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Thermal Stability of LED Molecules Triphenylamine-Based Aromatic Polyamides: Spectral and Electrochemistry Applications

AZHAR KAMIL RASHID

Department of Chemistry, College of Education for Pure Science/Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq

Corresponding author: Tel: +964 7714794280; E-mail: azhar_almasody@yahoo.co.uk

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By using the aromatic nucleophilic displacement reaction of 4-fluorobenzonitrile with three aniline-derivatives using sodium hydride as the base synthesized new dinitriles intermediates (**A-CN**), (**B-CN**) and (**C-CN**). After alkaline hydrolysis of these resultants three di acid monomers *e.g.*, 4,4'-dicarboxy-4"-ethylenetriphenylamine (**A-OH**), 4,4'-dicarboxy-4"-isopentyl-triphenylamine (**B-OH**), 4'-dicarboxy-4"-phenoxy-triphenylamine (**C-OH**) were obtained. A series of poly(amine-amide)s were prepared by the phosphorylation poly-condensation reaction with different aromatic diamines. The chemical structures of all the resultant compounds and poly(amine-amide)s were identified by FTIR, ¹H and ¹³C NMR techniques. These aromatic poly(amine-amide)s exhibited excellent thermal stability with high glass transition temperatures (*T_g*). Solutions diluted in N-methyl pyrrolidone of these polyamides appeared a strong UV-visible absorption in the blue region. These polymers exhibited cyclic voltammetry of the resulting polyamides films cast onto an ITO-coated glass substrate in dry acetonitrile containing 0.1 M of tetrabutylammonium perchlorate as an electrolyte exhibited one oxidation redox couples.

Keywords: LED-molecules, Thin layer, Emitting diodes.

INTRODUCTION

Materials with hole-transporting behaviour have been widely used in the polyamides light-emitting devices (PLEDs). They are highly interested due to their potential applications in many devices like flat panel displays and lighting sources. Organic light emitting diodes are described as a promising candidate for solid state lighting device [1,2]. The energy circumstance world is confronting today, it is basic to have a minimal effort, substantial territory, low energy utilization lighting elective and that is the place natural light transmitting diodes turn out to be critical [3-6]. The interest in organic semiconductors is not completely new, the first studies date back to early 20th century [7-9]. Discovery of electroluminescence in single crystals of anthracene lead to research efforts being focused on molecular crystals in the latter half of 20th century [10,11]. Conducting polymers along with organic photoconductors initiated the first applications of organic materials as conductive coatings [12,13]. The interest in undoped organic semiconductors was revived by fabrication of first organic heterojunction photovoltaic cell [14]. Also, the first reports of organic thin film transistors based on polymers [14,15] and oligomers [16] were published around the same time. However, the demonstration of high efficiency organic light emitting diodes by both vacuum sublimation of organic

molecules [1,17] and by solution processing of polymers [18] rekindled extensive interest in the field of organic semiconductors. The overlapping of those π -orbitals organic materials creates degeneracy that ends up in the formation of crammed bands called highest occupied molecular orbital (HOMO or bonding molecular orbital) and empty bands called lowest unoccupied molecular orbital (LUMO or antibonding molecular orbital).

EXPERIMENTAL

4-Ethylene-aniline (Merck, 99.7 %), 4-isopentyl-aniline (Acros, 98.7), 4-phenoxy-aniline (Merck, 99.8), 4-fluorobenzonitrile (Acros, 98.7 %), sodium hydride (Fluka, 60 %), N,N-dimethylformamide (Acros, 99.6 %), potassium hydroxide (Fluka, 99.8 %), ethanol (Merck, 99.7 %), acetic acid (Merck, 98 %), hydrochloric acid (Merck, 36 %), dimethyl sulfoxide-*d*₆, (Merck, 99.8 %), chloroform-*D*₁, (CDCl₃) (Merck, 99.8 %), *p*-phenylenediamine (Merck, 98 %), 1,5-diaminonaphthalene (Fluka, 98.8 %), pyridine (Merck, 97.8 %), triphenylphosphite (Fluka, 99 %), calcium chloride (Merck, 99.6 %), N-methylpyrrolidone (Fluka, 99.6 %) were used without further purification.

