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Synthesis and Characterization of Novel Polyamide-ethers Based on Bis-imidazole Containing Bulky Aryl Pendant Groups

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Abstract: A series of novel polyamide-ethers (PAEs) based on bis-imidazole containing bulky aryl pendant groups was prepared by direct polycondensation of a diamine, 4-(1-(4-(4-(2-(4-aminophenyl)-4,5-diphenyl-1H-imidazol-1-yl)phenoxy)phenyl)-4,5-diphenyl-1H-imidazol-2-yl)benzenamine (DABI), and various dicarboxylic acids. All the resulting polyamide-ethers were amorphous with inherent viscosities ranged from 0.52 to 0.61 dL/g and were readily soluble in many organic solvents which could be solution-cast into transparent and tough films. The glass transition temperatures (T_g) of these polymers were affected considerably by their chemical structure and ranged from 230 to 310 °C. They had useful levels of thermal stability associated with relatively high temperatures of 10% weight loss (T_{10}) in the range of 329-399 °C in air atmosphere.

Keywords: Polyamide-ether, polycondensation, solubility, thermal properties, bis-imidazole.

Introduction

Polyamides occupy an important place in the world of polymers because they offer excellent physical and chemical properties, thermal and oxidative stability, flame resistance, and superior mechanical and dielectric properties^[1,2]. However, in addition to these useful properties, for many applications polymers need to have good film-forming ability and adequate organo-solubility. In order to answer these requirements, structural modifications of polyamides often became essential. The earliest, simplest, and best known commercial aramids (the shortened form of aromatic polyamides) are poly(*p*-phenylene terephthalamide) (PPPT) and poly(*m*-phenylene isophthalamide) (PMPI). Both can be transformed upon solution by wet spinning into flame, cut-resistant, and high tensile strength synthetic fibers, or they can be cast into varnishes or enamels yielding similar properties. The transformed materials have applications in advanced fabrics, coatings, and fillers, as advanced composites in the aerospace and armament industry, as asbestos substitutes, electrical insulation, bullet-proof body armor, industrial filters, and protective and sport clothing, among others^[3].

It is known that ether linkages inserted in aromatic main chains provide them with a significantly lower energy of internal rotation^[4]. Aramids containing ether linkages or asymmetrical groups are significantly more flexible and soluble than conventional aramids^[4-6]. In general, these structural modifications lead to lowering of glass transition temperatures, as well as significant improvement in solubility and processability.

The heterocycles are interesting chemical structures to modify the properties of aramids and other thermally stable polymers because they usually impart excellent thermal stability with improved solubility. Heterocycle rings have been widely incorporated into the chains of thermally stable polymers such as polyesters, polyamide-

imides, polyazomethines, polyureas, polycyanurates, and polyamides. Generally, the heterocyclic units in the main chain, and in the pendant structure, impart excellent thermal stability with improved solubility, which justifies the research efforts directed toward them^[7-12].

The incorporation of bulky pendant groups can provide beneficial effects for solubility, because this approach produces a separation of chains, a weakening of hydrogen bonding, and a lowering of chain packing with a gain of free volume, which diminishes the T_g s. On the contrary, bulky side groups also restrict molecular mobility, so that the overall observable effect is an increase in T_g s. This counteracts the chain separation effect, and simultaneously improves the solubility^[13-22].

So in order to prepare novel processable polyamide-ethers (PAEs) with enhanced thermal stabilities, new diamine monomer containing ether linkage based on bis-imidazole heterocyclic group and containing bulky aromatic pendant groups was synthesized and used for the preparation of PAEs. The incorporation of aryl groups into the polymer backbone is expected to affect their properties as well as enhance the solubility in organic solvents and improve the processability.

Experimental

Materials

All materials and solvents were purchased either from Merck or Fluka, through a local agency. Hydrazine monohydrate, Pd/C and reagent-grade dicarboxylic acids such as isophthalic acid, adipic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, diphenic acid, solvents such as glacial acetic acid, ethanol and methanol were used as received. N-methyl-2-pyrrolidinone (NMP) and pyridine were purified by

distillation over calcium hydride under reduced pressure and stored over 4 Å molecular sieves. Tetrahydrofuran (THF) was dried by sodium before use.

Measurements

Elemental analysis was run in a Flash EA 1112 series analyser. FTIR spectra were recorded on a Bruker Tensor 27 spectrometer. The IR spectra were obtained using KBr pellets. NMR spectrum was recorded at room temperature using Bruker Spectrometer operating at 400 and 500 MHz for ^1H and at 100 MHz for ^{13}C NMR using deuterated chloroform (CDCl_3) and dimethyl sulfoxide ($\text{DMSO}-d_6$) and tetramethyl silane as an internal standard. The inherent viscosities were measured using an Ubbelohde viscometer with polymer concentration of 0.5 g/dL in NMP at 25 °C. Melting points were recorded on an electrothermal Stuart SMP3. DSC was recorded on a Mettler Toledo DSC822 at a heating rate of 10°C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed with TGA 50 from Shimadzu analyzer at a heating rate of 10 °C/min under air atmosphere and in the temperature range of 30-1,000 °C. Glass transition temperatures (T_g)s were read at the middle of the transition in the heat capacity.

