

Synthesis and characterization of organo-soluble polyamides containing triaryl imidazole pendant and ether linkage moieties: thermal, photophysical, and chemiluminescent properties

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A new symmetrical diamine monomer containing a triaryl imidazole pendant group was successfully synthesized by the nucleophilic substitution of hydroquinone with the synthesized 2-(2-chloro-5-nitrophenyl)-4, 5-diphenyl-1H-imidazole (I). A series of novel polyamides were prepared from the diamine monomer and various aliphatic and aromatic dicarboxylic acids via phosphorylation polyamidation. These polyamides are readily soluble in many organic solvents; their inherent viscosities ranged from 0.68 to 0.89 dl/g and gave tough and flexible films by solution-casting. They had useful levels of thermal stability associated with relatively high T_g s (186–278°C), 10% weight loss temperatures in the range of 355–482°C, and char yields at 600°C in air up to 67%. All the polyamides have fluorescence emission in dilute (0.2 g/dl) DMAc solution with maxima at 425–495 nm and with the quantum yields in the range 14–28%. The chemiluminescence activity of polyamides was also studied in the presence of peroxyoxalate. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: fluorescent; polyamides; polycondensation; solubility; thermal properties

INTRODUCTION

Aromatic polyamides are difficult to process as high performance polymers due to their high softening temperatures and/or insolubility in most organic solvents.^[1–4] Therefore, research was focused to incorporate new functionalities to develop structurally modified aromatic polyamides with increased solubility. These studies include introduction of flexible segments into the polymer chain,^[5–12] replacing symmetrical aromatic rings by unsymmetrical ones,^[13–17] and forming a non-coplanar structure.^[18–21] Generally, one of the successful approaches to increase the solubility and processability of polymers without sacrificing high thermal stability is the introduction of bulky pendant groups into polymer backbone.^[22–30] Other reports have described the incorporation of imidazole and its derivatives into polymeric frameworks.^[31–33] The rigidity, symmetry and aromaticity of the imidazole ring contribute to thermal and chemical stability and enhanced mechanical properties of the resulting polymer at elevated temperatures; in addition, increased polarizability resulting from the nitrogen atom in imidazole ring improves the solubility of the polymer in organic solvents.^[33] Imidazole rings, useful *n*-type building blocks with high electron affinity and good thermal stability, have been successfully incorporated in small molecules and polymers as the electron-transport component of organic light emitting diodes OLEDs.^[34–40] Lophine, 2, 4, 5-triphenylimidazole, and its derivatives have significant analytical applications for their fluorescent and chemiluminescent properties.^[41,42]

The present investigation focused on the synthesis and characterization of a series novel polyamides from a new diamine

monomer, 4-(4-(4-amino-2-(4,5-diphenyl-1H-imidazol-2-yl) phenoxy) phenoxy) -3-(4, 5-diphenyl-1H-imidazol-2-yl) benzenamine, and various dicarboxylic acids by direct polycondensation. These polymers bear flexible ether linkages in the backbone and bulky triaryl imidazole pendant groups that create functionalities and impart properties such as thermal stability and solubility to the polyamides. It is expected that the presence of voluminous pendant groups to result in a less ordered polymer matrix, to enhance the solubility and processing characteristics of these polymers while maintaining a good thermal stability. The polyamides were tested for different physical properties including viscosity, solubility, thermal stability, fluorescence, and chemiluminescent behavior.

EXPERIMENTAL

Materials

All starting materials and reagents were purchased either from Merck or Fluka Co. *N*-methyl-2 pyrrolidinone (NMP), *N,N*-dimethyl acetamide (DMAc), dimethyl sulfoxide (DMSO), and *N,N*-dimethyl formamide (DMF) were purified by distillation over calcium

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hydride under reduced pressure and stored over 4 Å molecular sieves. Tetrachloroethane (TCE) and pyridine (Py) were purified by distillation over anhydrous potassium carbonate. LiCl was dried for 10 hr at 180°C under vacuum. All other reagents such as benzyl, 2-chloro-5-nitrobenzaldehyde, hydroquinone, hydrazine monohydrate, and dicarboxylic acids such as pyridine-2, 6-dicarboxylic acid, terephthalic acid, isophthalic acid, adipic acid and sebacic acid, and solvents were reagent-grade quality and used as received without further purification.

Monomer synthesis

2-(2-chloro-5-nitrophenyl)-4,5-diphenyl-1H-imidazole (I)

In a 250 ml round-bottomed two-necked flask equipped with a condenser, a magnetic stirrer bar and a nitrogen gas inlet tube, a mixture of 1.86 g (0.01 mol) 2-chloro-5-nitrobenzaldehyde, 2.1 g (0.01 mol) benzil, 5.39 g (0.07 mol) ammonium acetate, and 20 ml of glacial acetic acid was refluxed for 24 hr. Upon cooling, the precipitated white solid was collected by filtration and washed with mixture of C₂H₅OH/H₂O (50/50, v/v). 3.55 g (yield 95%) yellow crystals were obtained with the melting point 218–220°C. FT-IR (KBr) at cm⁻¹: 3453 (NH), 3124 (C–H aromatic), 1684 (C=N), 1532 and 1345 (NO₂). Anal. Calcd. (%) for C₂₁H₁₄ClN₃O₂: C, 67.20; H, 3.73; N, 11.20. Found: C, 67.00; H, 3.65; N, 11.35.

2-(2-(4-(4-nitro-2-(4,5-diphenyl-1H-imidazol-2-yl)phenoxy)phenoxy)-5-nitrophenyl)-4,5-diphenyl-1H-imidazole (II)

In a 250 ml round-bottomed two-necked flask equipped with a condenser, a magnetic stirrer bar and a nitrogen gas inlet tube, a mixture of 1.1 g (10 mmol) hydroquinone, 7.5 g (20 mmol) (I), and 2.76 g (20 mmol) anhydrous potassium carbonate in 20 ml of dry DMAc was refluxed at 140°C for 12 hr and then cooled. The mixture was then poured into water and the precipitate was collected by filtration and recrystallized from ethanol. The yield of the reaction was 97% (7.6 g), and the melting point was 275–278°C. FT-IR (KBr disk) at cm⁻¹: 3453 (NH), 3069 (C–H aromatic), 1608 (C=N), 1588 (C=C), 1532, 1350 (NO₂), and 1234 (C–O). Anal. Calcd. for C₄₈H₄₂N₆O₆: C, 73.08%; H, 4.06%; N, 10.66%. Found: C, 72.93%; H, 4.12%; N, 10.55%.