FT-IR spectrum of the synthesized compounds was recorded with a Spotlight 400 Perkin Elmer spectrometer. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) measurements were performed with a JEOL spectrometer. UV-visible absorption

and photoluminescence spectra were recorded in N-methyl pyrrolidone with concentration (10^{-5} M) on a Cary 60 UV-visible spectrophotometer. Thermal data were obtained from a Perkin Elmer DSC6 instrument. The data were recorded under nitrogen atmosphere at a heating rate of 20 °C/min with a SDT Q600 thermo gravimetric analyzer. The thermal decomposition data were recorded at a heating rate of 20 °C/min under nitrogen atmosphere with a SDT Q600 thermo gravimetric analyzer (TGA Instrument).

Monomer synthesis: The monomers (**(A-OH)**, **(B-OH)** and **(C-OH)** have synthesized *via* the aromatic nucleophilic reaction of 4-fluorobenzonitrile with three aniline-derivatives to provide three dicynides intermediates **(A-CN)**, **(B-CN)** and **(C-CN)** as follow:

Synthesis of 4,4'-dicyano-4''-ethylenetriphenylamine (A-CN): A mixture of 1.40 g (0.02 mol) of sodium hydride and 80 mL of DMF was stirred at room temperature for about 30 min. To the mixture, 2.38 g (0.02 mol) of 4-ethylenedianiline and 4.84 g (0.02 mol) of 4-fluorobenzonitrile were added in sequence. The mixture was heated with stirring at 120 °C for 24 h under nitrogen and then precipitated into 150 mL of cold water [19,20]. The products were filtered and recrystallized from ethanol to give pale yellowish solid 4.2 g (yield: 65 %), m.p.: (177-180) °C, FTIR: 2216 cm^{-1} (CN), ^1H NMR (400 MHz, $\text{CDCl}_3\text{-d}_1$, δ ppm): 7.60-7.70 (d, 2H, Ha), 7.34-7.44 (d, 4H, Hd), 6.76-6.86 (d, 4H, Hc), 6.58-6.68 (t, 1H, H_i), 6.53-6.63 (d, 2H, Hb), 5.56-5.66 (d, 1H, H₃), 5.13-5.23 (d, 1H, H₂). ^{13}C NMR (400 MHz, $\text{CDCl}_3\text{-d}_1$, δ ppm): 150.2 (C₅), 145.1 (C₄), 136.1 (C_{=H}), 133.1 (C₇), 132.3 (C₁), 129.7 (C₂), 124.9 (C₃), 123.4 (C₆), 118.62 (CN), 114.3 (C_{=CH₂}), 107.0 (C₈). In same procedure other intermediates **(B-CN)** and **(C-CN)** were synthesized:

Characteristics properties of 4,4'-dicyano-4''-isopentyl-triphenylamine (B-CN): 5.40 g (yield: 74.5 %), m.p.: 187-190 °C. FTIR: 2222 cm^{-1} (CN), ^1H NMR (400 MHz, $\text{CDCl}_3\text{-d}_1$, δ ppm): 7.34-7.44 (d, 4H, Hd), 7.01-7.11 (d, 2H, Ha), 6.76-6.86 (d, 4H, Hc), 6.50-6.61 ((d, 2H, Hb), 2.93 (s, 3H, HCH₃g), 2.18-2.26 (m, 1H, Hg), 1.25 (s, 3H, He), 0.86-0.96 (d, 6H, Hh). ^{13}C -NMR (400 MHz, $\text{CDCl}_3\text{-d}_1$, δ ppm): 150.22 (C₅), 142.71 (C₄), 135.21 (C₁), 133.11 (C₇), 129.42 (C₂), 127.13 (C₃), 123.44 (C₆), 118.62 (CN), 107.08 (C₈), 42.02 (C-CH₁), 35.63 (C-CH₂), 20.34 (C₂CH₃), 15.93 (C_{CH₃}).