Synthesis

Monomer synthesis

The synthetic pathway leading to the synthesis of target diamine is shown in Scheme 1.

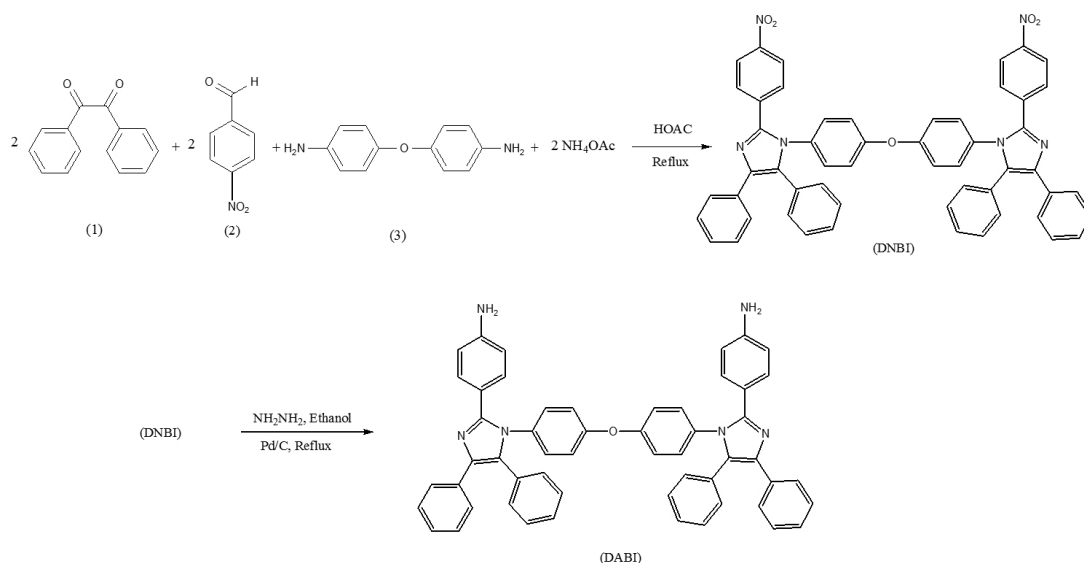
Synthesis of 1-(4-(4-(2-(4-nitrophenyl)-4,5-diphenyl-1H-imidazol-1-yl)phenoxy)phenyl)-2-(4-nitrophenyl)-4,5-diphenyl-1H-imidazole (DNBI). In a 500 mL, two-necked, round-bottomed flask equipped with a reflux condenser, a magnetic stirrer and nitrogen gas inlet tube, benzil (8.4 g, 0.04 mol), 4-nitrobenzaldehyde (6.04 g, 0.04 mol), 4,4'-diamino diphenyl ether (4 g,

0.02 mol) and ammonium acetate (3.08 g, 0.04 mol) in 200 ml acetic acid were mixed and heated at 120 °C. The progress of reaction was monitored by thin layer chromatography (TLC). After completion of reaction, the reaction mixture was cooled to room temperature. Then the product was filtered, washed with water and recrystallized from ethanol to afford 21.8 g (64%) of **DNBI** as yellow solid with melting point of 248-250 °C.

FT-IR (KBr): 3063 (C–H aromatic), 1598 (C=N), 1518 (asym N=O), 1499 (C=C), 1341 (sym N=O), 1242 (C–O), 855 (*p*-Ar) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 6.92 (d, 4H, J = 8.4 Hz), 7.09 (d, 4H, J = 8.4 Hz), 7.15 (d, 4H, J = 7.2 Hz), 7.23-7.29 (m, 12H), 7.58 (d, 4H, J = 7.2 Hz), 7.65 (d, 4H, J = 8.4 Hz), 8.12 (d, 4H, J = 8.4 Hz); ^{13}C NMR (CDCl_3 , 100 MHz), δ : 119.56, 123.53, 127.17, 127.30, 128.35, 128.53, 128.61, 129.10, 129.94, 129.98, 131.09, 132.33, 132.54, 133.73, 136.46, 139.51, 144.42, 147.15, 156.38; MS, m/z : 848. *Anal.* Calcd. for $\text{C}_{54}\text{H}_{36}\text{N}_6\text{O}_5$: C, 76.40; H, 4.27; N, 9.90; O, 9.42; Found: C, 76.48; H, 4.23; N, 9.88; O, 9.40.

