

# Synthesis and Characterization of Novel Photoactive Poly(ether-amide)s Based on Highly Substituted Phenanthrimidazole

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**ABSTRACT:** A new aromatic diamine monomer containing ether linkage based on the phenanthrimidazole ring, 1,1'-(4,4'-oxy bis(1,4-phenylene))bis(2-(4-aminophenyl)-1H-phenanthro[9,10-d]imidazole) was synthesized through four-components condensation of 4,4'-diamino diphenyl ether, 4-nitrobenzaldehyde, phenanthrene-9,10-dione and ammonium acetate in presence of acetic acid, followed by palladium-catalyzed hydrazine monohydrate reduction. This new monomer was further confirmed by FT-IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectroscopy. A series of new aromatic polyamides containing phenanthrimidazole ring in the main chain was prepared by direct polycondensation of the prepared diamine with four commercially available aromatic and aliphatic diacids. These polymers are essentially amorphous and were soluble in polar aprotic solvents such as DMF, NMP, DMAc, and DMSO. Inherent viscosities of polyamides were in the range 0.42–0.53 dL/g indicating the formation of medium molecular weight polymers. Polyamides exhibited glass-transition temperature (*T<sub>g</sub>*) in the range 260–280 °C. The 10% weight loss temperature in air atmosphere measured by TGA was in the range 454–526 °C indicating their good thermal stabilities. The photophysical properties of diamine and polyamides were investigated by UV-Visible and fluorescence spectroscopy.

**KEYWORDS:** Polyamides; Polycondensation; Bis-phenanthrimidazole; Thermal stability.

## INTRODUCTION

Aromatic polyamides are thermally stable polymers with an attractive combination of excellent chemical, physical and mechanical properties that make them

practical as high-performance materials for advanced technologies [1-6]. However, the applications of aromatic polyamides are often hampered by problems in their

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fabrication due to their high glass transition temperatures ( $T_g$ ), or high melting temperatures ( $T_m$ ), and limited solubility in organic solvents [7, 8]. To get the better of these limitations, the modification of the macromolecule structure is necessary. The properties of polyamides can be dramatically altered by minor variations in the structures of the diacid and diamine monomers. Due to, much of research efforts have been focused on the synthesis of structurally modified aromatic polyamides having improved solubility and processability with retention of their high thermal stability [9-13].

In general, many efforts have been devoted to enhancing the solubility of polyamides, and this has included the introduction of noncoplanar groups, incorporation of unsymmetrical structure, and the introduction of bulky side groups into the polymer backbone. It is known that ether linkages inserted in aromatic main chains provide them with a significantly lower energy of internal rotation. Aramids containing ether linkages or asymmetrical groups are significantly more flexible and soluble than conventional polyamides [13-16]. These modifications work by breaking chain symmetry and regularity and by destroying hydrogen bonding, generally leading to better solubility and processability.

On the other hand, the synthesis and characterization of the macromolecules restrain heterocyclic rings in the main chain has been the topic of considerable interest, because of their relatively good thermal stability with improved solubility and some attractive novel properties. Among different heterocycles, imidazole can be readily obtained by condensation of 1,2-diketone, aldehyde, amine and ammonium acetate in presence of acetic acid. So in order to prepare novel processable polyamides with enhanced thermal stabilities, new diamine monomer containing ether linkage based on phenanthrimidazole ring and bearing bulky aromatic pendant groups in the 1, 2-positions of the phenanthrimidazole ring was synthesized and used for the preparation of polyamides. The incorporation of aryl groups and ether linkage into the polymer backbone is expected to affect their properties as well as enhance the solubility in organic solvents and improve the processability.

## EXPERIMENTAL SECTION

### Materials

All chemicals were purchased from Merck. *N*-methyl-2-pyrrolidinone (NMP) was purified by distillation over

calcium hydride under reduced pressure and stored over 4 Å molecular sieves. Other materials were used as received without any purification.