4-(4-(4-amino-2-(4,5-diphenyl-1H-imidazol-2-yl)phenoxy)phenoxy)-3-(4,5-diphenyl-1H-imidazol-2-yl)benzenamine (III)

In a 250-ml round-bottomed three-necked flask equipped with a dropping funnel, a reflux condenser and a magnetic stirrer bar, 7.88 g (0.01 mol) (II) and 0.2 g Pd/C (10%) was dispersed in 80 ml of ethanol. The suspension solution was heated to reflux, and 8 ml of hydrazine monohydrate was added slowly to the mixture. After a further 5 hr of reflux, the solution was filtered hot to remove Pd/C, and the filtrate was cooled to precipitate white crystals. The product was collected by filtration and dried in vacuum at 80°C. The yield of the reaction was 85% (6.21 g), and the melting point was 157–160°C. FT-IR (KBr disk) at cm⁻¹: 3362, 3216 (NH₂), 3443 (NH imidazole), 3044 (C–H aromatic), 1618 (C=N), 1603 (C=C), and 1198 (C–O). ¹H NMR (500 MHz, CD₃SOCD₃): δ 5.18 (s, 4H), 6.5–6.6 (dd, 2H, J = 8.35 Hz), 6.7 (d, 2H, J = 8.35 Hz), 6.9 (s, 4H), 7.1–7.5 (m, 22H), 11.93 (s, 2H). ¹³C NMR, δ 113.90, 115.41, 118.19, 121.12, 122.72, 126.34, 126.98, 127.60, 128.23, 128.52, 129.05, 131.06, 135.18, 136.39, 143.07, 143.35, 145.23, 148.83, 153. Anal. Calcd. for C₄₈H₃₆N₆O₂: C, 79.11%; H, 4.94%; N, 11.53%. Found: C, 79.69%; H, 4.58%; N, 11.78%.

Polyamide synthesis

The following general procedure was used for the preparation of all the polyamides. In a three-necked flask equipped with a condenser, a mechanical stirrer and a nitrogen gas inlet tube, 0.728 g (1 mmol) the diamine monomer (III), 1 mmol of a dicarboxylic acid, and 0.6 g lithium chloride were dissolved in a mixture of 1 ml pyridine, 1.2 ml TPP, and 8 ml NMP. The mixture was heated at 110°C for 14 hr with stirring under dry N₂ atmosphere. The system was then cooled to room temperature and the solution was poured into 300 ml methanol. The precipitate was filtered and washed with hot water. For further purification, the obtained polyamides were extracted in hot methanol for 24 hr and then dried at 100°C under vacuum. The inherent viscosities of the polyamides in NMP were in the range of 0.58–0.89 dL/g, measured at a concentration 0.5 g/dL at 25°C.

PA-a: The yield 90%, FT-IR (KBr, cm⁻¹): 3448 (NH imidazole), 3060 (C–H aromatic), 1674 (C=O amide), 1598 (C=N imidazole), 1492 (C=C), 1373 (C–N), 1244 (C–O). ¹H NMR (DMSO-d₆): δ 12.31 (s-2H), 11.29 (s-2H), 6.78–8.65 (m-33H). (C₅₅H₃₇N₆O₄)_n Anal. Calcd. C, 78.11; H, 4.38; N, 9.94. Found C, 77.78; H, 4.55; N, 9.65.

PA-b: The yield 87%, FT-IR (KBr, cm⁻¹): 3528 (NH imidazole), 3078 (C–H aromatic), 1668 (C=O amide), 1601 (C=N imidazole), 1488 (C=C), 1375 (C–N), 1243 (C–O). ¹H NMR (DMSO-d₆): δ 12.33 (s-2H), 10.63 (s-2H), 7–8.51 (m-34H). (C₅₆H₃₈N₆O₄)_n Anal. Calcd. C, 78.32; H, 4.43; N, 9.79. Found C, 78.12; H, 4.62; N, 9.31.

PA-c: The yield 85%, FT-IR (KBr, cm⁻¹): 3382 (NH imidazole), 3049 (C–H aromatic), 1665 (C=O amide), 1608 (C=N imidazole), 1490 (C=C), 1375 (C–N), 1230 (C–O). ¹H NMR (DMSO-d₆): δ 12.15 (s-2H), 10.36 (s-2H), 7.12–8.71 (m-34H). (C₅₆H₃₈N₆O₄)_n Anal. Calcd. C, 78.32; H, 4.43; N, 9.79. Found C, 78.55; H, 4.65; N, 9.53.

PA-d: The yield 91%, FT-IR (KBr, cm⁻¹): 3448 (NH imidazole), 3043 (C–H aromatic), 2964 (C–H aliphatic), 1659 (C=O amide), 1603 (C=N imidazole), 1482 (C=C), 1371 (C–N), 1235 (C–O). ¹H NMR (DMSO-d₆): δ 12.35 (s-2H), 10.15 (s-2H), 6.94–9.58 (m-30H), 2.25 (t-4H), 1.47 (m-4H). (C₅₄H₄₂N₆O₄)_n Anal. Calcd. C, 77.34; H, 5.01; N, 10.02. Found C, 77.18; H, 5.22; N, 10.35.

PA-e: The yield 84%, FT-IR (KBr, cm⁻¹): 3455 (NH imidazole), 3044 (C–H aromatic), 2937 (C–H aliphatic), 1663 (C=O amide), 1605 (C=N imidazole), 1487 (C=C), 1375 (C–N), 1220 (C–O). ¹H NMR (DMSO-d₆): δ 12.15 (s-2H), 10.44 (s-2H), 7.02–8.25 (m-30H), 2.28 (t-4H), 1.31 (m-12H). (C₅₈H₅₀N₆O₄)_n Anal. Calcd. C, 77.85; H, 5.59; N, 9.40. Found C, 77.48; H, 5.72; N, 9.15.

