** Polymer characterization.

Polyimide	FTIR (cm <sup>-1</sup> )	<sup>1</sup> H NMR (ppm)	Elemental analysis (%)	
			Calc.	Found
PI-PMDA	3060 (-NH-) amide, 1781 (C=O) asym.str.imide, 1729 (C=O) sym.str.imide, 1662 (C=O) amide, 1596 (C-N) out-of-plane bending & (N-H), 1366 (C-N) str.imide, 722 (C-N) imide ring deform.	7.03 d (4H, benzene) 7.13 d (2H, naphthyl) 7.36 d (2H, naphthyl) 7.47 dd (2H, naphthyl) 7.64 dd (2H, naphthyl) 7.74 d (2H, py) & d (2H, naphthyl) 7.98 d (4H, benzene) 8.14 d (2H, naphthyl) 8.42 d (2H, py) 8.51 s (2H, py) 8.70 s (2H, PMDA) 10.10 s (2H, amide)	C: 71.52 H: 3.31 N: 9.27	C: 71.78 H: 3.30 N: 9.25
PI-BTDA	3055 (-NH-) amide, 1780 (C=O) asym.str.imide, 1723 (C=O) sym. str.imide, 1663 (C=O) amide, 1596 (C-N) out-of-plane bending & (N-H), 1366 (C-N) str.imide, 721 (C-N) imide ring deform.	7.01 d (4H, benzene) 7.11 d (2H, naphthyl) 7.38 d (2H, naphthyl) 7.46 dd (2H, naphthyl) 7.70 dd (2H, naphthyl) 7.79 d (2H, naphthyl) 7.83 d (2H, py) 8.01 d (4H, benzene) 8.19 d (2H, BTDA) 8.23 d (2H, naphthyl) 8.30 s (2H, BTDA) 8.35 d (2H, py) 8.58 d (2H, BTDA) 8.61 s (2H, py) 10.36 s (2H, amide)	C: 72.47 H: 3.37 N: 8.32	C: 72.51 H: 3.30 N: 8.33
PI-6FDA	3390-2920 (-NH-) amide, 1784 (C=O) asym.str. imide, 1729 (C=O) sym.str.imide, 1660 (C=O) amide, 1600 (C-N) out-of-plane bending & (N-H), 1371 (C-N) str.imide, 721 (C-N) imide ring deform.	7.02 d (4H, benzene) 7.12 d (2H, naphthyl) 7.34 d (2H, naphthyl) 7.43 dd (2H, naphthyl) 7.59 dd (2H, naphthyl) 7.70 d (2H, 6FDA) & d (2H, py), d (2H, naphthyl) 7.80 s (2H, 6FDA) 7.94 d (2H, 6FDA) 8.06 d (4H, benzene) 8.22 d (2H, naphthyl) 8.40 d (2H, py) 8.68 s (2H, py) 10.08 s (2H, amide)	C: 66.78 H: 3.00 N: 7.42	C: 66.50 H: 2.98 N: 7.50

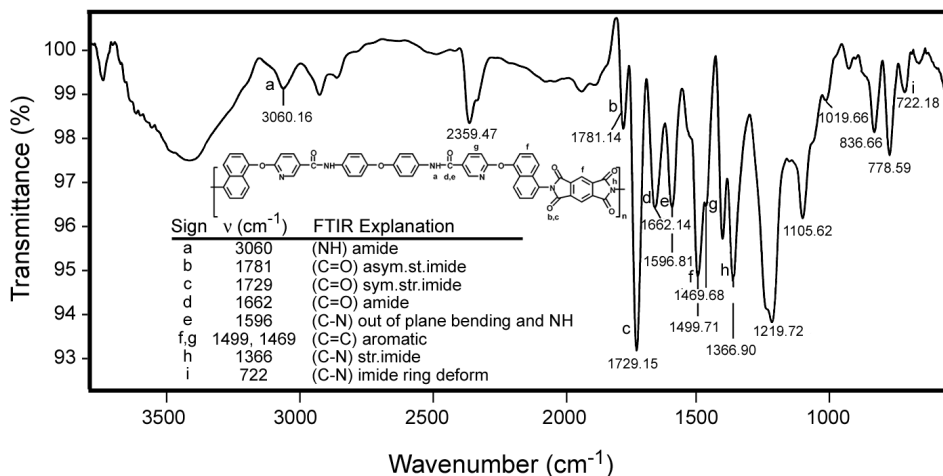


Figure 3. FTIR Spectrum of PI-PMDA.