### Instruments

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a 400 MHz Bruker Advance DRX instrument using DMSO- $d_6$  as a solvent and tetramethyl silane as an internal standard. FT-IR spectra were recorded using a Bruker Tensor 27 spectrometer on KBr pellets. Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) analysis were performed using TGA-50 and Mettler Toledo 822° in an air atmosphere, respectively. The inherent viscosities of the polymers were determined for the solutions of 0.5 g/dL in NMP at 25 °C using an Ubbelohde viscometer. Absorption and fluorescence spectra were recorded on a Varian Cary Eclipse spectrophotometer.

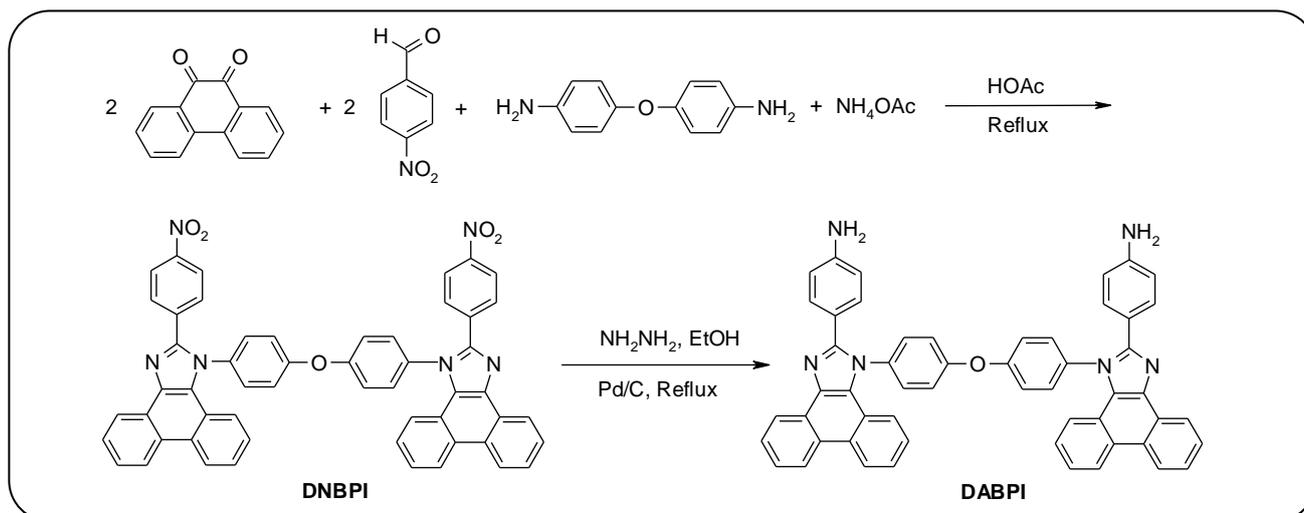
### Monomer Synthesis

*Synthesis of 4-(1-(4-(4-(2-(4-aminophenyl)-1H-phenanthro[9,10-d]imidazol-1-yl)phenoxy)phenyl)-1H-phenanthro[9,10-d]imidazol-2-yl)benzenamine (DABPI):*