Synthesis of 4-(1-(4-(4-(2-(4-aminophenyl)-4,5-diphenyl-1H-imidazol-1-yl)phenoxy)phenyl)-4,5-diphenyl-1H-imidazol-2-yl)benzenamine (DABI). To a 250 mL two-necked flask equipped with a dropping funnel and a reflux condenser (6.78 g, 8 mmol) of DNBI and 0.16 g of palladium on activated carbon (Pd/C, 10%), were dispersed in 80 mL of ethanol. The suspension solution was heated to reflux, and 4 mL of hydrazine monohydrate was added slowly to the mixture. After a further 5 h of reflux, THF was added to the mixture and filtered hot to remove Pd/C, and the filtrate was cooled to precipitate orange powder. The product was collected by filtration, recrystallized from ethanol and dried in vacuum at 80 °C. The yield of the reaction was 83% (5.65 g), and the melting point was 207-209 °C.

FT-IR (KBr): 3333 (asym N–H), 3211 (sym N–H), 3052 (C–H aromatic), 1608 (C=N), 1500 (C=C), 1241 (C–O), 835 (*p*-Ar) cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6$)



Scheme 1. Synthesis of **DABI**.

δ : 5.31 (br, 4H, NH), 6.43 (d, 4H, $J = 8.4$ Hz), 6.84 (d, 4H, $J = 8.4$ Hz), 7.05 (d, 4H, $J = 8.4$ Hz), 7.21-7.28 (m, 20H), 7.45 (d, 4H, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz), δ : 113.60, 117.95, 119.33, 126.69, 126.79, 128.56, 128.70, 128.92, 129.79, 130.73, 131.21, 131.62, 133.27, 135.20, 136.64, 147.74, 149.40, 149.46, 156.14; MS, m/z : 788. *Anal.* Calcd. for $\text{C}_{54}\text{H}_{40}\text{N}_6\text{O}$: C, 82.21; H, 5.11; N, 10.65; O, 2.03; Found: C, 82.25; H, 5.09; N, 10.60; O, 2.06.

Polymer synthesis

The synthetic pathway leading to the synthesis of polyamide-ethers (PAEs) is shown in Scheme 2. In a 50 mL two necked round bottomed flask equipped with a reflux condenser, a nitrogen gas inlet tube, and a magnetic stirrer bar, a mixture of 1 mmol diamine, 1 mmol a dicarboxylic acid, 1.2 mmol triphenyl phosphite (TPP), 0.5 mL pyridine, 0.3 g LiCl, and 5.0 mL NMP was heated under a stream of N_2 at 120 °C for 10 h. After cooling, the obtained polymer solution was poured into a large volume of methanol giving rise to a precipitate which was washed thoroughly with a large volume of hot water, collected by filtration and dried at 80 °C in a vacuum oven for 24 h. The inherent viscosity of these polymers was measured at 0.5 g/dL in NMP were in the range of 0.52-0.61 dL/g at 25 °C.

PAE-1: yield = 85%, $\eta_{\text{inh}} = 0.61$ dL/g. FT-IR (KBr): 3350 (N-H amide), 3051 (C-H aromatic), 1662 (C=O amide), 1599 (C=N), 1500 (C=C), 1330 (C-N), 1233 (C-O) cm^{-1} . ^1H NMR (500 MHz, $\text{DMSO}-d_6$): $\delta = 6.49$ –7.81 (m, 44H aromatic), 10.64 (br, 2H amide) ppm.

$[\text{C}_{68}\text{H}_{46}\text{N}_6\text{O}_3]_n$ (995) $_n$: Calculated: C, 82.07; H, 4.66; N, 8.45; O, 4.82; Found: C, 82.01; H, 4.69; N, 8.41; O, 4.89

PAE-2: yield = 88%, $\eta_{\text{inh}} = 0.52$ dL/g. FT-IR (KBr): 3328 (N-H amide), 3050 (C-H aromatic), 2927 (C-H aliphatic), 1668 (C=O amide), 1600 (C=N), 1498 (C=C), 1325 (C-N), 1238 (C-O) cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO}-d_6$): $\delta = 1.60$ (t, 4H, CH_2), 2.34 (t, 4H, CH_2), 6.58-7.63 (m, 36H aromatic), 10.24 (br, 2H amide) ppm.

$[\text{C}_{60}\text{H}_{46}\text{N}_6\text{O}_3]_n$ (899) $_n$: Calculated: C, 80.16; H, 5.15; N, 9.35; O, 5.34; Found: C, 80.10; H, 5.18; N, 9.40; O, 5.32.

PAE-3: yield = 86%, $\eta_{\text{inh}} = 0.58$ dL/g. FT-IR (KBr): 3314 (N-H amide), 3055 (C-H aromatic), 1671 (C=O amide), 1599 (C=N), 1500 (C=C), 1321 (C-N), 1240 (C-O) cm^{-1} . ^1H NMR (500 MHz, $\text{DMSO}-d_6$): $\delta = 6.92$ –8.70 (m, 40H aromatic), 10.75 (br, 2H amide) ppm.