Procedure for chemiluminescence measurement

Bis (2, 4, 6-trichlorophenyl) oxalate (TCPO) was prepared from the reaction of 2, 4, 6-trichlorophenol with oxalyl chloride in the presence of triethylamine as described in the literature.^[43] Solution A was made with 1.0 ml of TCPO (0.01 M) and 0.5 ml of solution of monomer (10⁻⁵ M) and polymer (0.2 g/dl) in DMAc. Solution B contained 2 ml of 3.0 M hydrogen peroxide and the 1.0 ml of catalyst sodium salicylate (0.1 M) in methanol. Solution A was transferred into the instrument glass cell via polypropylene syringe. Then 100 μl of B stock solution was injected in the 3 cm quartz cuvette containing solution A, and the chemiluminescence spectrum was recorded.

Measurements

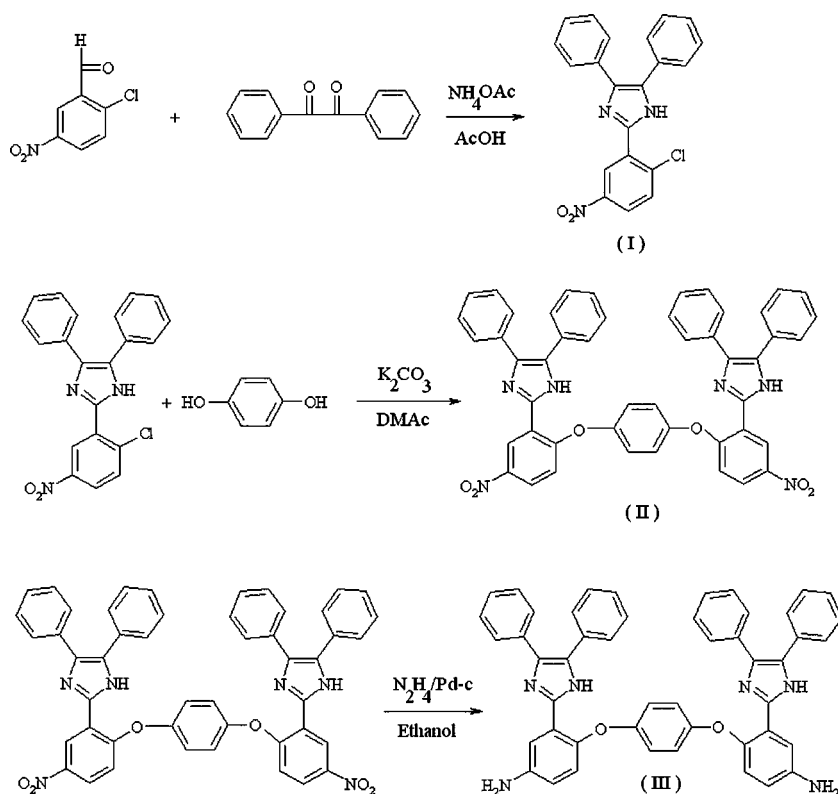
Elemental analysis was run in a Flash EA 1112 series analyzer. FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer. ¹H and ¹³C NMR spectra were recorded on a 500 MHz Bruker

Advance DRX spectrometer in DMSO- d_6 , using tetramethyl silane as an internal reference. The *inherent* viscosities were measured at 0.5 g/dl concentration using an Ubbelohde viscometer at 25°C. Thermogravimetric analysis (TGA) was conducted with a TGA-50 analyzer in the temperature range of 50–600°C under air atmosphere at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) analysis was performed on a Perkin-Elmer Pyris 6 DSC at a heating rate of 10 °C/min under air atmosphere. Dynamic mechanical thermal analysis (DMTA) was carried out on a Polymer Laboratories instrument (Model MK-II, Surrey, UK) over a temperature range of 25–350°C at 1 Hz and a heating rate of 5 °C/min. Glass transition temperatures (T_g s) were taken as the midpoint of the change in slope of the baseline in DSC curve from the second heating scan after quick cooling from 350°C at a cooling rate of 200 °C/min, and the maximum of $\tan \delta$ curve in DMTA experiments. UV-visible and fluorescence emission spectra were recorded on a Cecil 5503 and a Perkin-Elmer LS-3B spectrophotometers, respectively. X-ray powder diffraction (XRD) patterns were recorded by X-ray diffractometer (XRD, GBC MMA Instrument) with Be Filtered Cu K_α radiation (1.5418 Angstrom) operating at 35.4 kV and 28 mA. The scanning range of 2θ was set between 4 and 50° with scan rate of 0.05°/sec. Chemiluminescence detection was carried out with a homemade apparatus equipped with a model BPY47 photocell (Leybold, Huerch, Germany). The apparatus was connected to a personal computer via a suitable interface. Experiments were carried out with magnetic stirring in flattened bottom glass cells of 15 mm diameter at room temperature. The polyamides solubility's were determined by mixing 5 g polymer in 100 ml of solvent, followed by stirring at room temperature.

RESULTS AND DISCUSSION

Monomer synthesis and characterization

The first objective of this study was to prepare a new diamine monomer with fluorescent activity based on imidazole moiety. The synthetic route for the preparation of this new diamine with triaryl imidazole pendant group, 4-(4-(4-amino-2-(4, 5-diphenyl-1H-imidazol-2-yl)phenoxy) phenoxy)-3-(4, 5-diphenyl-1H-imidazol-2-yl) benzenamine (**III**), is depicted in Scheme 1. Condensation of benzil with 2-chloro-5-nitrobenzaldehyde and ammonium acetate is well known as a classical but convenient synthetic method for preparation of triaryl imidazole. The dinitro precursor (**II**), was synthesized by the nucleophilic aromatic substitution reaction of hydroquinone with the compound (**I**), was reduced with traditional hydrazine-Pd/C system to give the diamine monomer (**III**) with high purity. Elemental analysis, FT-IR, and ^1H and ^{13}C NMR spectroscopic techniques confirmed the structure of the diamine (**III**). The conversion of the nitro groups into amine groups was confirmed by the disappearance of the typical IR nitro absorptions at 1345 and 1549 cm^{-1} ($-\text{NO}_2$ asymmetric and symmetric stretching), and by the present of the primary amino group absorption pair at 3458 and 3367 cm^{-1} due to N–H stretching. The ^1H NMR spectrum of the diamine (**III**), in Fig. 1, also showed the broad singlet at 5.18 ppm related to the protons of the primary amine group. The proton of imidazole ring appeared as a singlet signal at 11.93 ppm in the ^1H NMR spectrum. Aromatic protons at δ 6.5–6.6 (dd, 2H, $J = 8.35$ Hz), 6.7 (d, 2H, $J = 8.35$ Hz), 6.9 (s, 4H), and 7.1–7.5 (m, 22H) ppm, showed the expected multiplicity and integration values. These results clearly confirmed that the diamine monomer (**III**) prepared herein is consistent with the proposed structure.



