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Synthesis and identification of organosoluble polyamides bearing a triaryl imidazole pendent: Thermal, photophysical, chemiluminescent, and electrochemical characterization with a modified carbon nanotube electrode

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ABSTRACT

A novel monomer containing a triaryl imidazole pendent group was successfully synthesized by nucleophilic substitution of bisphenol A with 2-(2-chloro-5-nitrophenyl)-4,5-diphenyl-1H-imidazole (I). A series of new polyamides (PAs) with inherent viscosities of 0.95–1.2 dL/g was prepared by direct polycondensation of the diamine with various dicarboxylic acids. These PAs were readily soluble in many organic solvents and gave tough and flexible films by solution casting. These PAs exhibited T_{gS} between 189 °C and 252 °C, and 10% weight loss temperatures in excess of 400 °C with up to 68% char yield at 600 °C in air. All of the PAs emitted a greenish-yellow light in dilute THF solution, with photoluminescence (PL) quantum yields in the range of 10–25%. The chemiluminescent activity and electrochemical oxidation of the PAs were also investigated.

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1. Introduction

Aromatic polyamides are difficult to process as high-performance polymers due to their high softening temperatures and/or insolubility in most organic solvents [1,2]. Therefore, research has focused on the development of structurally modified aromatic polyamides with increased solubility by introducing flexible segments into the polymer chain, replacing symmetrical aromatic rings by unsymmetrical ones, and forming a non-coplanar structure [3–9]. Generally, one of the successful approaches to increase the solubility and processability of polymers without sacrificing high thermal stability is the introduction of bulky pendent groups into the polymer backbone [10–20]. Other reports have described the incorporation of imidazole and its derivatives into polymeric frameworks [20-22]. 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 [23]. 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 [24–30]. Lophine, 2,4,5-triph-enylimidazole, and its derivatives have significant analytical applications for their fluorescent and chemiluminescent properties [31,32].

Carbon nanotubes (CNTs) are well characterized due to their novel mechanical, electronic, structural and chemical properties [33]. The modification of electrode substrates with multi-walled carbon nanotubes (MWCNTs) for use in analytical sensing is reported to result in high sensitivities, low detection limits, resistance to surface fouling and reduction of overpotentials.

The present investigation focused on the synthesis and characterization of five polyamides (PAs) from a novel diamine monomer, 4-(4-(2-(4-(4-amino-2-(4,5-diphenyl-1H-imidazol-2-yl) phenoxy) phenyl) propan-2-yl) phenoxy)-3-(4,5-diphenyl-1H-imidazol-2yl) aniline, bearing triaryl imidazole pendent groups and ether linkages that impart properties such as thermal stability and solubility to the polyamides. The presence of voluminous pendent groups is expected to result in a less ordered polymer matrix and 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, water sorption, thermal stability, UV-visible absorption, fluorescence, chemiluminescent, and their electrochemical behavior on an MWCNT-modified electrode.



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2. Experimental section

2.1. Materials

All starting materials including the dicarboxylic acids, such as pyridine-2, 6-dicarboxylic acid, terephthalic acid, isophthalic acid, adipic acid, sebacic acid, and other reagents, were purchased from either Merck or Fluka. N-Methyl-2 pyrrolidinone (NMP) and pyridine (Py) were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves. Lithium chloride (LiCl) was dried for 10 h at 180 °C under vacuum. All other reagents and solvents were used as received.

2.2. Synthesis of monomer (Scheme 1)

2.2.1. 2-(2-chloro-5-nitrophenyl)-4,5-diphenyl-1H-imidazole (I)

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 h in a 250 mL round-bottomed two-necked flask equipped with a condenser, a magnetic stir bar and a nitrogen gas inlet tube. Upon cooling, the precipitated white solid was collected by filtration and washed with ethanol and water. Yellow crystals (3.55 g, yield of 95%) were obtained with a melting point (mp) of 218–220 °C. Fourier transform infrared (FT-IR) (KBr, cm⁻¹): 3453 (NH), 3124 (C—H aromatic), 1684 (C=N), 1532 and 1345 (NO₂). Elemental analysis calculated (Anal. Calcd.) (%) for C₂₁H₁₄ClN₃O₂: C, 67.20; H, 3.73; N, 11.20. Found: C, 67.00; H, 3.65; N, 11.35.