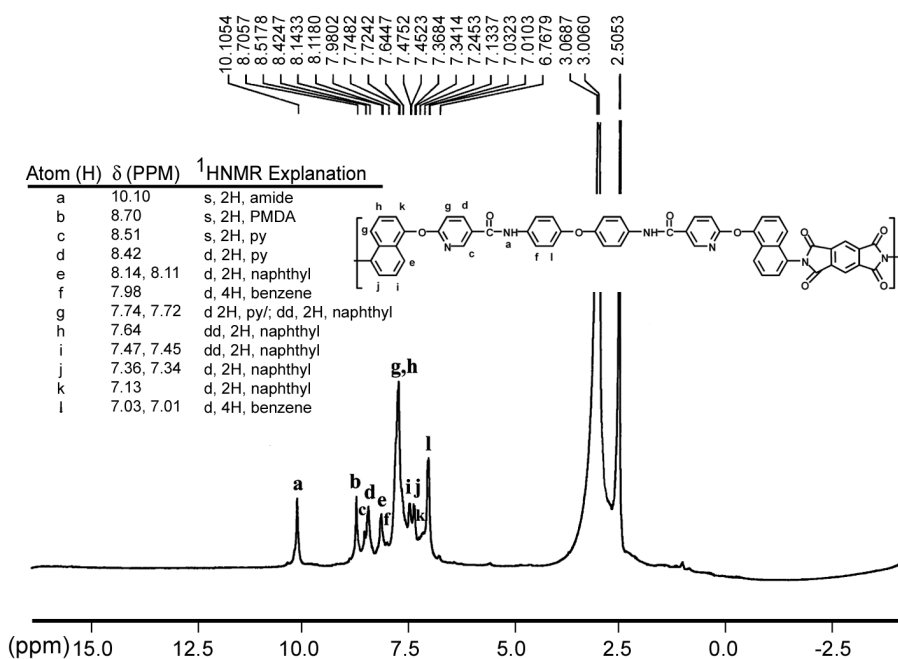


Figure 4. <sup>1</sup>H NMR Spectrum of PI-PMDA.

Table 2. Properties of poly(ether amide imide)s.

Polyimide	$\eta_{inh}$ (dL/g)		Moisture uptake (%)		Thermal analysis $T_{10}$ (°C)		Yield (%)	
	a	b	a	b	a	b	a	b
PI-PMDA	0.88	0.93	1.67	1.88	415	445	80	83
PI-BTDA	0.42	0.60	2.05	2.01	405	438	81	90
PI-6FDA	0.40	0.52	4.20	2.30	385	430	78	88

a: Prepared through two-step imidization method. b: Prepared through one-step ionic liquid method



**Table 3.** Solubility of polyimides.

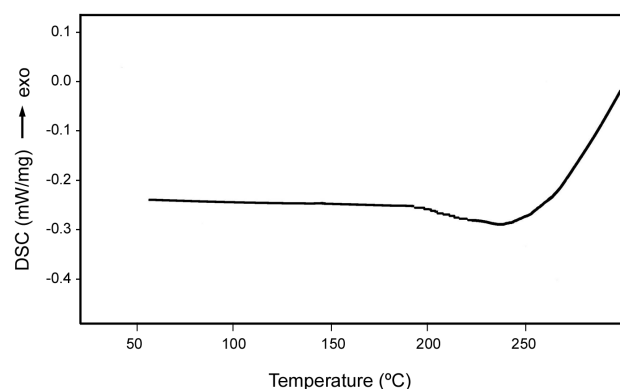
Solvent \ Polyimide	PI-PMDA	PI-BTDA	PI-6FDA
NMP	+	+	+
DMAC	+	+	+
DMSO	+	+	+
DMF	±	+	+
<i>m</i> -Cresol	±	+	+
CH <sub>2</sub> Cl <sub>2</sub>	-	-	-

Inherent viscosity, as a suitable criterion for evaluation of molecular weights, was obtained at a concentration of 0.5 g/dL in NMP at 30°C within 0.45-0.88 dL/g range for polyimides prepared via a two-step method, and 0.52-0.93 dL/g for polyimides prepared via IL of one-step method. As a result, reasonable molecular weights were obtained for the polymers while using IL of one-step method led to higher values of viscosity (Table 3). The role of IL as solvent and catalyst in mechanism of polycondensation of aromatic dianhydrides with aromatic diamines has been evidently confirmed that the solubility of starting materials could be improved by addition of imidazolium type zwitterion which led to higher molecular weights of resulting polyimides. The non-volatility and thermal stability of ionic liquids should make them attractive solvents for polycondensation processes that usually require high temperatures and the removal of the volatile byproducts. On the whole, ionic liquids have been found to be convenient solvents for the synthesis of polyimides requiring milder reaction conditions for the synthesis of high-molecular weight polymers [26-28].

The moisture uptake of polymers was about 1.67-2.20% for polyimides prepared via a two-step

method, and 1.88-2.30% for polyimides prepared via IL of one-step method (Table 3). A relatively high amount of moisture uptake in these polyimides could be mainly related to the presence of amide structures in the backbones of polyimides.