$[\text{C}_{62}\text{H}_{42}\text{N}_6\text{O}_3]_n$ (919) $_n$: Calculated: C, 81.03; H, 4.61; N, 9.14; O, 5.22; Found: C, 81.10; H, 4.58; N, 9.19; O, 5.13.

PAE-4: yield = 90%, $\eta_{\text{inh}} = 0.56$ dL/g. FT-IR (KBr): 3221 (N-H amide), 3056 (C-H aromatic), 1679 (C=O amide), 1599 (C=N), 1500 (C=C), 1323 (C-N), 1237 (C-O) cm^{-1} . ^1H NMR (500 MHz, $\text{DMSO}-d_6$): $\delta = 6.56$ –8.38 (m, 39H aromatic), 10.96 (br, 2H amide) ppm.

$[\text{C}_{61}\text{H}_{41}\text{N}_7\text{O}_3]_n$ (920) $_n$: Calculated: C, 79.63; H, 4.49; N, 10.66; O, 5.22; Found: C, 79.67; H, 4.53; N, 10.62; O, 5.18.

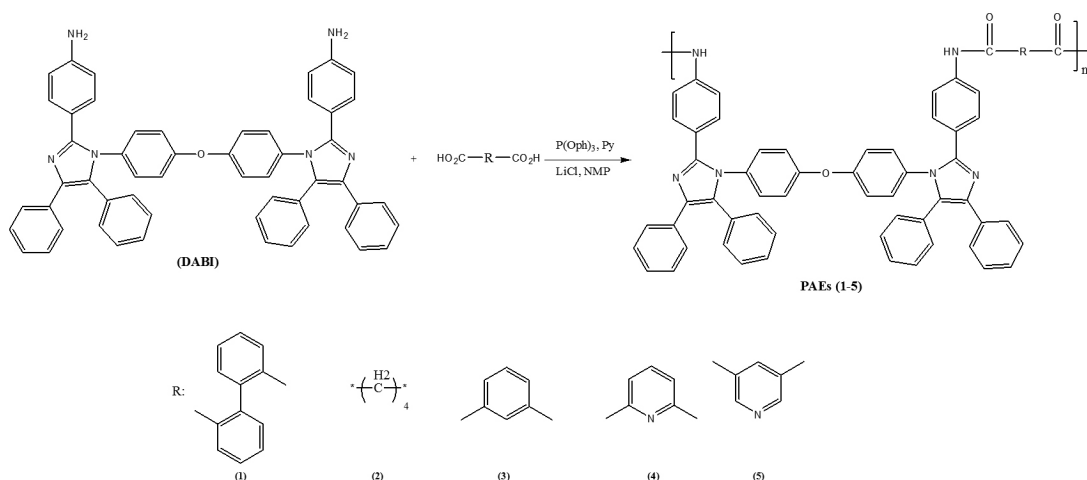
PAE-5: yield = 88%, $\eta_{\text{inh}} = 0.54$ dL/g. FT-IR (KBr): 3387 (N-H amide), 3058 (C-H aromatic), 1676 (C=O amide), 1601 (C=N), 1500 (C=C), 1326 (C-N), 1240 (C-O) cm^{-1} . ^1H NMR (500 MHz, $\text{DMSO}-d_6$): $\delta = 6.91$ –9.27 (m, 39H aromatic), 10.73 (br, 2H amide) ppm.

$[\text{C}_{61}\text{H}_{41}\text{N}_7\text{O}_3]_n$ (920) $_n$: Calculated: C, 79.63; H, 4.49; N, 10.66; O, 5.22; Found: C, 79.58; H, 4.52; N, 10.64; O, 5.26.

Results and Discussion

Monomer synthesis

Structure of the imidazole ring with both rigidity and polarizability was of interest. Thus, heteroaromatic monomer containing the bis-imidazole unit have been designed, synthesized and exploited to prepare novel heteroaromatic polymers with good thermal stability and processability. The key step for the preparation of monomer (**DABI**) used in this study is the synthesis of **DNBI** (Scheme 1). The suggested mechanism



Scheme 2. Synthesis of PAEs.

for preparation of **DNBI** is shown in Scheme 3. The structures of **DNBI** and **DABI** were characterized by elemental, FTIR, ^1H and ^{13}C NMR analyses. ^1H and ^{13}C NMR spectra of **DABI** are given in Figures 1, 2. Data from elemental analysis were in good agreement with the calculated values. These characterizations demonstrated that chemical composition of **DNBI** and **DABI** are consistent with the expected structures.