2.2.2. 2-(2-(4-(2-(4-(4-nitro-2-(4,5-diphenyl-1H-imidazol-2-yl) phenoxy) phenyl) propan-2-yl) phenoxy) -5-nitrophenyl)-4,5-diphenyl-1H-imidazole (II)

A mixture of 2.28 g (10 mmol) Bisphenol A, 7.5 g (20 mmol) (I), 2.76 g (20 mmol) anhydrous potassium carbonate in 20 mL of dry DMAc was refluxed at 140 °C for 12 h in a 250 mL round-bottomed two-necked flask equipped with a condenser, a magnetic stir bar and a nitrogen gas inlet tube. After cooling, the mixture was poured into water and the precipitate was collected by filtration and recrystallized from ethanol. The yield of the reaction was 96% (8.7 g); mp 210–212 °C. FT-IR (KBr) at cm⁻¹: 3443 (NH), 3059 and 2963 (C—H aromatic and aliphatic), 1603 (C=N), 1537 and 1345 (NO₂). Anal. Calcd. (%) for C₅₇H₄₂N₆O₆: C, 75.47; H, 4.63; N, 9.27. Found: C, 75.52; H, 4.6; N, 9.33.

2.2.3. 4-(4-(2-(4-(4-amino-2-(4, 5-diphenyl-1H-imidazol-2-yl) phenoxy) phenyl) propan-2-yl) 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 stir bar, 9.06 g (0.01 mol) (II) and 0.2 g of 10% Pd/C were dispersed in 80 mL ethanol. The suspension was heated to reflux, and 8 mL of hydrazine monohydrate was added slowly to the mixture. After an additional 5 h of reflux, the solution was filtered hot to remove the Pd/C. Upon cooling of the filtrate, white crystals precipitate, which were collected by filtration and dried under vacuum at 80 °C. The yield was 88% (7.5 g); mp 150-152 °C. FT-IR (KBr) at cm⁻¹: 3433 and 3373 (NH₂), 3442 (NH imidazole), and 1219 (C-O). ¹H NMR (500 MHz, DMSO-d₆): δ 1.54 (s, 6H), 5.25 (s, 4H), 6.64–6.66 (dd, 2H, J = 8.35 Hz), 6.79–6.86 (m, 6H, J = 8.35 Hz), 7– 7.14 (t, 4H, J = 8.35 Hz), 7.20-7.24 (t, 2H, J = 8.35 Hz), 7.25-7.28 (t, 4H, J = 8.75), 7.30–7.37 (m, 12H), δ 7.46–7.49(t, 4H, J = 8.75 Hz), δ 11.90 (s, 2H). ¹³C NMR (500 MHz, DMSO-d₆): δ 31.59, 42.29, 114.79, 115.52, 116.37, 116.85, 122.80, 124.09, 127.27, 127.88, 128.17, 128.40, 128.94, 129.03, 129.40, 131.93, 136.09, 137.32, 143.37, 143.96, 144.82, 146.41, 157.01. Anal. Calcd.

(%) for $C_{57}H_{46}N_6O_2$: C, 80.82; H, 5.43; N, 9.92. Found: C, 80.83; H, 5.75; N, 9.72.

2.3. Synthesis of polyamides (Scheme 2)

The following general procedure was used for the preparation of all of the polyamides. The diamine (III) (1 mmol), dicarboxylic acid (1 mmol), and lithium chloride (0.6 g) were dissolved in a mixture of pyridine (1 mL), TPP (1.2 mmol), and NMP (8 mL) in a three-necked flask equipped with a condenser, a mechanical stir and a nitrogen gas inlet tube. The mixture was heated at 110 °C for 14 h with stirring under a dry N₂ atmosphere. The system was then cooled to room temperature and the solution was poured into 300 mL of methanol. The precipitate was filtered and washed with hot water. For further purification, all of the polyamides were extracted in methanol for 24 h. The extracted polyamides were then filtered and dried at 100 °C under vacuum. The inherent viscosities of the polymers in NMP were in the range of 0.95–1.2 dL/g, as measured at a concentration 0.5 g/dL at 25 °C.