Scheme 1. Three step synthesis procedure for the preparation of monomer.

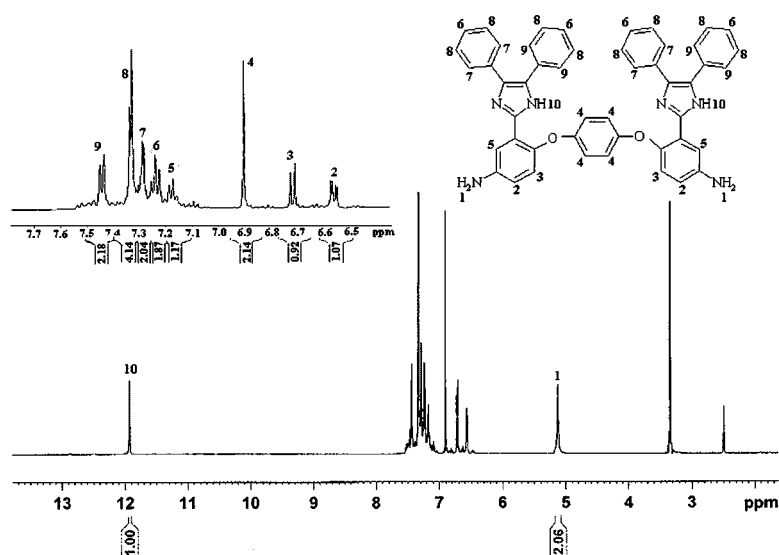


Figure 1. ^1H NMR spectrum of the diamine monomer.

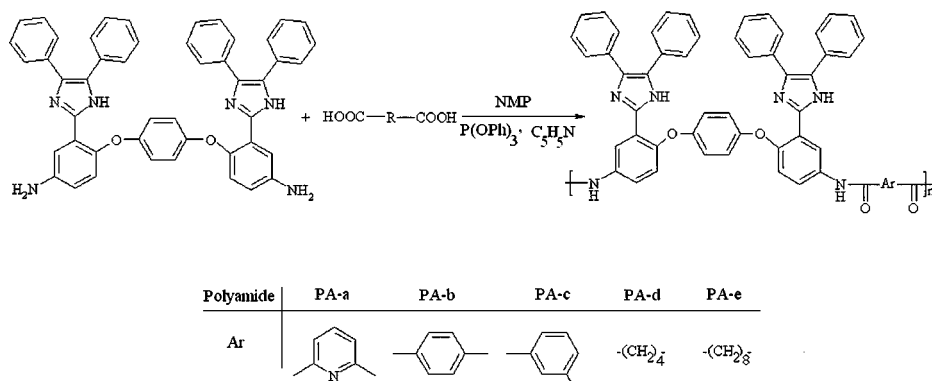
Polyamides synthesis and characterization

A series of novel polyamides containing aryl-ether linkages in the main chain and triaryl imidazole pendant groups were prepared according to the direct phosphorylation polycondensation,^[44] from the diamine compound (III) with aromatic and aliphatic dicarboxylic acids, as shown in Scheme 2. The polymerization was carried out via solution polycondensation using triphenyl phosphite and pyridine as condensing agents. To optimize the reaction conditions of this new diamine with dicarboxylic acids, the inherent viscosity of the polyamide PA-b was measured during polyamidation which has reached to its maximum of 0.89 dl/g after 13 hr at 110°C. The obtained polyamides had inherent viscosities in the range of 0.68–0.89 dl/g, as shown in Table 1. All the polymers could afford transparent, tough, and flexible films via solution casting. The chemical structures of the polyamides were confirmed by elemental analysis, FT-IR, and ^1H NMR spectroscopic techniques. The characteristic FT-IR absorption bands of the amide group appeared around 3530 cm^{-1} (N–H stretching) and 1650 cm^{-1} (C=O stretching). The assignment of the total protons in ^1H NMR spectrum of the polyamide PA-b, in Fig. 2, is consistent with the proposed chemical structure of the polyamide PA-b.

Polyamides properties

A first approach for structural characterization was made by X-ray method. The WAXD studies indicated that all of these polymers displayed almost amorphous patterns in nature, and this could be attributed to the presence of pendant groups which reduce attraction between molecules and hindrance macromolecular packing regularly.

The solubility of the new polyamides was determined at concentration of 5% (w/v) in a number of solvents and the results are tabulated in Table 1. All the polyamides exhibited excellent solubility in polar aprotic solvents such as NMP, DMAc, DMF, DMSO, and even in less polar solvents like pyridine and *m*-cresol at room temperature. The good solubility of the polyamides should be the result of the introduction of the bulky triphenyl imidazole pendant groups which disturb a dense chain packing; consequently, the solvents molecules were able to penetrate easily to interact with the ether and amide linkages in the backbone and imidazole rings in the pendant moiety. In addition, the solubility varies depending upon the dicarboxylic acid used. The polyamides (PA-d and PA-e) which were synthesized from aliphatic dicarboxylic acids exhibited good solubility behavior in dioxane and tetrachloroethane (TCE). The methylene units



Scheme 2. Synthesis procedure for preparation of PAs.