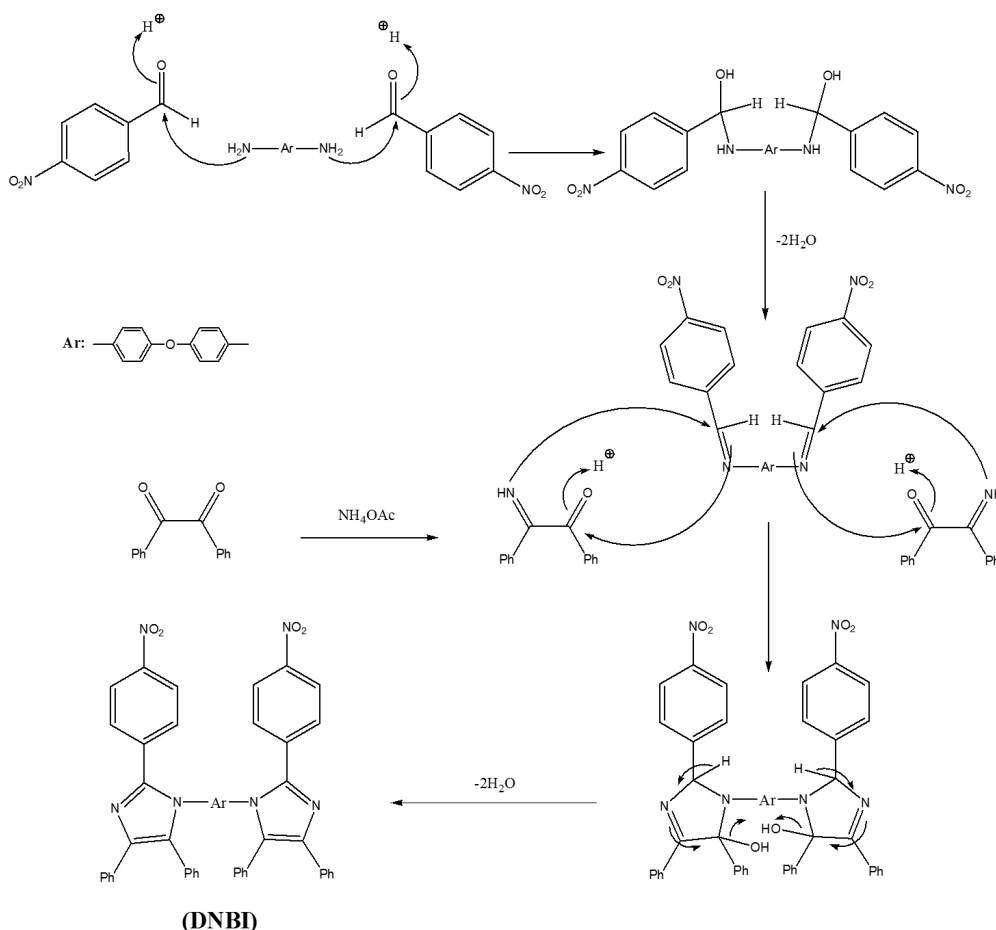
Polymer synthesis

Among various methods for polyamidation reaction, the direct phosphorylation polycondensation method has been developed by several investigators and especially by Yamazaki et al.^[23]. A series of new **PAEs** based on bis-imidazole, containing bulky aryl pendant groups and ether linkages was prepared in good yields (86-91%) from the diamine monomer **DABI** and various commercially available dicarboxylic acids by the direct polycondensation using triphenyl phosphite and pyridine as condensing agents. The synthetic route for these new **PAEs** is depicted in Scheme 2. In all the polymerizations, the yields were good after the polymers were repeatedly washed with hot methanol to completely remove the low molecular weight oligomers and the phosphorylation by-products. The obtained polymers had viscosity in the

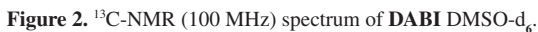
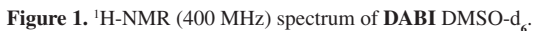
range of 0.52-0.61 dL/g in a concentration of 0.5 g/dL in NMP at 25 °C, which indicated moderate molecular weight. The structures of the synthesized **PAEs** were characterized by elemental analysis, FT-IR and ^1H NMR spectroscopic methods. The FT-IR spectra of **PAE-3**, as shown in Figure 3 as representative, exhibited the N-H stretching of the amide group around 3230 cm^{-1} , 3055 cm^{-1} (C-H stretching), 1671 cm^{-1} (C=O stretching), 1599 cm^{-1} (C=N stretching), 1500 cm^{-1} (C=C stretching) and at 1240 cm^{-1} (C-O stretching). In the ^1H NMR spectra of the resulting **PAEs**, as illustrated for the representative **PAE-5** in Figure 4, the existing aromatic protons resonate in the region 6.91-9.27 ppm. Besides, the signals appeared at the most downfield region, about 10.70 ppm is attributed to the protons of the amide linkages. In the ^{13}C NMR spectrum of the representative polymer as shown in Figure 5, the resonance peak appearing in the region of 171.88 is related to C=O of the amide group. The elemental analysis data were also in good agreement with theoretical values for the proposed polymer structures.