PA-a: Yield: 86%, FT-IR (KBr, cm⁻¹): 3442 (NH imidazole), 3060 (C—H aromatic), 2973(C—H aliphatic), 1684 (C=O amide), 1588 (C=N imidazole), 1492 (C=C), 1370 (C—N), 1224 (C—O).1H NMR (DMSO-d₆): δ 12.36 (s-2H), 10.68 (s-2H), 6.99–8.75 (m-37H), 1.72 (s-6H). Anal. Calcd. C, 78.86; H, 4.75; N, 9.91. Found C, 78.18; H, 4.95; N, 9.61.

PA-b: Yield: 90%, FT-IR (KBr, cm⁻¹): 3428 (NH imidazole), 3049 (C—H aromatic), 2975 (C—H aliphatic), 1668 (C=O amide), 1607 (C=N imidazole), 1498 (C=C), 1370 (C–N), 1235 (C–O). ¹H NMR (DMSO-d₆): δ 12.21(s-2H), 10.61(s-2H), 6.95–8.28(m-38H), 1.61(s-6H). Anal. Calcd. C, 79.92; H, 4.92; N, 8.61. Found C, 79.32; H, 4.90; N, 8.31.

PA-c: Yield: 85%, FT-IR (KBr, cm⁻¹): 3362 (NH imidazole), 3059 (C—H aromatic), 2968 (C—H aliphatic), 1664 (C=O amide), 1610 (C=N imidazole), 1487 (C=C), 1370 (C–N), 1229 (C–O). ¹H NMR (DMSO-d₆): δ 12.11 (s-2H), 10.56 (s-2H), 7.15–8.61 (m-38H), 1.65 (s-6H). Anal. Calcd. C, 79.92; H, 4.92; N, 8.61. Found C, 79.45; H, 4.65; N, 8.51

PA-d: Yield: 95%, FT-IR (KBr, cm⁻¹): 3447 (NH imidazole), 3044 (C—H aromatic), 2953 (C—H aliphatic), 1669 (C=O amide), 1603 (C=N imidazole), 1482 (C=C), 1370 (C–N), 1225 (C–O). ¹H NMR (DMSO-d₆): δ 12.11(s-2H), 10.56(s-2H), 6.93–9.38 (m-34H), 2.16 (t-4H), 1.63 (s-6H), 1.55 (m-4H). Anal. Calcd. C, 78.91; H, 5.63; N, 8.77. Found C, 78.23; H, 5.82; N, 8.65.

PA-e: Yield: 91%,FT-IR (KBr, cm⁻¹): 3452 (NH imidazole), 3054 (C—H aromatic), 2917 (C—H aliphatic), 1665 (C=O amide), 1608 (C=N imidazole), 1485 (C=C), 1375 (C–N), 1219(C–O). ¹H NMR (DMSO-d₆): δ 12.11 (s-2H), 10.56 (s-2H), 6.99–8.27 (m-34H), 2.18 (t-4H), 1.65 (s-6H), 1.28 (m-12H). Anal. Calcd. C, 79.44; H, 5.93; N, 8.30. Found C, 79.29; H, 5.42; N, 8.36.