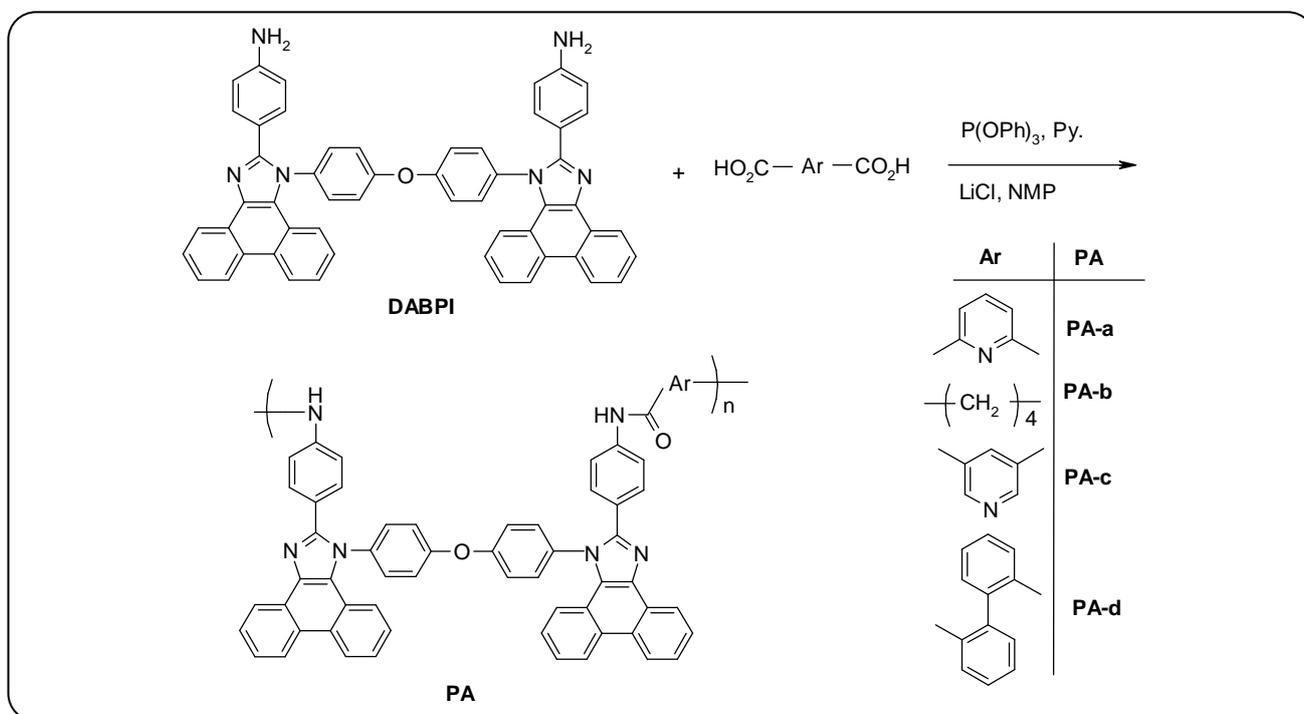
1-(4-(4-(2-(4-nitrophenyl)-1H-phenanthro[9,10-d]imidazol-1-yl)phenoxy)phenyl)-2-(4-nitrophenyl)-1H-phenanthro[9,10-d]imidazole (DNBPI) was prepared according to the literature [17]. DABPI was synthesized according to the following procedure as shown in scheme 1: To a 250-mL three-necked flask equipped with a dropping funnel and a reflux condenser (5gr, 5.9 mmol) of DNBPI and 0.3 g of palladium on activated carbon (Pd/C, 10%), were dispersed in 100 mL of ethanol. The suspension solution was heated to reflux, and 10 mL of hydrazine monohydrate was added slowly to the mixture. After a further 5 h of reflux, the solution was filtered hot to remove Pd/C, and the filtrate was cooled to precipitate orange crystals. The product was collected by filtration and dried in vacuum at 80 °C. The yield of the reaction was 83% (3.60 g), and the melting point was 273–275 °C.

### 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. [18]. The synthetic pathway leading to the synthesis of polyamides is shown in Scheme 2.



Scheme 1: Synthesis of DABPI.



Scheme 2: Synthesis of polyamides (PA).

A flask was charged with a mixture of DABPI (0.259 g, 0.33 mmol), dicarboxylic acid (0.33 mmol), triphenylphosphite (0.3 mL), pyridine (0.3 mL), NMP (5 mL) and LiCl (0.3 g). The reaction mixture was maintained at 130 °C under N<sub>2</sub> atmosphere for 12 h. After cooling, the reaction mixture was poured into a large amount of methanol, producing a precipitate. The precipitate was filtered, washed with hot methanol and

then with hot water several times, which afforded polyamide.