Polymer solubility

As a general rule, high solubility is a desired prerequisite for polymer processing. All investigated polymers were found to be highly soluble in several



Scheme 3. The suggested mechanism for preparation of **DNBI**.



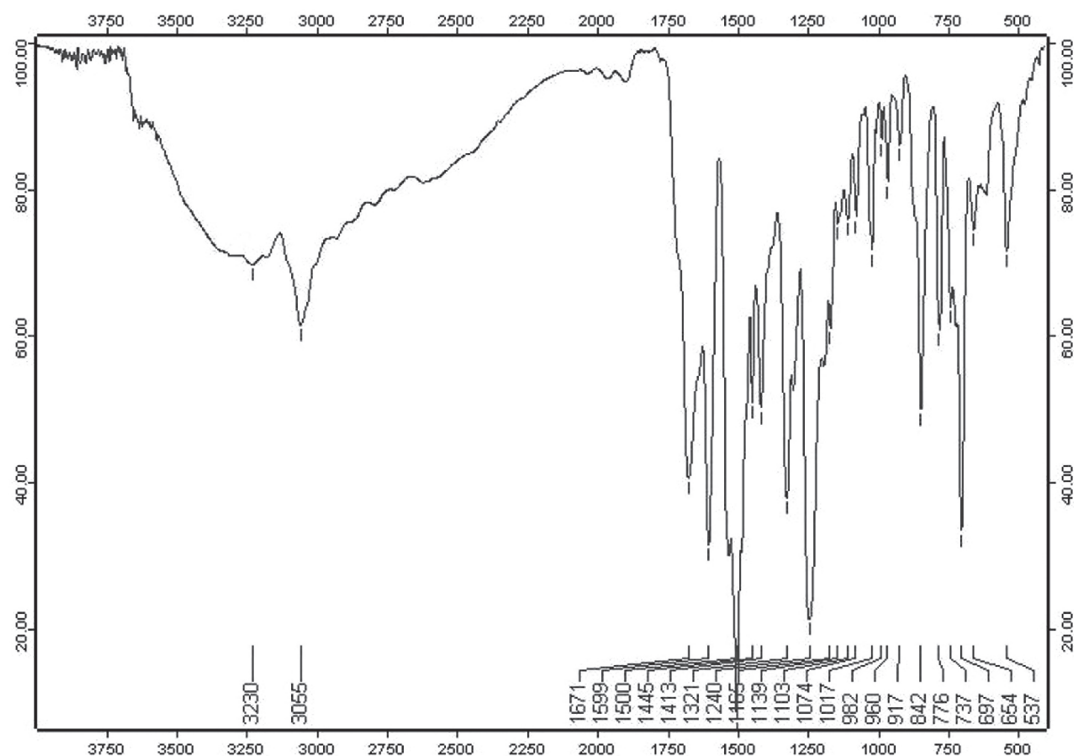


Figure 3. FT-IR spectrum of PAE-3.