2.4. Preparation of MWCNT suspension and modified working electrode (CPE)

To eliminate metal oxide catalysts within the nanotubes, MWCNTs were refluxed in 2.0 M HNO₃ for 15 h, and then washed thoroughly with twice-distilled water and dried at room temperature [34]. The purified MWCNTs were dispersed in acetonitrile (0.1 mg MCNTs/10 mL) by ultrasonic agitation to obtain a relative stable suspension. The modified electrode was made by mixing (w/w) of 3% polymer (or 3% monomer), 5% MWCNT, and graphite powder in ether and hand mixing with a mortar and pestle. The solvent was evaporated by stirring. A 1:1 (w/w) mixture of the above modified electrode and paraffin was blended by hand mixing until a uniformly wetted paste was obtained. The resulting paste was inserted in the bottom of a glass tube (with internal radius and length of 1.0 mm and 10 cm, respectively). The electrical connection was implemented by copper wire leads fit into the glass tube. When necessary, a new surface was obtained by pushing out an excess of paste and polishing it on with weighing paper.

2.5. 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 previously described [35]. Solution A was composed of 1.0 mL of TCPO (0.01 M) and 0.5 mL of a monomer solution (10^{-5} M) and polymer (0.2 g/dL) in THF. Solution B contained 2 mL of 3.0 M hydrogen peroxide and 1.0 mL of the catalyst sodium salicylate (0.1 M) in methanol. Solution A was transferred into the instrument glass cell via polypropylene syringe. Then, 100 µL of stock solution B was injected in the 3 cm quartz cuvette containing solution A, and the chemiluminescence spectrum was recorded.

2.6. Procedures for water absorption test

Water sorption values were determined gravimetrically for PA powders and films. The PAs films were made by solution casting of 0.6 g of polymer in 10 mL of DMAc. The polymer films were dried, first at 90 °C overnight to remove most of the solvent and then at 180 °C in a vacuum oven for 8 h. The obtained polymer films were used for water absorption tests by immersion in a flask containing distilled water: (A) at 25 °C and (B) at 70 °C. Powdered polymeric samples of about 200 mg, which were previously dried at 120 °C for 8 h, were placed in an open space with a relative humidity of 75%. Samples of the above tests were weighed periodically over the course of 48 h.

2.7. 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-d₆ using tetramethyl silane as an internal reference. The inherent viscosities were measured at a 0.5 g/dL concentration using an Ubbelohde viscometer at 25 °C. Thermogravimetric analysis (TGA) was conducted with a TGA-50 analyzer over the temperature range of 50-600 °C under an air atmosphere at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) analysis was performed on a Perkin-Elmer Pyris six calorimeter at a heating rate of 10 °C /min under flowing nitrogen (20 cm³/min). Glass transition temperatures (T_{σ}) were read at the middle of the transition in the heat capacity and were taken from the second heating scan after quick cooling from 350 °C at a cooling rate of 200 °C/min. 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. Relaxation temperatures were determined from the corresponding peak top temperatures of the damping (tan δ) curves. UV–visible and fluorescence emission spectra were recorded on Cecil 5503 and Perkin-Elmer LS-3B spectrophotometers, respectively. Electrochemical experiments were performed using the AUTOLAB PGSTAT 30 electrochemical analysis system and GPES 4.9 software package (Eco Chemie, Netherlands). A three-electrode system, composed of a CPE (surface area of 0.015 cm^2) as the working electrode, a saturated Ag/AgCl electrode as the reference electrode and a platinum wire as the auxiliary electrode, was used. X-ray powder diffraction (XRD) patterns were recorded by an 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 2 θ was set between 4° and 50° with a scan rate of 0.05° s⁻¹. 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 (Micropars, Tehran, Iran). Experiments were carried out with magnetic stirring in the flattened-bottom glass cells (15 mm diameter) at room temperature.