Characteristics properties of 4,4'-dicyano-4''-phenoxy-triphenylamine (C-CN): 5.30 g (yield: 68 %), m.p.: 192-195 °C. FTIR: 2219 cm^{-1} (CN). ^1H NMR (400 MHz, $\text{CDCl}_3\text{-d}_1$, δ ppm): 7.34-7.46 (d, 6H, H_{d,f}), 7.09-7.20 (d, 2H, He), 6.70-6.86 (d, 6H, Hc,a), 6.54-6.64 (d, 2H, Hb), ^{13}C NMR (400 MHz, $\text{CDCl}_3\text{-d}_1$, δ ppm): 157.08 (C₉), 150.24 (C₅), 148.84 (C₁), 139.61 (C₄), 133.04 (C₇), 130.87 (C₃), 128.43 (C₁₁), 123.48 (C₆), 118.62 (C₁₀), 118.93 (C_{CN}), 116.34 (C₃), 107.04 (C₈).

Synthesis of 4,4'-dicarboxy-4''-ethylenetriphenylamine (A-OH): A mixture of 15.5 g of potassium hydroxide and 3.21 g (0.02 moles) of the dinitrile compound **(A-CN)** in 60 mL of ethanol and 60 mL of distilled water was stirred at about 100 °C until no further ammonia was generated. The time taken to reach this stage was about 24 h. The solution was cooled and the pH value was adjusted by dilute hydrochloric acid to near 3. The yellowish precipitate formed was collected by

filtration, washed with water. Recrystallization from acetic acid gave pale yellow crystals 3.30 g (92 % yields): m.p.: 281-284 °C. FTIR: 1678 cm^{-1} (C=O), 3400-2800 cm^{-1} (O-H). ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ ppm): 12.68 (s, 2H, H_{COOH}), 7.76-7.86 (d, 4H, Hd), 7.61-7.69 (d, 2H, Ha), 6.80-6.88 (d, 4H, Hc), 6.58-6.66 (t, 1H, H_i), 6.53-6.63 (d, 2H, Hb), 5.55-5.66 (d, 1H, H₃), 5.11-5.23 (d, 1H, H₂). ^{13}C NMR (400 MHz, $\text{DMSO-}d_6$, δ ppm): 169.3 (C_{COOH}), 151.1 (C₅), 145.1 (C₄), 136.1 (H-C=), 132.3 (C₁), 131.2 (C₇), 129.7 (C₂), 124.6 (C₈), 124.9 (C₆), 124.9 (C₃), 114.3 (C_{=CH₂}). In same procedure, other monomers **(B-OH)**, **(C-OH)** were synthesized.

Characteristics properties of 4,4'-dicarboxy-4''-isopentyltriphenylamine (B-OH): 3.70 g (92 % yields): m.p.: 276-278 °C. FTIR: 1683 cm^{-1} (C=O), 3300-2800 cm^{-1} (O-H). ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ ppm): 12.68 (s, 2H, H_{COOH}), 7.76-7.86 (d, 4H, Hd), 7.01-7.11 (d, 2H, Ha), 6.80-6.88 (d, 4H, Hc), 6.50-6.61 (d, 2H, Hb), 1.20-1.31 (d, 3H, He), 2.88-2.98 (q, 1H, Hf), 2.18-2.26 (m, 1H, Hg), 0.86-0.95 (d, 6H, Hh). ^{13}C NMR (400 MHz, $\text{DMSO-}d_6$, δ ppm): 169.33 (C_{COOH}), 115.11 (C₅), 142.71 (C₄), 135.23 (C₁), 131.22 (C₇), 129.47 (C₂), 127.19 (C₃), 124.63 (C₈), 124.94 (C₆), 42.08 (CCH-1), 35.66 (CCH-2), 20.32 (C₂CH₃), 15.93 (C_{CH₃}).

Characteristics properties of 4,4'-dicarboxy-4''-phenoxy-triphenylamine (C-OH): 3.80 g (89 % yield): m.p.: 292-295 °C. FTIR: 1681 cm^{-1} (C=O), 3300-2700 cm^{-1} (O-H). ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ ppm): 12.68 (s, 2H, H_{COOH}), 7.76-7.86 (d, 4H, Hd), 7.36-7.46 (d, 2H, He), 7.10-7.20 (d, 2H, Hf), 6.70-6.86 (d, 6H, Hc,a), 6.55-6.65 (d, 2H, Hb). ^{13}C NMR (400 MHz, $\text{DMSO-}d_6$, δ ppm): 169.33 (C_{COOH}), 157.08 (C₉), 151.14 (C₅), 148.64 (C₁), 139.01 (C₄), 131.24 (C₇), 130.97 (C₃), 128.43 (C₁₁), 124.64 (C₈), 124.98 (C₆), 118.92 (C₁₀).