## RESULTS AND DISCUSSION

### Monomer synthesis and characterization

The objective of this study was the preparation of novel thermally stable PAs with improved solubility containing substituted bis-phenanthrimidazole rings

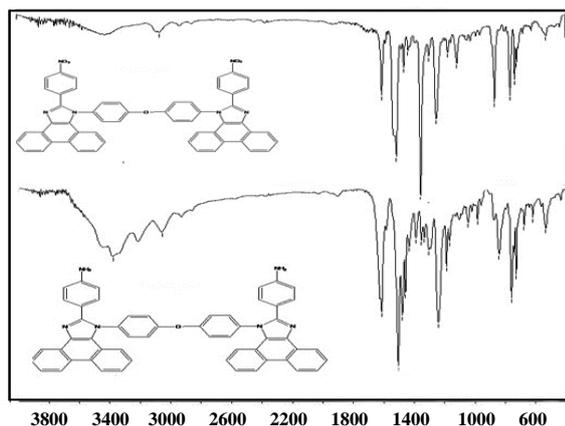


Fig. 1: FT-IR spectra of (DNBPI) and (DABPI).

in the main chain. For this purpose, a new diamine (DABPI) was synthesized through a two-step procedure, as illustrated in Scheme 1. Firstly, DNBPI was synthesized according to the literature [17]. DABPI was readily obtained in high yield by the Pd/C-catalyzed reduction of the DNBPI with hydrazine monohydrate in refluxing ethanol. The purity of all compounds was checked by thin-layer chromatography, which showed one spot in ethylacetate/*n*-hexane mixture (2:8). The structure of DABPI was characterized by FT-IR and  $^1\text{H}$  NMR spectroscopic techniques. The nitro groups of compound (DNBPI) showed two characteristic absorption bands at 1341 and 1545  $\text{cm}^{-1}$  ( $-\text{NO}_2$  asymmetric and symmetric stretching). After reduction, these absorption peaks disappeared and the primary amino group in compound (DABPI) showed the typical absorption pair at 3476 and 3377  $\text{cm}^{-1}$  because of N-H stretching. The FT-IR spectra of compounds DNBPI and DABPI were presented in Fig. 1.

The FT-IR spectra of DABPI exhibited 3476, 3377  $\text{cm}^{-1}$  (unsymmetrical and symmetrical stretching of  $\text{NH}_2$ ); 1609  $\text{cm}^{-1}$  (C=N stretching); 1499, 1472  $\text{cm}^{-1}$  (C=C stretching) and 1235  $\text{cm}^{-1}$  (C-O stretching) absorptions.

The  $^1\text{H}$  NMR spectrum of compound DABPI was presented in Fig. 2. The signal at 5.39 ppm is due to the  $-\text{NH}_2$  protons. Aromatic protons at 6.46–8.89 ppm showed the expected multiplicity and integration values.

#### Polymers synthesis and characterization

New classes of polyamides were prepared from the direct polycondensation of DABPI with dicarboxylic acids by means of triphenyl phosphite, pyridine, and LiCl.

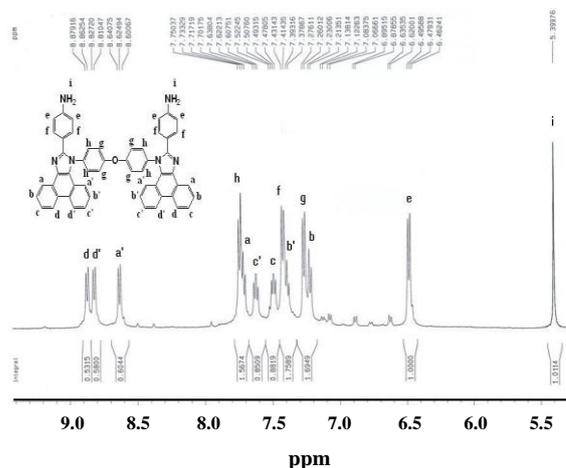


Fig. 2: The  $^1\text{H}$  NMR spectrum of DABPI.

The prepared polyamides with the yields of 90–95% showed inherent viscosities ( $\eta_{\text{inh}}$ ) in the range of 0.48–0.53 dL/g. All of the polymers were characterized by using FT-IR and  $^1\text{H}$  NMR. The spectroscopic data of PAs is shown in Table 1. The characteristic FT-IR absorptions of the polymers (Fig. 3) are about 3400  $\text{cm}^{-1}$  related to N-H, 1660  $\text{cm}^{-1}$  due to C=O in amide groups, 1600  $\text{cm}^{-1}$  (C=N stretching), 1500  $\text{cm}^{-1}$  (C=C stretching) and 1240  $\text{cm}^{-1}$  (C-O stretching). The signal at about 11 ppm in  $^1\text{H}$  NMR is due to the  $-\text{NH}$  proton of the amide group. Aromatic protons appeared at 6.5–8.8 ppm in all PAs. The signals at 1.5 and 2.3 ppm in PA-b are related to protons of the methylene groups.