3. Results and discussion

3.1. Monomer synthesis and characterization

The objective of this study was to prepare a novel diamine fluorescent material based on an imidazole pendent. Scheme 1 shows the synthesis of this new diamine compound, 4-(4-(2-(4-(4-amino-2-(4,5-diphenyl-1H-imidazol-2-yl) phenoxy) phenyl) propan-2-yl) phenoxy)-3-(4,5-diphenyl-1H-imidazol-2-yl) benzenamine (III). Condensation of benzil with 2-chloro-5-nitrobenzaldehyde and ammonium acetate is a classical but convenient synthetic method for preparation of triaryl imidazole. The dinitro compound (II) containing the triaryl imidazole pendent group was synthesized by nucleophilic aromatic substitution reaction of bisphenol A with compound (I) in DMAc solvent and in the presence of K₂CO₃. The catalytic hydrogenation of dinitro to the corresponding diamine was accomplished by means of hydrazine hydrate in ethanol in the presence of a catalytic amount of palladium on activated carbon. Elemental analysis, FT-IR, and ¹H and ¹³C NMR spectroscopic techniques confirmed the structures of these compounds. The nitro groups of compound (II) gave two characteristic absorption bands at 1345 and 1537 cm⁻¹ (–NO₂ asymmetric and symmetric stretching). After reduction, these absorptions disappeared and the primary amino group showed the typical absorption pair at 3458 and 3367 cm⁻¹ due to N-H stretching. The ¹H NMR spectrum of the compound (III) is illustrated in Fig. 1. The signals at 1.54 ppm, 5.25 ppm, and 11.90 ppm are due to the protons of CH₃, –NH₂, and –NH of the imidazole ring, respectively. Aromatic protons at δ 7.46–7.49(t, 4H, J = 8.75 Hz), 7.30–7.37 (m, 12H), 7.25– 7.28 (t, 4H, J = 8.75), 7.20-7.24 (t, 2H, J = 8.35 Hz), 7-7.14 (t, 4H, J = 8.35 Hz), 6.79–6.86 (m, 6H, J = 8.35 Hz), 6.64–6.66 (dd, 2H, J = 8.35 Hz), showed the expected multiplicity and integration values. These results and the assigned ¹³C NMR signals in the experimental section confirmed that the diamine (III) prepared herein is consistent with the proposed structure.

3.2. Polymer synthesis and characterization

A series of novel polyamides PA(a-e) containing bisphenol A and triaryl imidazole pendent group moieties were prepared by polycondensation of the diamine compound (III) with five aromatic and aliphatic dicarboxylic acids according to the phosphorylation technique [36], as depicted in Scheme 2. To optimize the reaction conditions of this new diamine with dicarboxylic acids, the inherent viscosity of polyamide PA-b was measured during polyamidation. The maximum viscosity of 1.12 dL/g was reached after 13 h at 110 °C. The polymer structures were confirmed by elemental analysis, FT-IR, and ¹H NMR spectroscopic techniques. The characteristic FT-IR absorption bands of the amide group appeared at \sim 3442 cm⁻¹ (N–H stretching) and 1684 cm⁻¹ (C=O stretching). The ¹H NMR spectrum of polyamide PA-b is illustrated in Fig. 2. The assignment of each proton is given in the figure and the total protons in the spectrum are consistent with the proposed chemical structure of polymer.





Scheme 1. Three-step synthesis procedure for monomer preparation.



Fig. 1. ¹H NMR spectrum of the diamine monomer.

The X-ray diffraction studies indicated that all of the PAs displayed almost amorphous patterns, which could be attributed to the presence of bulky pendent groups, thus reducing the attraction between molecules and hindering regular macromolecular packing.



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

3.3. Properties of polymers

3.3.1. Solubility, viscosity and water absorption

The solubility of the PAs was determined at a 5% (W/V) concentration in a number of solvents and the results are tabulated in Table 1. All of the prepared polyamides exhibited excellent solubil-

ity in polar aprotic solvents, such as NMP, DMAc, DMF, and DMSO, and even in less polar solvents like pyridine and m-cresol at room temperature. However, they showed reduced solubility in dioxane and tetrachloroethane due to the low dielectric constant of the solvent. Good solubility should result from the introduction of the bulky pendent triphenyl imidazole group in the polymer backbone.

Table 1

Solubility behavior and inherent viscosities of the PAs.