Polymer synthesis

Synthesis of poly(amine-amide) (PBA): The poly(amine-amide) **(PBA)** was synthesized as follow: A mixture of 1.80 g (0.005 mol) of the dicarboxylic acid monomer **(A-OH)**, 0.92 g (0.005 mol) of benzidine, 0.5 g of calcium chloride, 4.5 mL of triphenylphosphite, 1.5 mL of pyridine and 4.5 mL of N-methyl-2-pyrrolidone was heated with stirring at 105 °C for 3 h. The resulting viscous polymer solution was poured slowly into 300 mL of stirring methanol giving rise to a stringy fiber-like precipitate that was collected by filtration, washed thoroughly with hot water and methanol and dried at 80 °C for 24 h, 2.0 g (77 % yield). FTIR was 3356 (N-H stretching) and 1648 cm^{-1} (C=O) stretching. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ ppm): 10.25 (s, 1H, H_{NH-CO}), 6.58-7.81 (d, 8H, Ha-h). ^{13}C NMR (400 MHz, $\text{DMSO-}d_6$, δ ppm): 119.72-151.12 (C₁₋₁₂).

Synthesis of poly(amine-amide)s (PBB), (PBC), (PANA), (PANB), (PANC): The obtained poly(amine-amide)s: **(PBB)** 2.11 g (74 % yield), 3314 cm^{-1} (N-H stretching) and 1644 cm^{-1} (amide carbonyl), **(PBC)** 2.22 g (76.5 % yield) IR spectral bands appeared at 3314 and 3304 due to N-H stretching, **(PANA)** 2.12g (77.3 % yield), 3314 cm^{-1} (N-H stretching) and 1644 cm^{-1} (amide carbonyl), **(PANB)** 2.33 g (78.4 % yield), IR spectral bands at 3364 cm^{-1} (N-H stretching) and 1648 cm^{-1} (amide carbonyl), **(PANC)** 2.40 g weight (78 % yield), 3357 cm^{-1} (N-H stretching) and 1648 cm^{-1} (amide carbonyl). ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ ppm): 10.25 (s, 1H, H_{NH-CO}) was for

all poly(amine-amide)s. **Scheme-I** shows the Synthetic routes for all intermediate compounds and poly(amine-amide)s resultant.

RESULTS AND DISCUSSION

Monomer synthesis: New substituted aromatic dicarboxylic monomers with triphenylamine units (**A-OH**), (**B-OH**) and (**C-OH**) were synthesized by the aromatic nucleophilic substitution reaction of aromatic diamines with 4-fluorobenzonitrile, trailed by the alkaline hydrolysis of the intermediate dicyano compounds (**A-CN**), (**B-CN**) and (**C-CN**). The chemical structures of the moderate dicyano compounds and the dicarboxylic acid monomers were portrayed by FTIR, ^1H and ^{13}C NMR spectroscopic procedures. The FTIR spectra of dicyano compounds gave a cyano bunch trademark band at 1216 cm^{-1} ($\text{C}\equiv\text{N}$ stretching). The cyano group absorption peak disappeared after hydrolysis and the carboxylic acid group showed a typical carbonyl absorption band at 1678 cm^{-1} ($\text{C}=\text{O}$ stretching) together with the appearance of expansive groups around $3400\text{--}2800\text{ cm}^{-1}$ (O-H stretching) (Fig. 1).