Thermal behaviours of the poly(ether imide)s were studied in air at a heating rate of 10°C/min using DSC technique. In their DSC curves, the midpoint of the changing slope of the baseline was considered as T<sub>g</sub> and the results are collected in Table 4. Thermal stability of the polyimides was estimated in air at a heating rate of 10°C/min using TGA method. The initial decomposition temperature of the polymers was about 335-360°C for polyimides prepared through a two-step, and 352-374°C for polyimides prepared through IL one-step method. The 10% weight loss which is an important criterion for evaluation of thermal stability was in the range of 430-445°C for polyimides prepared by the two-step method, while it was 457-474°C for polyimides prepared in IL by one-step method. These data together with the maximum decomposition temperature (T<sub>max</sub>) and weight of remaining polymer



**Figure 5.** DSC Curve of PI-PMDA.

**Table 4.** Thermal analysis of the polyimides.

Polyimide	T <sub>g</sub> (°C)	T <sub>0</sub> (°C)	T <sub>10</sub> (°C)	T <sub>max</sub> (°C)	Char yield at 600°C (°C)
PI-PMDA	235	360	445	485	46
PI-BTDA	221	347	438	475	44
PI-6FDA	210	335	430	470	42

T<sub>g</sub>: Glass transition temperature obtained from DSC. T<sub>0</sub>: Initial decomposition temperature. T<sub>10</sub>: Temperature for 10% weight loss. T<sub>max</sub>: Maximum decomposition temperature. Char yield: weight of polymer remained.

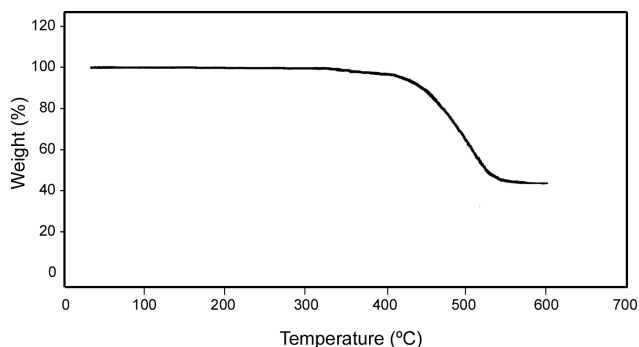


Figure 6. TGA Diagram of PI-PMDA.

at 600°C are tabulated in Table 4.

The representative DSC and TGA curves are shown in Figures 5 and 6, respectively. According to the obtained data, poly(ether imide)s display high thermal stability and among them PMDA-derived polymer shows the highest thermal stability which is attributed to the greater rigidity of this structure in comparison to other products. Also, it is revealed that polyimides prepared by IL one-step method have higher thermal stability with respect to the polyimides prepared by the conventional two-step method which could be related to increased molecular weights of polymers obtained by the former method and therefore improved thermal properties [26,29].

Wide angle X-ray diffraction studies of the polymers were achieved with specimens in powder form. The results indicate that the polymers are almost amorphous. This is attributed to the presence of flexible ether groups and introduction of packing-disruptive bulky naphthyl side groups which resulted

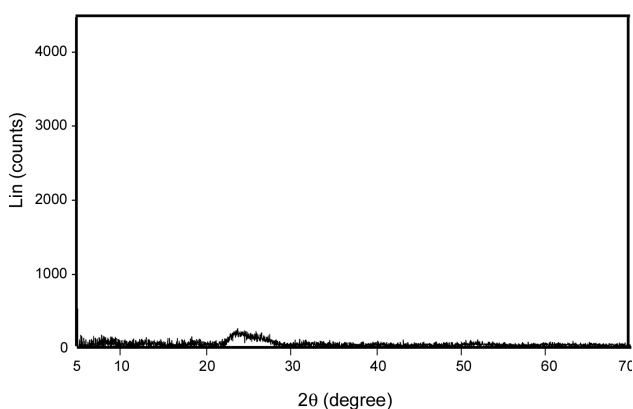


Figure 7. Wide angle X-ray diffraction pattern of PI-PMDA.

in increased chain distances and decreased chain interactions. A typical wide angle X-ray diffraction pattern is shown in Figure 7.

## CONCLUSION

A new diamine-containing pyridine polar unit, ether groups, amide structures, and bulky naphthyl groups with fully aromatic structure were successfully prepared via two steps reactions. Soluble and thermally stable poly(ether imide)s were obtained through a conventional two-step and one-step ionic liquid-aided polyimidization methods. The presence of flexible ether groups, pyridine polar structures, amide units, and bulky naphthyl moieties on the one hand and avoiding any weak linkages and providing fully aromatic structures on the other hand result in production of polyimides with improved solubility and high thermal stability. The counter-balancing of thermal stability versus solubility is effectively improved by design of suitable diamines and their related polyimides. The inherent viscosities and thermal properties of the polyimides synthesized via IL method are higher than the viscosities and thermal properties of the same polyimides prepared using the conventional two-step method. It is concluded that IL could be beneficially used for synthesis of polyimides with improved properties.

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