Polymer code	NMP	DMSO	DMAc	DMF	m-cresol	THF	Dioxan	Pyridine	TCE	$\eta_{\rm inh}({\rm dL/g})$
PA-a	++	++	++	++	++	+	±	++	_	1.05
PA-b	++	++	++	++	++	+	±	++	_	1.12
PA-c	++	++	++	++	++	+	±	++	_	1.2
PA-d	++	++	++	++	++	+	+	++	±	1.12
PA-e	++	++	++	++	++	+	+	++	±	0.95

Five grams polymer in 100 mL solvent. (DMAc: N,N-dimethyl acetamide; DMF: N,N'-dimethyl formamide; NMP: N-methyl pyrrolidone; DMSO: dimethyl sulfoxide; TCE: tetrachloroethane).

(++: soluble at room temperature; +: soluble on heating at 60 °C; ±: partially soluble on heating at 60 °C; -: insoluble on heating at 60 °C).

Dense chain packing of the polymer chains was probably disturbed by the bulky pendent group; consequently, the solvent molecules were able to penetrate more easily to solubilize the polymer chains. We believe that the presence of the polar imidazole group in the pendent unit also contributes to the increased solubility of these polyamides. The solubility varies depending upon the dicarboxylic acid used. The polyamides synthesized from aliphatic dicarboxylic acids (PA-d and PA-e) exhibited good solubility behavior in dioxane and tetrachloroethane (TCE). The methylene units, instead of the rigid phenyl, improve the solubility of these polyamides in comparison with the PA(a-c). Thus, all of these polymers can be readily processed from solution. The obtained polyamides had inherent viscosities in the range of 0.95–1.2 dL/g for a concentration of 0.5 g/dL in NMP at 25 °C, as shown in Table 1. All of the polymers yielded transparent and light yellowish, tough, and flexible films via solution casting. The polymers showed moisture intake ranging from 7.98% to 9.22% (at 75% room humidity). Water absorption of the polymer films at room temperature and at 70 °C were in the range of 11.49-12.88% and 14.51-15.43%, respectively. A structurally flexible polymer with bulky chemical groups in its structure is reported to be capable of more water uptake than a linear, rigid polymer [37].

3.3.2. Photophysical properties

The photoluminescence (PL) spectra of the diamine and PAs in dilute (0.2 g/dL) THF solution are shown in Fig. 3A. The diamine and the polymers exhibited strong absorption at 245-320 nm, which was assigned to a π - π ^{*} transition resulting from the conjugation between the aromatic rings and nitrogen atoms. The UV-vis absorption of polyamide films also showed similar absorbance. An excitation wavelength of 315 nm was used in all cases. The maximum emission ($\lambda_{max(em)}$) of the diamine monomer in THF solution was observed at 420 nm. The monomer showed strong fluorescent blue light. The PL spectra of polymers in THF solutions exhibited broad emission from 400 nm to 600 nm, with a high-intensity maximum around 390 nm for the aliphatic PAs (PA-d and PA-e). The aromatic PAs (PA-a, PA-b and PA-c) exhibited two maxima: higher intensity peak at 450 nm and a lower intensity peak at 545 nm. The polymers emit greenish-yellow light; in addition, their PL spectra in THF solution and in the solid state were very similar in terms of the spectral shapes and peak positions. To measure the PL quantum yields (Φ_f), dilute polymer solutions (0.2 g/dL) in THF were prepared. A 0.1 N solution of quinine in H₂SO₄ $(\Phi_f = 0.53)$ was used as a Ref. [28]. The Φ_f values were 0.31 for the monomer, 0.23–0.25 for the aliphatic PAs, and 0.10–0.13 for the aromatic PAs. The blue shift and higher fluorescence quantum yield of the aliphatic polyamides compared with the aromatic polyamides could be attributed to reduced conjugation and capability of charge-transfer complex formation by the aliphatic diacids with the electron-donating diamine moiety in comparison to the stronger electron-accepting aromatic diacids [38]. Because of the lower capability of charge-transfer, the polyamides PA-d and PAe showed a light color and high optical transparency.