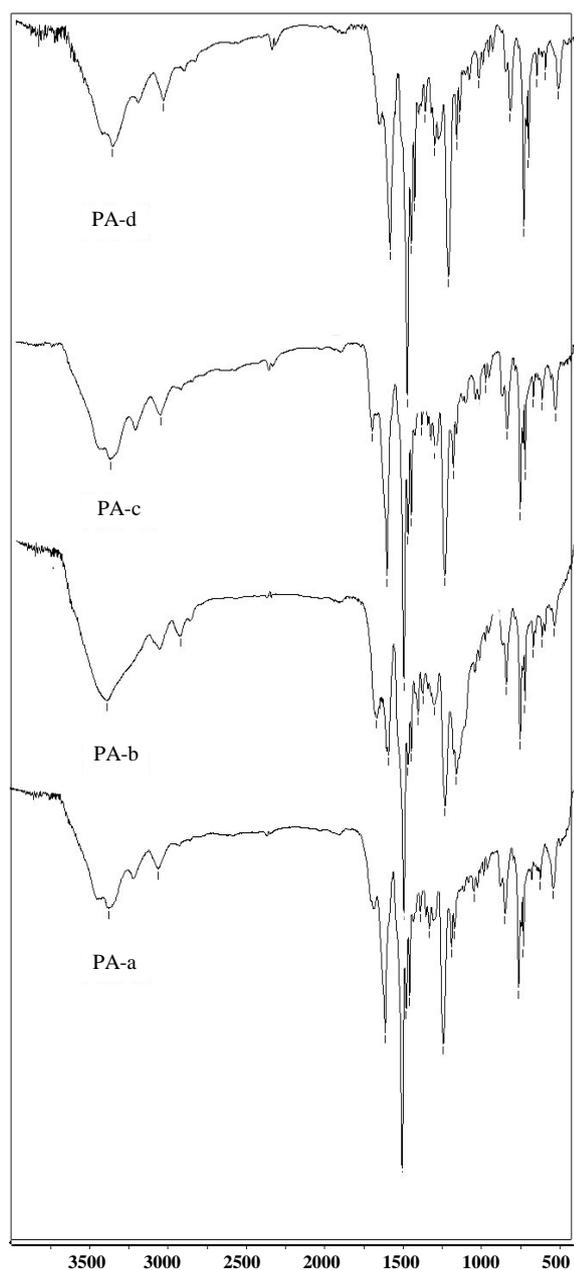
#### Thermal properties of PAs

The thermal behaviors of PAs were evaluated by Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA). Thermal analysis data of PAs is shown in Table 2. There were no melting peaks detected in DSC which support the generally amorphous nature of the polymers. The DSC thermograms of polymers showed  $T_g$  in the range of 260–280  $^{\circ}\text{C}$ . PA-b 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 its diacid residue, and the highest  $T_g$  of 285  $^{\circ}\text{C}$  was observed for PA-d derived from diphenic acid because of the highest rigidity which inhibited the molecular motion.

The thermal stability of polymers was evaluated by TGA in an air atmosphere (Fig. 4). To compare thermal

**Table 1: Spectroscopic data of polyamides.**

Entry	FT-IR (cm <sup>-1</sup> )	<sup>1</sup> H NMR (DMSO, 400 MHz, ppm)
PA-a	3375, 1608, 1499, 1472, 1236	6.5-7.8 (m, 35H aromatic), 11 (br, 2H amide)
PA-b	3397, 1672, 1499, 1473, 1236	1.5 (t, 4H), 2.3 (t, 4H), 7.7-8.8 (m, 32H aromatic), 11(br, 2H amide)
PA-c	3376, 1607, 1499, 1472, 1237	6.5-8.9 (m, 35H aromatic), 11 (br, 2H amide)
PA-d	3384, 1609, 1499, 1473, 1237	7.2-7.7 (m, 40H aromatic), 10 (br, 2H amide)

**Fig. 3: FT-IR spectra of polyamides.**

behavior, the temperatures of 5% weight loss ( $T_5$ ) and the temperatures of 10% weight loss ( $T_{10}$ ) values were determined from the original TGA curves. The temperatures for 10% weight loss, which are important criteria for evaluating the thermal stability of the polymers, were in the range of 454-526 °C indicating their high thermal stability.