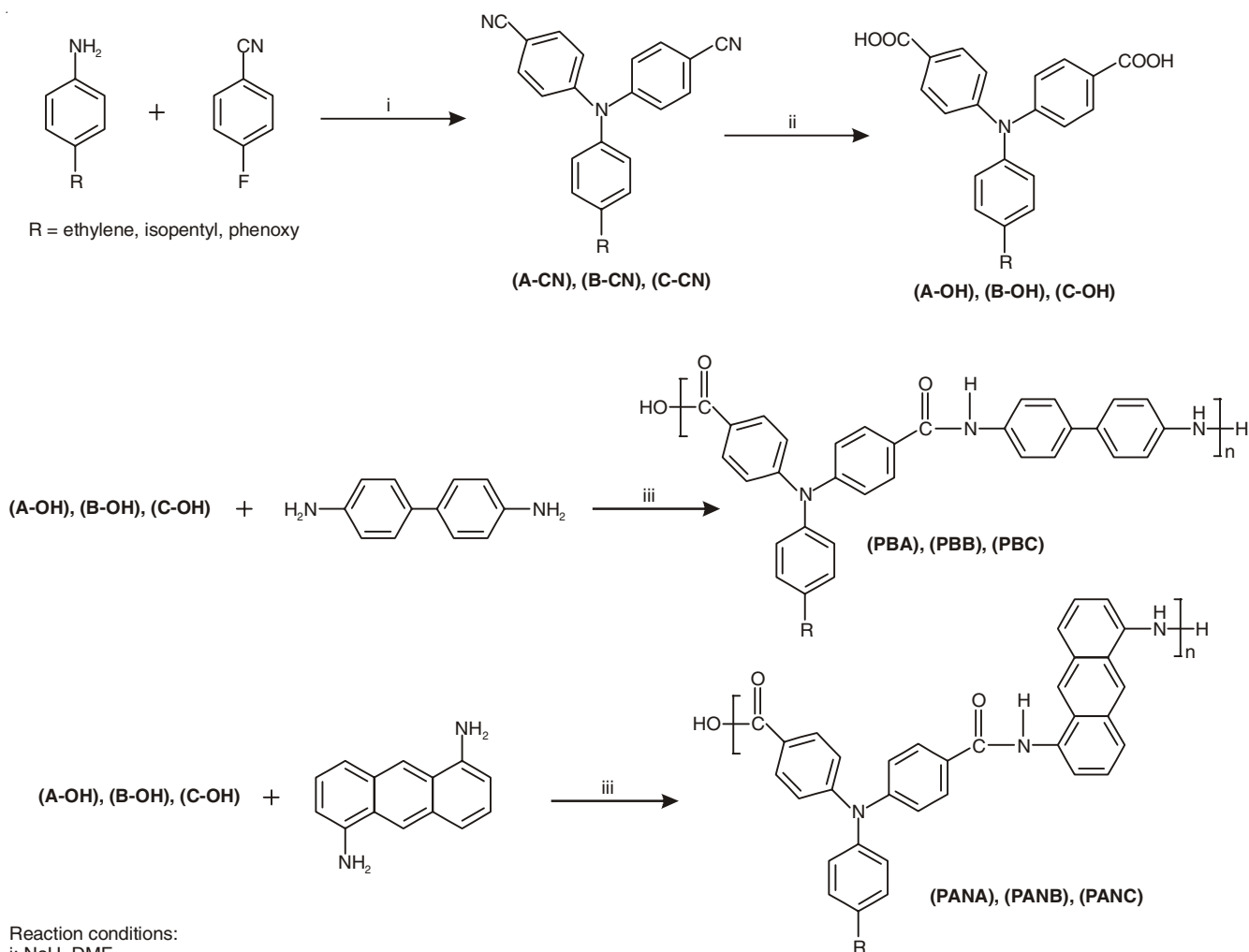
These structures of intermediates and monomers were likewise affirmed by high-resolution NMR spectra. (**A-CN**) indicates ^1H NMR range of two major doublet peaks at 7.34-

7.44 (d, 4H, Hd) of four protons (H_d) and 6.76-6.86 (d, 4H, Hc) of four protons (H_c). Doublet peaks at 6.53-6.63 (d, 2H, Hb) and 7.60-7.70 (d, 2H, Ha) because of two phenylene protons (H_b) and (H_a) individually.

(**A-OH**) shows singlet peak because of the proton of carboxylic group at 12.68 (s, 2H, H_{COOH}) as a result of substitution hydrogen atoms of (COOH) by deuterium of DMSO solvent and development of H-bonding.