3.3.3. Chemiluminescence characteristics

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 [39]. We used this technique to study the chemiluminescence arising from the reaction of TCPO with hydrogen peroxide in the presence of the monomer and PAs. In preliminary experiments, the addition of a few drops of a stock solution of H₂O₂ to a THF solution containing TCPO and monomer resulted in a very intense blue chemiluminescence light that was similar to the photoluminescence light of the monomer (i.e., $\lambda_{max(em)} = 420$ nm). This experiment was repeated with the PAs, and a very intense greenish-yellow chemiluminescence light was observed, as shown in Fig. 3B. The higher chemiluminescence intensity of the aliphatic polyamides in comparison to those from the aromatic polyamides may be due to reduced conjugation, resulting in a lower capability of charge-transfer complex formation. The colors of the emitted light for both photoluminescence and chemiluminescence are essentially analogous, thus the emission wavelength maxima in both processes should be identical.

3.3.4. Thermal properties

The DSC, DMTA, and TGA methods were applied to evaluate the thermal properties of the PAs, and the thermal analysis data are summarized in Table 2. The T_g values of these PAs were measured by DSC, and ranged from 189 °C to 252 °C, depending upon the stiffness of dicarboxylic acid in the polymer chain. The DSC curves of the PAs are shown in Fig. 4. The lowest T_g value of the polyamide PA-e in these series polymers can be explained in terms of the flexible methylene linkages in its diacid component. Among all of the synthesized PAs, the polyamide PA-b, which is based on terephthalic acid, showed the highest T_g value, likely because of its



Fig. 3. Fluorescence emission spectra (A) and chemiluminescence spectra (B) of the monomer and PAs.

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Thermal stability	data and kine	etic parameters	for thermal decomp	osition of polyamides.	
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Polymer	T_g (°C)	T_{10} (°C)	Char yield (%)	E_a (kJ mol ⁻¹)	$A(S^{-1})$	ΔS (J mol ⁻¹ k ⁻¹)	ΔH (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)
PA-a	239	462	61	157.81	2.12×10^9	-75.12	150.80	214.12
PA-b	252	479	68	160.25	$3.14 imes10^9$	-71.91	153.22	214.06
PA-c	247	442	51	157.81	$1.97 imes 10^8$	-75.63	149.30	212.91
PA-d	206	423	34	144.95	$3.35 imes 10^8$	-90.35	137.96	213.94
PA-e	189	395	23	121.13	1.25×10^7	-117.62	114.21	212.18

Tg; glass transition temperature, Ti: initial decomposition temperature, T10: temperature for 10% weight loss. Char yield: weight of polymer remained at 600 °C.



Fig. 4. DSC curves of the PAs.

high rigidity inhibiting the molecular motion. None of the PAs showed clear melting endotherms in the DSC thermograms, suggesting the amorphous nature of these PAs. The bulky pendent group increases the steric hindrance for close-chain packing, thus increasing the fractional free volume between the polymer chains and decreasing the intra- and inter-chain interaction.

Viscoelastic relaxation behaviors of these PAs were subjected to DMTA experiments. The DMTA results displayed the dynamic storage modulus and tan δ as a function of temperature. Two relaxation processes were observed above room temperature for all of the PAs. The β -relaxation processes 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 δ curves were regarded as the T_gs 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 an air atmosphere. The TGA curves for the polyamides are shown in Fig. 5. The initial decomposition temperatures (T_i) , the temperatures of 10% weight loss (T_{10}) and the residual weight values were determined from original thermograms and are tabulated in Table 2. All of the polymers exhibited good thermal stability with insignificant weight loss up to 400 °C in air. The temperatures for 10% weight loss, which are important criteria for evaluating the thermal stability of the polymers, were in the range of 395-479 °C, indicating their high thermal stabilities. There was a small weight loss at the beginning of the TGA curves of the polymers, over the temperature range from 100 °C to 200 °C, which can be attributed to the loss of absorbed water (moisture) hydrogen-bonded with amide linkages that was not removed in the drying operation. The residual weight retentions at 600 °C for the resulting PAs were in the range of 21-68%. These results imply significantly higher thermal stability of the aromatic PAs, likely due to the rigid structure of the aromatic diacids in comparison to that of the flexible aliphatic diacids.



Fig. 5. TGA thermograms of the PAs.