#### **Polymer solubility**

The solubility of PAs was tested qualitatively in various organic solvents and the results were tabulated in Table 3. Almost all of the prepared PAs exhibited excellent solubility in polar aprotic solvents such as NMP, DMAc, DMF, and DMSO at room temperature. The good solubility of these PAs 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 PAs through better penetration of solvent molecules, the formation of *H*-bonding and dipole-dipole interaction with polar molecules of organic solvents.

#### **Photophysical properties of polyamides**

The photophysical properties of diamine (DABPI) and PAs were investigated by UV-Visible and fluorescence spectroscopy in NMP solution. The UV-Vis absorption and emission spectra of diamine (DABPI) (0.2 g/dL=10<sup>-3</sup> M) and PA-c (0.2 g/dL) in NMP solutions were shown in Fig. 5 and Fig. 6, respectively. The extracted data were listed in Table 4.

The diamine (DABPI) with an extended conjugated system showed wide range absorption peak with a maximum at 348 nm corresponding to the  $\pi$ - $\pi^*$  transition of the aromatic chromophores. As seen from Scheme 1, the DNBPI and DABPI are related, but their chemical

**Table 2: Thermal analysis data of PAs.**

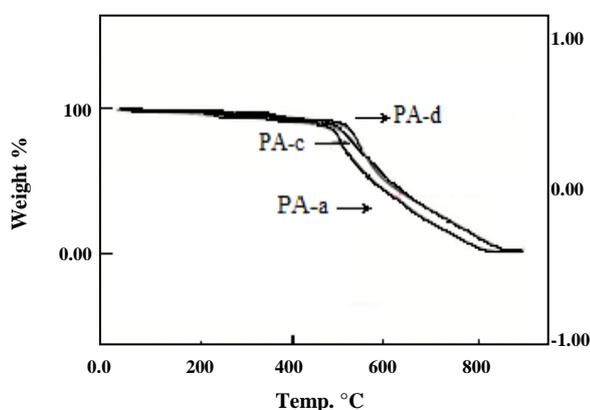
Entry	Yield (%)	$\eta_{inh}$ (dL/g)	$T_g$ (°C)	$T_5$ (°C)	$T_{10}$ (°C)
PA-a	93	0.51	280	261	491
PA-b	90	0.48	260	253	454
PA-c	91	0.50	265	253	454
PA-d	95	0.55	285	297	526

**Table 3: Solubility behavior of polyamides a.**

Polymer	NMP	DMSO	DMF	DMAc	THF	CH <sub>2</sub> Cl <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> OH	CH <sub>3</sub> OH
PA-a	++	++	++	++	++	+-	-	-
PA-b	++	++	++	++	++	++	+-	+-
PA-c	++	++	++	++	++	+-	-	-
PA-d	++	++	++	++	+-	+-	-	-

**Table 4: Wavelengths of maximum absorbance ( $\lambda_{abs}$ ) and Fluorescence emission ( $\lambda_{flu}$ ).**

Compound	DNBPI	DABPI	PA-a	PA-b	PA-c	PA-d
$\lambda_{abs}$ (nm)	260	348	374	396	380	384
$\lambda_{em}$ (nm)	435	473	419	449	443	451