Table 1. Solubility behavior and inherent viscosities of the polyamides

Code	NMP	DMSO	DMAc	DMF	<i>m</i> -cresol	THF	Dioxan	Py	TCE	η_{inh} (dl/g)
PA-a	++	++	++	++	++	+	±	++	—	0.75
PA-b	++	++	++	++	++	+	±	++	—	0.89
PA-c	++	++	++	++	++	+	±	++	—	0.70
PA-d	++	++	++	++	++	+	+	++	±	0.70
PA-e	++	++	++	++	++	+	+	++	±	0.68

5 g polymer in 100 ml solvent. ++: soluble at room temperature; +: soluble on heating at 60°C; ±: partially soluble on heating at 60°C; and —: insoluble on heating at 60°C.

instead of rigid phenyl improves solubility of these polyamides in comparison with the PA (a-c). Thus, all these polymers can be readily processed from solution.

The photoluminescence spectra of the diamine and polyamides in dilute (0.2 g/dl) DMAc solution are shown in Fig. 3(A). The diamine and the polymers exhibited strong absorption at 285–315 nm, which are assignable to a π – π^* transition resulting from the conjugation between the aromatic rings and nitrogen atoms. The excitation wavelength used is 315 nm in all cases. The monomer showed strong blue fluorescent light, and its maximum emission was observed at 405 nm. As can be seen in Fig. 3(A), the photoluminescence spectra of polymers in DMAc solutions exhibited broad emission with maxima at 425–443 nm for the aliphatic polyamides PA-d and PA-e, and at 485–495 nm for the aromatic polyamides PA-a, PA-b, and PA-c. The fluorescence images from the polymer solutions are shown in Fig. 4. To measure the photoluminescence quantum yields (Φ_f), dilute

polymer solutions (0.2 g/dl) in DMAc were prepared. A 0.1 N solution of *quinine* in H_2SO_4 ($\Phi_f=53\%$) was used as a reference.^[38] The Φ_f values were 30% for the monomer, 25–28% for the aliphatic polyamides, and 14–17% for the aromatic polyamides. The photoluminescence of this monomer in DMAc solution showed lower Φ_f than that reported for lophine in hexane (48%) in the literature.^[38] This difference in fluorescence property can be attributed to the different polarity of the used solvent (solvent effect) and also as a result of energy dissipation by intramolecular rotation around flexible ether linkages in this monomer. The blue shift and higher fluorescence quantum yield of the aliphatic polyamides compared with the aromatic polyamides could be attributed to the effectively reduced conjugation and capability of charge-transfer complex formation by aliphatic diacids with the electron-donating diamine moiety in comparison with that of the stronger electron-accepting aromatic diacids.^[45] Because of the lower

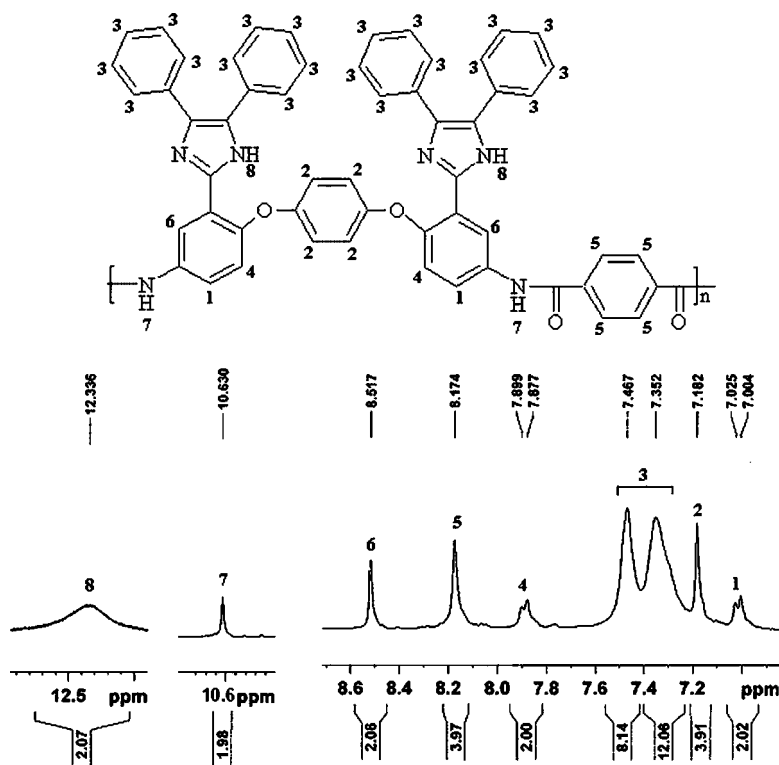


Figure 2. 1H NMR spectrum of the polyamide PA-b.

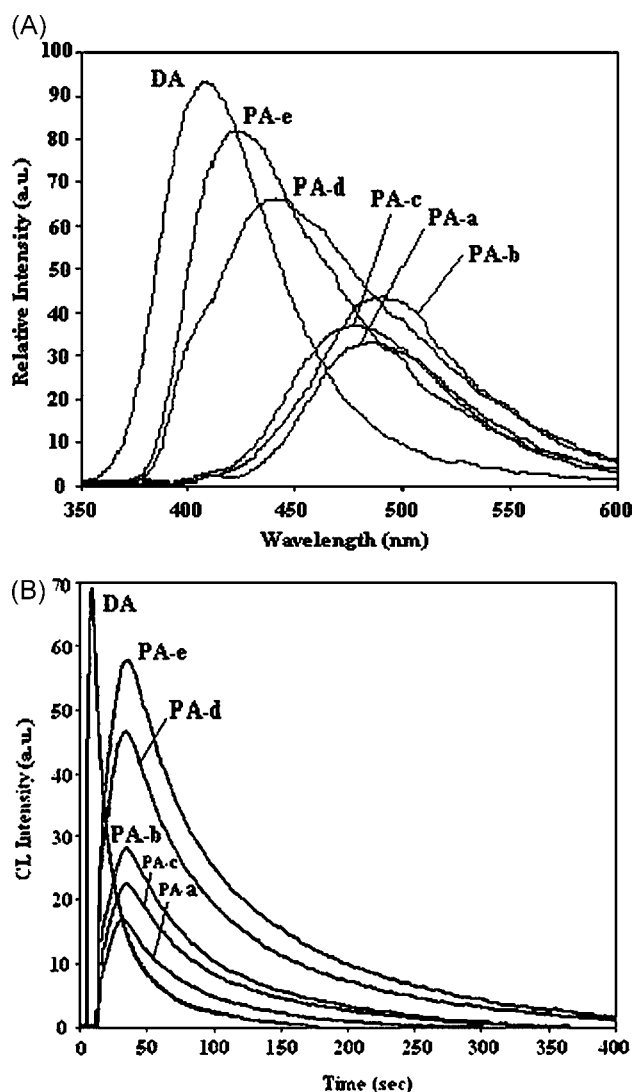


Figure 3. Photoluminescence (A) and chemiluminescence emission (B) spectra of the monomer and polyamides.