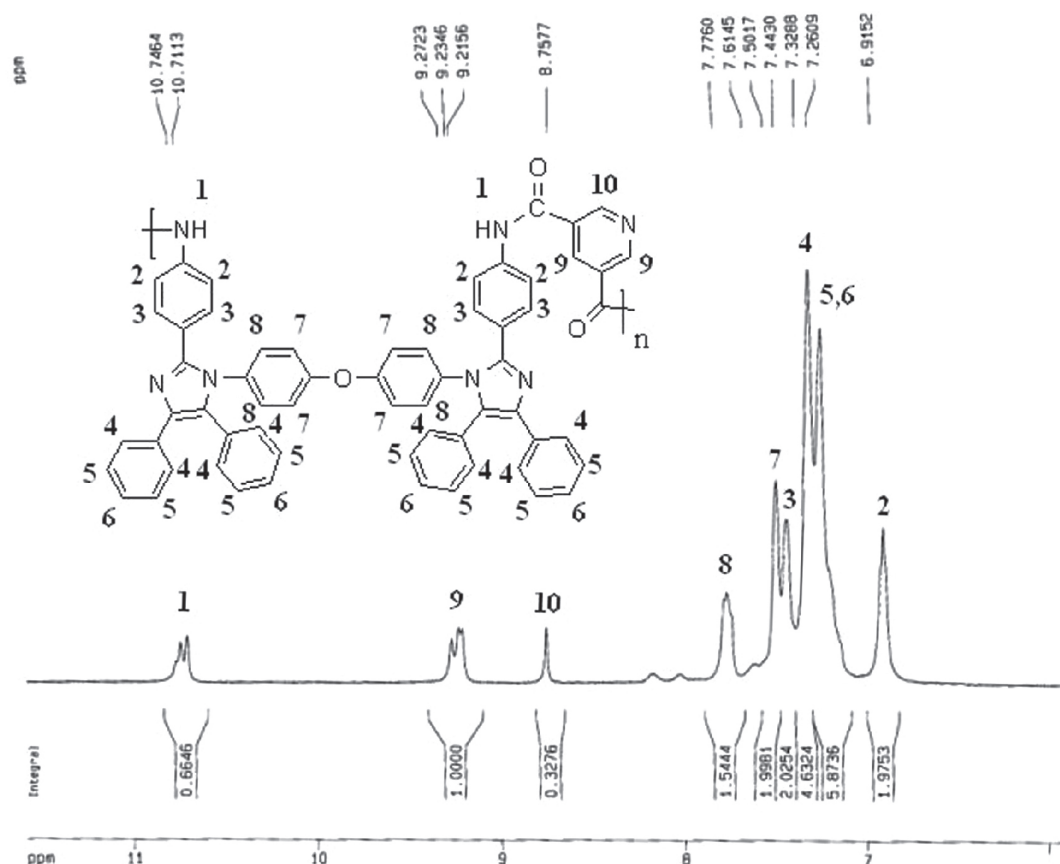


Figure 4. ^1H -NMR (500 MHz) spectrum of PAE-5 DMSO-d_6 .

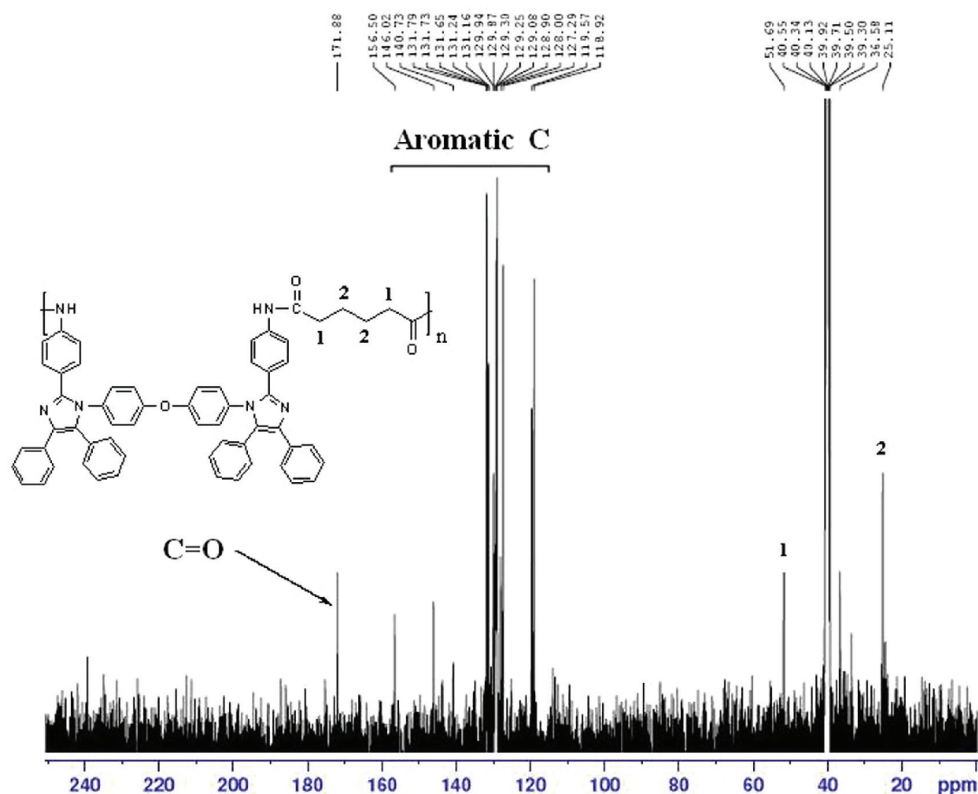


Figure 5. ¹³C-NMR (100 MHz) spectrum of PAE-2 DMSO-*d*₆.

Table 1. Solubility behavior of PAEs (1-5)^a.

Polymer	NMP	DMSO	CHCl ₃	DMF	DMAc	C ₂ H ₅ OH	CH ₃ OH	EtOAc
PAE-1	++	++	–	++	++	+-	–	+-
PAE-2	++	++	–	++	++	++	+-	+-
PAE-3	++	++	–	++	++	+-	+-	++
PAE-4	++	++	–	++	++	+-	+-	+-
PAE-5	++	++	–	++	++	+-	+-	+-

^a15 mg PA in 1 mL solvent. Solubility: ++ Soluble at room temperature, +- Partially soluble at room temperature, – Insoluble.

organic polar solvents such as NMP, DMSO, DMF and DMAc at room temperature (Table 1). The good solubility of these PAEs was governed by the structural modification through the incorporation of bulky aryl pendant groups in the polymer backbone which resulted in increased chain-packing distances and decreased inter-chain interactions. These factors and also the amorphous nature contributed to the enhanced solubility of these PAEs through better penetration of solvent molecules, formation of *H*-bonding and dipole-dipole interaction with polar molecules of organic solvents.