**Fig. 4: TGA thermograms of PAs.**

structures are differentiated by introducing various substituents, for instance, nitro or amine. Such a structural modification could be expected to result in some changes in the  $\pi$ -conjugated length and in the absorption and emission spectra. It was also noted that replacement of nitro group with an amine donor in phenyl moiety of the phenanthro[9,10-d]imidazole molecules resulted in

a large hypsochromic shift (88 nm), which implied that DABPI seems to possess a larger conjugated system than DNBPI. In comparison to the absorption band maxima of PAs, the absorption band maxima of DABPI is red shifted. The red shift absorption of the diamine monomer compared with the PAs could be attributed to the effectively increased conjugation and resonance effect between  $\pi$ -clouds of phenyl and phenanthrimidazole core. In polyamides, exchange of proton by the acyl groups in the  $-NH_2$  group decreases the dihedral angle between the lone pair of electrons on the nitrogen atom and the p-electrons on the carbon atom of the C-N bond (from 23° to 17°), as well as, the dihedral angle between the phenyl and phenanthrimidazole ring (from 35° to 30°) [19].

## CONCLUSIONS

A series of new polyamides were readily prepared via direct polycondensation of a new diamine and various aromatic and aliphatic dicarboxylic acids. The introduction of a bulky moiety of bis-phenanthrimidazole into the polymer backbone resulted in polyamides

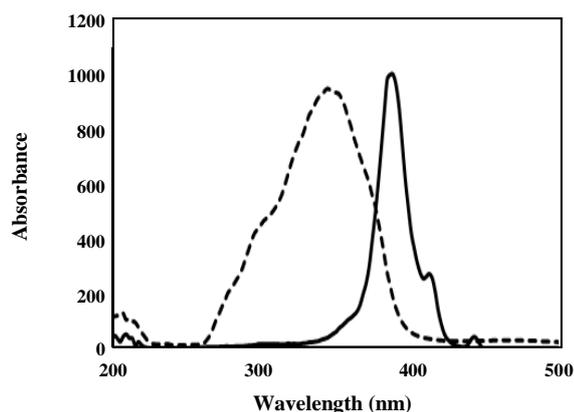


Fig. 5: UV-vis spectrum of diamine (- -) and PA-c (-).

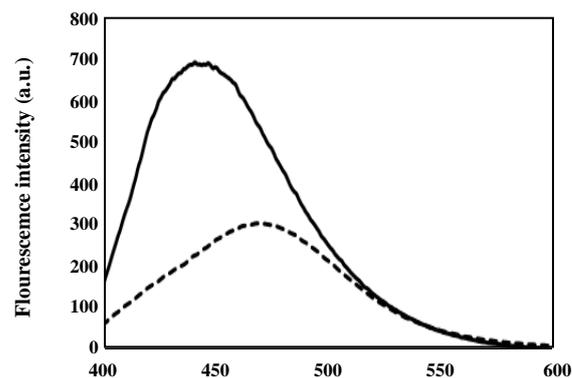


Fig. 4: Fluorescence emission spectrum of diamine (- -) and PA-c (-).

with good solubility in polar aprotic solvents because of a decrease in the ability for polymer chains to pack and reduction of inter-chain interactions, and this also increased  $T_g$  of the polymer up to 260 °C, as a result of a decrease in the segmental mobility due to side chain-side chain and side chain-main chain interaction through *H*-bonding. They had useful levels of thermal stability associated with relatively high temperatures of 10% weight loss ( $T_{10}$ ) in the range of 454-526 °C in an air atmosphere.