capability of charge transfer, the aliphatic polyamides showed a light color and high optical transparency. The photoluminescence efficiencies of these polyamides are comparable and also higher than those reported for some other aromatic polyamides in the literature.^[46–49]

The chemiluminescence light of the reaction between hydrogen peroxide and an activated derivative of oxalic acid such as bis (2, 4, 6-trichlorophenyl) oxalate (TCPO), in the presence of a fluorophore has been widely studied.^[50] The peroxyoxalate-chemiluminescence reaction can be described in three basic steps. In the first step, an aryl oxalate ester like TCPO reacts with H_2O_2 to produce a key chemical intermediate, C_2O_4 , containing the necessary excitation energy. The second step involves the chemiexcitation of a fluorophore to electronically excited states by the reactive intermediate via conversion of the chemical energy into electronic excitation energy. The final step is the emission of light energy by returning the excited fluorophore molecule to the ground state. We have used this technique to study the chemiluminescence arising from the reaction of TCPO with hydrogen peroxide in the presence of diamine monomer

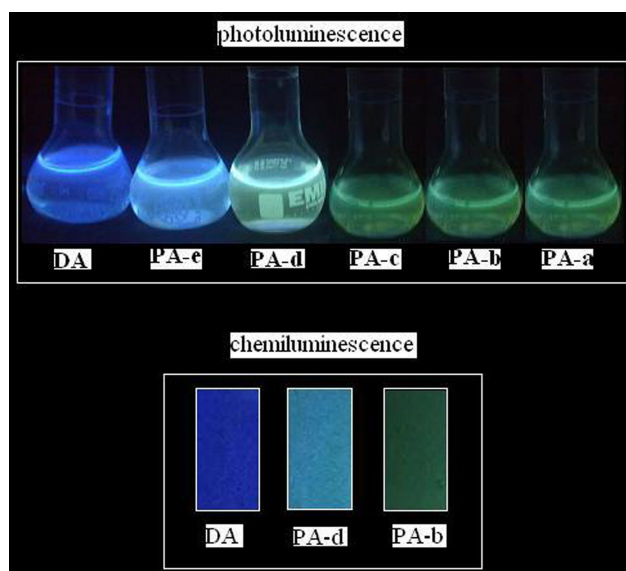


Figure 4. The fluorescence images of the monomer and polyamide solutions. This figure is available in color online at wileyonlinelibrary.com/journal/pat

and the prepared polyamides. In preliminary experiments, it was found that the addition of a few drops of the stock solution of H_2O_2 to a DMAc solution containing TCPO and monomer results in a very intense blue chemiluminescence light which was identical to the blue photoluminescence light of maximum 405 nm. This experiment was repeated with the PAs and the results are shown in Fig. 3(B). The chemiluminescence images from the polymer solutions are shown in Fig. 4. The higher chemiluminescence intensity of the aliphatic polyamides (PA-d and PA-e) compared with the aromatic polyamides (PA-a – PA-c) can be due to the same explanation which has been given for the photoluminescence. The color of emitted light for both processes of photoluminescence and chemiluminescence are essentially analogous, thus the emission maximum in both processes should be identical.

DSC, DMTA, and TGA methods were applied to evaluate the thermal properties of these polyamides, and the thermal analysis data are summarized in Table 2. The DSC curves of polymers are shown in Fig. 5(A). Neither crystallization exotherms nor melting endotherms were observed by DSC in the range of 30–350°C. The DSC results and the WAXD studies, X-ray diffraction patterns are shown in Fig. 5(B), indicated that all of these polymers are essentially amorphous in nature, and this could be attributed to the presence of pendant groups which reduce attraction between molecules and hindrance macromolecular packing regularly. The T_g values of the polyamides evaluated by DSC ranged from 186 to 278°C, depending upon the stiffness of the residue of dicarboxylic acid in the polymer chain. The lowest T_g value of the polyamide PA-e in this series polymers can be explained in terms of the flexible methylene linkages in its diacid component. Among all the synthesized polyamides, the polyamide PA-b based on terephthalic acid showed the highest T_g value because of the highest rigidity, which inhibited the molecular motion. The DMTA results displayed the dynamic storage modulus and $\tan \delta$ as a function of temperature, as shown in Fig. 5(C). Two relaxation processes were observed above room temperature for all of the polyamides. The β -relaxation processes

Table 2. Thermal characteristic and optical properties of the polyamides

Polymer	Thermal properties				Optical properties		
	T_g	T_5	T_{10}	Char yield	λ_{abs}	λ_{em}	Φ_f
	(°C)	(°C)	(°C)	(%)	(nm)	(nm)	(%)
PA-a	245	406	455	50.6	305	489	14
PA-b	278	425	481	66.8	315	495	17
PA-c	259	410	472	55.4	308	480	15
PA-d	226	331	402	39.6	294	443	25
PA-e	186	310	355	29.4	285	425	28

T_g : glass transition temperature; T_i : initial decomposition temperature; T_5 : temperature for 5% weight loss; T_{10} : temperature for 10% weight loss; Char yield: weight of polymer remained at 600°C; λ_{abs} : maximum absorption wavelength; λ_{em} : maximum emission wavelength; Φ_f : fluorescence quantum yield.

were observed from room temperature to 200°C, possibly due to the local molecular motions related to the diamine constituents of the polymer chain. The high-temperature relaxation is an α -relaxation process; the peak temperatures in the $\tan \delta$ curves were regarded as the T_g s of these polymers, which were generally in good agreement with T_g values obtained from DSC experiments.