3.3.4.1. *Kinetic study of thermal decomposition.* In order to study the effect of different functional groups in the resultant PAs on thermal stability, thermal kinetic investigations were carried out using the Coats–Redfern Eq. (1), assuming a first-order reaction [40–42]:

$$\ln[-\ln(1-\alpha)/T^{2}] = \ln[AR/\phi(1-2RT/E_{a})]E_{a}/RT,$$
(1)

where α is the fraction decomposed at temperature *T*, ϕ is the heating rate, *R* is the gas constant, and *A* is the Arrhenius frequency factor. The *E*_a values were calculated from the plots of ln [-ln (1 – α)/*T*²] versus 1/*T* and are given in Table 2. The entropy of activation ΔS in J mol⁻¹ K⁻¹ was calculated using the following equation:

$$\Delta S = R \ln(Ah/K_B T_S) \tag{2}$$

where K_B is the Boltzmann constant, h is Plank's constant and T_S is the DTG peak temperature [42]. Other kinetic parameters such as enthalpy of activation (ΔH), and Gibbs free energy (ΔG) can be calculated via the equations $\Delta H = E_a - RT_m$ and $\Delta G = \Delta H - T_m \Delta S$, respectively, and are included in Table 2. Positive values of ΔH indicate that the dissociation processes are endothermic in nature and enhanced with increasing temperature. The ΔG values for the dissociation constants are positive, indicating that the dissociation processes are non-spontaneous. The negative ΔS values for the decomposition step indicate that the all of the studied PAs have a more ordered structure after the transition than the reactants in their activated states.

3.3.5. Electrochemical behavior on MCNT-modified electrode

The redox behavior of the modified graphite-MWCNT-polymer paste as working electrode was monitored by cyclic voltammetry (CV). Modification of a graphite paste electrode with MWCNT can lead to a strong interfacial accumulation of materials and allow for highly sensitive adsorptive measurements. The measurements of graphite paste-MWCNT-polymer, as illustrated in Fig. 6, reveal



Fig. 6. Cyclic voltammograms of (a) the polyamide PA-b with CPE; (b) the polyamide PA-b with modified CPE; and (c) the monomer with modified CPE at a scan rate of 100 mV/s.

that the polymers are oxidized at a potential of 0.6-0.7 V. Electrooxidized products of the polymers cannot be reduced, as shown by the reverse peak in Fig. 6. The cyclic voltammograms of the compounds exhibiting one anodic peak at the forward scan of potential may be related to the oxidation of the imidazole group. In order to interpret the voltammograms of the resulting PAs, it was necessary to study the electrochemical behavior of the monomer and polymer in the absence of MWCNT. These results showed that the monomer has an electrochemical behavior similar to that of the polymers. The oxidation of the polymer in the absence of MWCNT was almost 50% less than that when MWCNT was present. Nanomaterials are more effective than conventional materials for two reasons. First, their extremely small size (typically 10-80 nm) vields a tremendous surface area-to-volume ratio, which in turn boosts the level of redox activity. Second, When materials are fabricated on the nanoscale, they achieve properties not found within their macroscopic counterparts.

4. Conclusions

A series of photoactive polyamides was prepared via direct phosphorylation polycondensation of a new symmetrical diamine monomer, 4-(4-(2-(4-(4-amino-2-(4,5-diphenyl-1H-imidazol-2-yl) phenoxy) phenyl) propan-2-yl) phenoxy)-3-(4,5-diphenyl-1H-imidazol-2-yl) aniline, with various aromatic and aliphatic dicarboxylic acids. The PAs had an inherent viscosity of 0.95–1.2 dL/g and emitted yellowish green light for both fluorescence and chemiluminescence. The introduction of the bulky triaryl imidazole pendent group into the polymer backbone significantly improved the solubility of the prepared PAs in various organic solvents. Most of these photoactive PAs exhibited a desired combination of properties necessary for high-performance materials, including high thermal stability and excellent solubility in organic solvents for fabrication, and showed reasonable electrochemical stability.

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