Thermal analyses

The thermal behaviour data of these PAEs were assessed by using DSC and TGA analysis. DSC was used to determine the glass-transition temperature values (*T_g*s) of the samples obtained with a heating rate of 10 °C/min under nitrogen. Neither crystallization exotherms nor melting endotherms were observed by DSC in the range of 50-400 °C, so that the polymers were considered to be essentially amorphous. The

Table 2. Thermal analysis data of different PAEs (1-5).

Polymer	<i>T_g</i> (°C) ^a	<i>T₅</i> (°C) ^b	<i>T₁₀</i> (°C) ^c	Char yield ^d (%)
PAE-1	310.6	334	399.7	55.6
PAE-2	230.1	303.6	389.3	48.7
PAE-3	248.2	253.8	399.5	53.6
PAE-4	231.1	235.2	329.8	39.5
PAE-5	246.2	298.1	384.4	23.6

^a*T_g*: Glass transition temperature. ^b*T₅*: Temperature for 5% weight loss. ^c*T₁₀*: Temperature for 10% weight loss. ^d(Char yield): Residual weight percentage at 600 °C.

amorphous nature of these PAEs can be attributed to their bulky pendant groups which decreased the inter-chain interaction resulting in loose polymer chain packaging and aggregates. The *T_g* values were read at the middle of the first break down observed in the DSC plots, and found to be in the range of 230-310 °C, as listed in Table 2. In general, molecular packing and chain rigidity are among the main factors influencing on *T_g* values. Therefore, the increased rotational barrier caused by the bulky pendant in diamines enhanced *T_g* values. As anticipated, the *T_g*

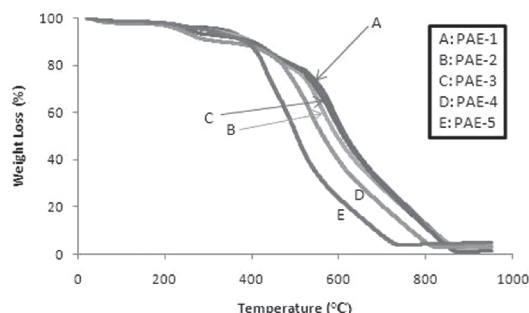


Figure 6. TGA curves of PAEs (1-5) at heating rate of 10 °C/min in air atmosphere.

values of these PAEs also depend on the stiffness of dicarboxylic acid component in the polymer chain and the increasing order of T_g generally correlated with that of chain rigidity. PAE-2 that obtained from adipic acid as an aliphatic dicarboxylic acid, showed lower T_g because of the presence of flexible aliphatic unit between the aromatic amide units and low rotation barrier of their diacid moieties, and the highest T_g of 310 °C was observed for PAE-1 derived from diphenic acid. As to the effect of pendant groups on the glass transition temperatures, the aromatic PAE-1 showed higher T_g value (310 °C) when compared with the aromatic PAE-3, PAE-4 and PAE-5.

The thermo-stability of the resulting PAEs was evaluated by TGA under air atmosphere at a heating rate of 10 °C min⁻¹. Figure 6 presents TGA curves of the PAEs, and corresponding weight loss temperatures of 5% (T_5) as well as weight loss temperatures of 10% (T_{10}) were all determined from original curves and listed in Table 2. The T_5 and T_{10} values of the aliphatic and aromatic PAEs stayed within 235-334 °C and 329-399 °C, respectively, and the amount of carbonized residue (char yield) of these polymers was from 23% to 55% at 600 °C in air atmosphere, depending on the structure of diacid component. PAE-4 and PAE-5 showed somewhat more reduced thermal stability than that of PAE-1, PAE-2 and PAE-3 which can be due to the presence of pyridine. PAE-1 containing diphenyl content in the main chain has the highest T_5 , T_{10} and thermal stability than the other PAEs. The results are summarized in Table 2.

Conclusions

The design and synthesis of novel thermally stable PAEs with improved solubility based on new aromatic diamine 4-(1-(4-(4-(2-(4-aminophenyl)-4,5-diphenyl-1H-imidazol-1-yl)phenoxy)phenyl)-4,5-diphenyl-1H-imidazol-2-yl) benzenamine (DABI) containing bis-imidazole ring in the polymer backbone was the main objective of this work. A series of PAEs containing ether linkages and bulky triaryl bis-imidazole pendant group were synthesized by phosphorylation polycondensation of DABI with commercially available dicarboxylic acids. The obtained polyamides had inherent viscosities in the range 0.52-0.61 dL/g. Most of the PAEs were soluble in polar aprotic solvents such as NMP, DMSO, DMF and DMAc at room temperature. T_{10} values for the polyamide-ethers were in the range 329-399 °C indicating their good thermal stability. T_g values of the

polymers were in the range 230-310 °C as a result of decrease in the segmental mobility due to side chain-side chain and side chain-main chain interaction through H-bonding.

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