The thermal stability of polymers was evaluated by TGA in air atmosphere. The TGA curves for the polyamides are shown in Fig. 5(D), and their analytical values are listed in Table 2. There is a small weight loss at the beginning of the TGA curves of the polymers, in the temperature range from 100 to 200°C, which can be attributed to the loss of absorbed water (moisture) which is hydrogen-bounded with amide linkages and has not been

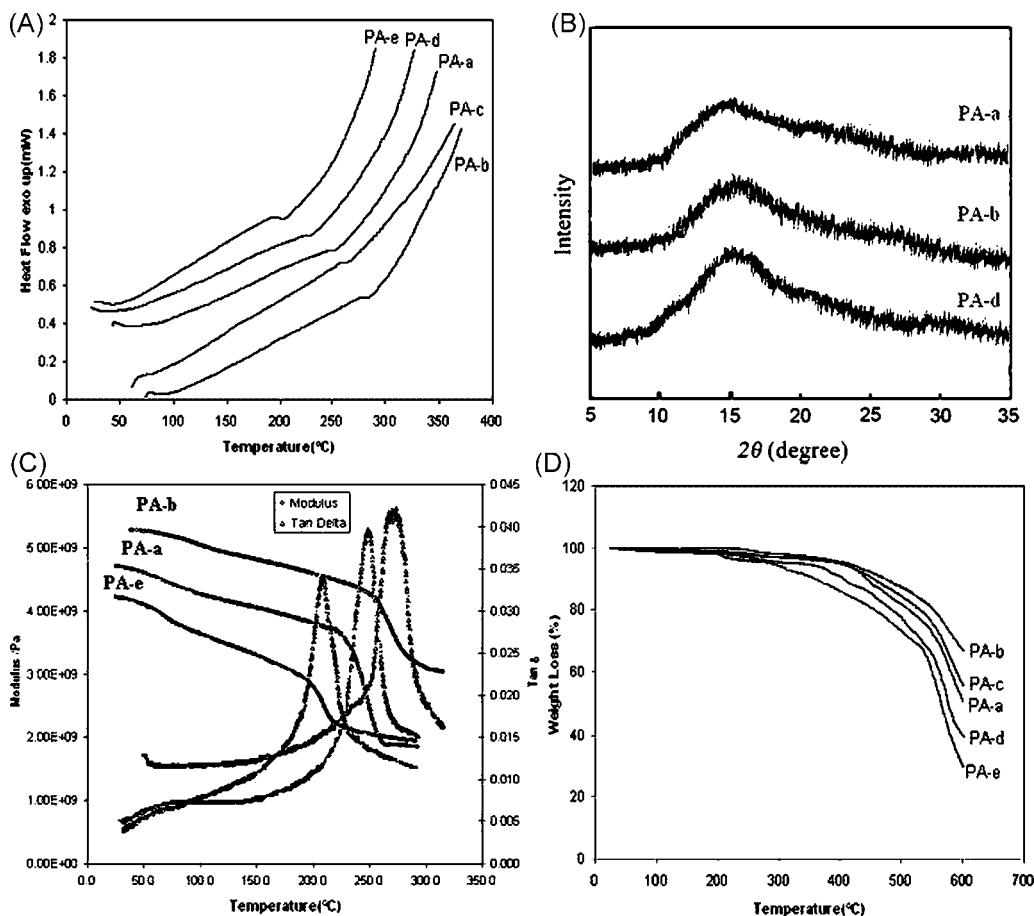


Figure 5. DSC curves (A), WAXD patterns (B), DMTA curves (C), and TGA curves (D) of polyamides.

removed in the precedent drying operation. Fig. 5(D) shows that the aromatic polyamides (PA-a, PA-b, and PA-c) start to gradually decompose near 400°C and are thermally stable up to 410°C as judged from their 5% weight loss temperatures. The aliphatic polyamides (PA-d and PA-e) are thermally stable up to 310°C, and they showed almost two-step decomposition path. The first step could be assigned to decomposition of the aliphatic chain while the second one could be associated to generalized polymer degradation. The residual weight retentions at 600°C for the resulting polyamides were in the range of 29–67%, implying the much better thermal stability of the aromatic polyamides.

CONCLUSIONS

In this work a series of novel photoactive polyamides containing bulky imidazole pendant groups and aryl-ether linkages in the backbone have been successfully prepared by direct phosphorylation polycondensation of a new symmetrical diamine monomer with various aromatic and aliphatic dicarboxylic acids. These polyamides exhibited the ability to dissolve in a variety of solvents and had high molecular weights as evidenced by their inherent viscosity of 0.68–0.89 dL/g and also good film forming ability by solution casting. In addition to excellent solubility, these polyamides also revealed high glass transition temperatures and high thermal stability. As a result, the present polyamides may find applications as new type of photoactive high-temperature polymeric materials.