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## REFERENCES

- [1] Mallakpour S., Taghavi M., A Facile, Microwave-Assisted Synthesis of Novel Optically Active Polyamides Derived from 5-(3-methyl-2-Phthalimidylpentanoylamino)Isophthalic Acid and Different Diisocyanates, *Eur. Polym. J.*, **44** (1): 87-97 (2008).
- [2] Majo M.A., Alla A., Bou J.J., Herranz C., Munoz-Guerra S., Synthesis and Characterization of Polyamides Obtained from Tartaric Acid and L-Lysine, *Eur. Polym. J.*, **40** (12): 2699-2708 (2004).
- [3] Behniafar H., Banihashemi A., Synthesis and Characterization of New Soluble and Thermally Stable Aromatic Poly(amide-imide)s Based on N-[3,5-bis(N-trimellitoyl)phenyl]phthalimide, *Eur. Polym. J.* **40** (7): 1409-1415 (2004).
- [4] Cui X., Li W., Yan D., Yuan C., Di Silvestro G., Synthesis and Characterization of Polyamides X 18, *J. Appl. Polym. Sci.*, **98** (4): 1565-1571 (2005).
- [5] Hearle J.W.S., "High-Performance Fibres", Woodhead Publishing Ltd, Cambridge (2001).
- [6] Mark H.F., "Encyclopedia of Polymer Science and Technology", Wiley Interscience, 12 Volume Set, 3rd Edition, New York (2004).
- [7] Imai Y., Recent Advances in Synthesis of High-Temperature Aromatic Polymers, *React. Funct. Polym.*, **30** (1-3): 3-15 (1996).
- [8] Liou G.Sh., Fang Y.K., Yen H.J., Synthesis, and Properties of Noncoplanar Rigid-rod Aromatic Polyamides Containing Phenyl or Naphthyl Substituents, *J. Polym. Res.*, **14** (2): 147-155 (2007).
- [9] Amini Nasab S.M., Ghaemy M., Synthesis and Characterization of New Polyamides and Polyimides Containing Dioxypyrimidine Moiety in the Main Chain with Bulky Imidazole Pendent Group: Solubility, Thermal and Photophysical Properties, *J. Polym. Res.*, **18** (6): 1575-1586 (2011).
- [10] Ghaemy M., Alizadeh R., Behmadi H., Synthesis of Soluble and Thermally Stable Polyimide from New Diamine Bearing N-[4-(9H-carbazol-9-yl)phenyl] Formamide Pendent Group, *Eur. Polym. J.*, **45** (11): 3108-3115 (2009).
- [11] Sava I., Iosip M.D., Bruma M., Hamciuc C., Robison J., Okrasa L., Aromatic Polyamides with Pendent Acetoxybenzamide Groups and Thin Films Made Therefrom, *Eur. Polym. J.*, **39** (4): 725-738 (2003).
- [12] Faghihi Kh., Mozaffari Z., New Polyamides Based on 2,5-bis[(4-carboxyanilino) carbonyl] Pyridine and Aromatic Diamines: Synthesis and Characterization, *J. Appl. Polym. Sci.*, **108** (2): 1152-1158 (2008).

- [13] In I., Kim S.Y., Soluble Wholly Aromatic Polyamides Containing Unsymmetrical Pyridyl Ether linkages, *Polymer*, **47** (2): 547-552 (2006).
- [14] Abdolmaleki A., Novel Aromatic Poly(amide-hydrazide)s Based on the Bipyridine. Part I: Synthesis, Characterization and Thermal Stability, *Polym. Degrad. Stab.*, **92** (2): 292-298 (2007).
- [15] Bottino F.A., Di Pasquale G., Scalia L., Pollicino L.A., Synthesis and Characterisation of New Polyamides Containing 6,6'-oxy or 6,6'-Carbonyldiquinoline Units, *Polymer*, **42** (8): 3323-3332 (2001).
- [16] Bottino F.A., Di Pasquale G., Pollicino A., Scalia L., Synthesis and Characterization of New Polyamides Containing 6,6'-Methylenediquinoline Units, *Polymer*, **39** (20): 4949-4954 (1998).
- [17] Saadati S.M., Mosslemin M.H., Behmadi H., Shams A., Synthesis, Characterisation and Fluorescence Studies of New Bis-phenanthrimidazole Derivatives, *J. Chem. Res.*, **37** (8): 487-512 (2013).
- [18] Yamazaki N., Higashi F., Kawataba J., Studies on Reactions of the N-phosphonium Salts of Pyridines. XI. Preparation of Polypeptides and Polyamides by Means of Triaryl Phosphites in Pyridine, *J. Polym. Sci. A: Polym. Chem.*, **12** (9): 2149-2154 (1974).
- [19] Dey J., Dogra S.K., Dual Fluorescence in 2-(4'-N,N-Dimethylamino-phenyl)benzazole and its Benzimidazole Analog – Effect of Solvent and pH on Electronic Spectra, *J. Phys. Chem.*, **98** (14): 3638-3644 (1994).