REFERENCES

- [1] P. E. Cassidy, *Thermally Stable Polymers*, Marcel Dekker, New York, **1980**.
- [2] J. Preston, H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, *Encyclopedia of Polymer Science and Technology*, Wiley, New York, **1988**.
- [3] H. H. Yang, *Aromatic High-strength Fibers*, Wiley, New York, **1989**.
- [4] J. Lin, D. C. Sherrington, *Adv. Polym. Sci.* **1994**, *111*, 177–219.
- [5] S. H. Cheng, S. H. Hsiao, T. H. Su, G. S. Liou, *Macromolecules* **2005**, *38*, 307–316.
- [6] D. J. Liaw, W. H. Chen, *Polymer* **2003**, *44*, 3865–3870.
- [7] C. P. Yang, S. H. Hsiao, K. H. Chen, *Polymer* **2002**, *43*, 5095–5104.
- [8] S. H. Hsiao, K. H. Lin, *Polymer* **2004**, *45*, 7877–7885.
- [9] M. Ghaemy, M. Barghamadi, *J. Appl. Polym. Sci.* **2008**, *110*, 1730–1738.
- [10] S. Mehdipour-Ataei, M. Hatami, *Polym. Adv. Technol.* **2007**, *18*, 292–298.
- [11] D. J. Liaw, B. Y. Liaw, *Polym. Adv. Technol.* **1998**, *9*, 740–745.
- [12] D. J. Liaw, B. Y. Liaw, K. L. Su, *Polym. Adv. Technol.* **1999**, *10*, 329–335.
- [13] S. H. Hsiao, C. F. Chang, *Macromol. Chem. Phys.* **1996**, *197*, 1255–1272.
- [14] S. H. Hsiao, K. Y. Chu, *J. Polym. Sci. A Polym. Chem.* **1997**, *35*, 3385–3391.
- [15] M. Ghaemy, S. M. Amini Nasab, R. Alizadeh, *J. Appl. Polym. Sci.* **2010**, *116*, 3725–3731.
- [16] S. H. Hsiao, C. W. Chen, G. S. Liou, *J. Polym. Sci. A Polym. Chem.* **2004**, *42*, 3302–3313.
- [17] R. R. Pal, P. S. Patil, M. M. Salunkhe, N. N. Maldar, P. P. Wadgaonkar, *Eur. Polym. J.* **2009**, *45*, 953–959.
- [18] J. Weber, Q. Su, M. Antonietti, A. Thomas, *Macromol. Rapid. Commun.* **2007**, *28*, 1871–1876.
- [19] D. J. Liaw, B. Y. Liaw, C. M. Yang, *Macromolecules* **1999**, *32*, 7248–7250.
- [20] Y. L. Liu, S. H. Tsai, *Polymer* **2002**, *43*, 5757–5762.
- [21] G. S. Liou, S. H. Hsiao, M. Ishida, M. Kakimoto, Y. Imai, *J. Polym. Sci. A Polym. Chem.* **2002**, *40*, 2810–2818.
- [22] S. Mallakpour, Z. Rafiee, *Polym. Adv. Technol.* **2008**, *19*, 1474–1478.
- [23] A. R. Hajipour, S. Zahmatkesh, A. E. Ruoho, *Polym. Adv. Technol.* **2008**, *19*, 1710–1719.
- [24] S. H. Chen, C. S. Shiau, L. R. Tsai, Y. Chen, *Polymer* **2006**, *47*, 8436–8443.
- [25] S. H. Cheng, S. H. Hsiao, T. H. Su, G. S. Liou, *Polymer* **2005**, *46*, 5939–5948.
- [26] D. J. Liaw, B. Y. Liaw, *Polymer* **2001**, *42*, 839–845.
- [27] M. Ghaemy, R. Alizadeh, H. Behmadi, *Eur. Polym. J.* **2009**, *45*, 3108–3115.
- [28] M. Ghaemy, M. Barghamadi, *J. Appl. Polym. Sci.* **2009**, *114*, 3464–3471.
- [29] S. Mallakpour, Z. Rafiee, *Polym. Adv. Technol.* **2008**, *19*, 1015–1023.
- [30] E. Hamciuc, I. Sava, M. Bruma, T. K. pnick, B. Schulz, B. Sapich, J. Wagner, J. Stumpe, *Polym. Adv. Technol.* **2006**, *17*, 641–646.
- [31] Y. Jung, J. Lee, S. Lee, H. Cho, H. Shim, *J. Polym. Sci. A Polym. Chem.* **2006**, *44*, 4611–4620.
- [32] T. Kanbara, N. M. Saito, T. Yamamoto, K. Kubota, *Macromolecules* **1991**, *24*, 5883–5885.
- [33] M. Ghaemy, R. Alizadeh, *Eur. Polym. J.* **2009**, *45*, 1681–1688.
- [34] K. Mullen, *Organic Light Emitting Devices: Synthesis, Properties and Applications*, Wiley-VCH, Weinheim, Germany, **2006**.
- [35] J. A. Mikroyannidis, D. Panayiotis, V. I. Panayiotis, K. Spiliopoulos, *Synth. Met.* **2004**, *145*, 87–93.
- [36] X. H. Zhou, J. C. Yan, J. Pei, *Macromolecules* **2004**, *37*, 7078–7080.
- [37] Y. Pan, X. Tang, L. Zhu, Y. Huang, *Eur. Polym. J.* **2007**, *43*, 1091–1095.
- [38] K. Feng, F. L. Hsub, D. Van DerVeer, K. Bota, R. Xiu, *J. Photochem. Photobiol. A Chem.* **2004**, *165*, 223–228.
- [39] G. Hadjikallis, S. C. Hadjiyannakou, M. Vamvakaki, C. S. Patrickios, *Polymer* **2002**, *43*, 7269–7273.
- [40] Y. Pan, X. Tang, *Eur. Polym. J.* **2008**, *44*, 408–414.
- [41] K. Nakashima, Y. Fukuzaki, R. Nomura, R. Shimoda, Y. Nakamura, N. Kuroda, S. Akiyama, K. Irgum, *Dyes Pigm.* **1998**, *38*, 127–136.
- [42] N. Fridman, M. Kaftory, S. Speiser, *Sens. Actuators B* **2007**, *126*, 107–115.
- [43] A. G. Mohan, N. J. Turro, *J. Chem. Educ.* **1974**, *51*, 528–529.
- [44] N. Yamazaki, M. Matsumoto, F. Higashi, *J. Polym. Sci. Polym. Chem.* **1975**, *13*, 1373–1380.
- [45] G. S. Liou, C. W. Chang, *Macromolecules* **2008**, *41*, 1667–1674.
- [46] G. S. Liou, K. H. Lin, *J. Polym. Sci. A Polym. Chem.* **2009**, *47*, 1988–2001.
- [47] G. S. Liou, S. H. Hsiao, N. K. Huang, Y. L. Yang, *Macromolecules* **2006**, *39*, 5337–5346.
- [48] G. S. Liou, H. J. Yen, *J. Polym. Sci. A Polym. Chem.* **2006**, *44*, 6094–6102.
- [49] G. S. Liou, S. M. Lin, H. J. Yen, *Eur. Polym. J.* **2008**, *44*, 2608–2618.
- [50] M. Stigbrand, T. Jonsson, E. Ponten, K. Irgum, R. Bos, *Chemiluminescence in Analytical Chemistry; La Campana* (Eds: A. M. La Campana, W. J. Baeyens), Marcell Dekker, New York, **2000**.