Two doublet peaks at 7.76-7.86 (d, 4H, Hd) and 6.80-6.88 (d, 4H, Hc) are because of (H_d) and (H_c) protons. Two doublet peaks at 7.61-7.69 (d, 2H, Ha) and 6.53-6.63 (d, 2H, Hb) are because of (H_a) and (H_b) protons. Triplet peak at 6.58-6.67 (t, 1H, H_1) due to H_1 of CH group. Two doublet peaks at 5.13-5.23 (d, 1H, H_2) and 5.55-5.66 (d, 1H, H_3) due to two protons H_2 and H_3 (Fig. 2).

The ^{13}C NMR spectra of the cyano and carboxylic groups affirmed that the cyano group was totally changed over into the carboxylic acid group. The ^{13}C NMR demonstrated that the disappearance of the resonance peak for the cyano carbon at 118.62 ppm and the appearance of the carboxylic peak at 169.30 ppm was strong evidence of that transformation. Other proof of this change is the moving of the carbon resonance signs of C8 adjoining the cyano or carboxyl group. The C8 of



Scheme-I: Synthetic routes of intermediate compounds of poly(amine-amide)s

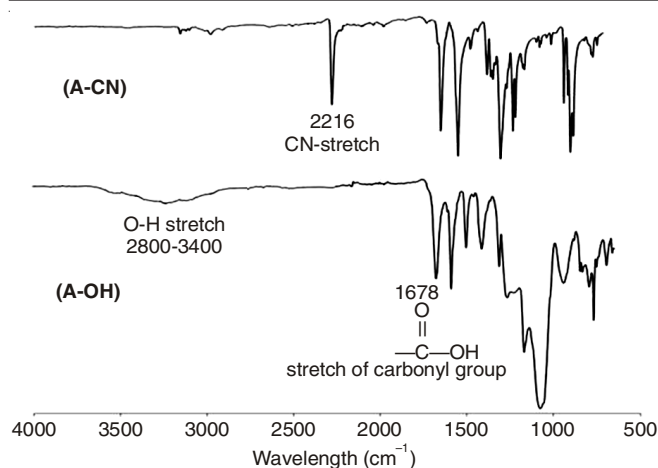
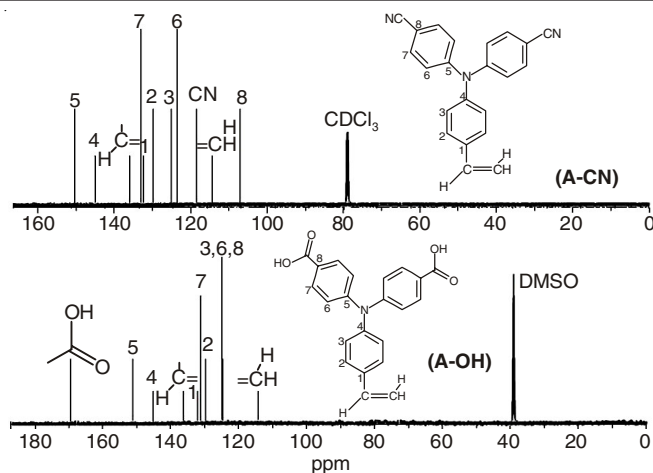
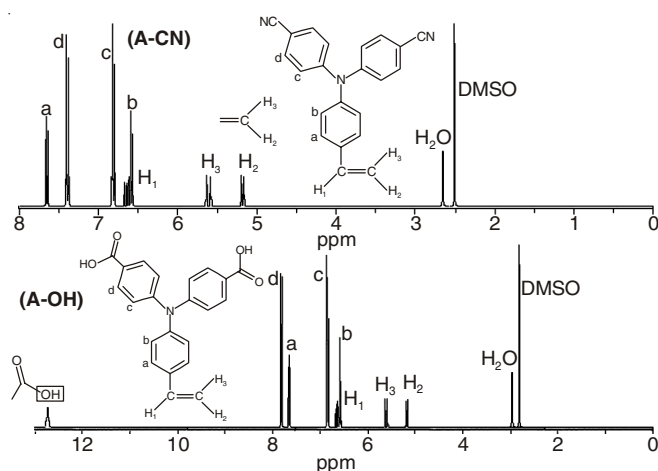


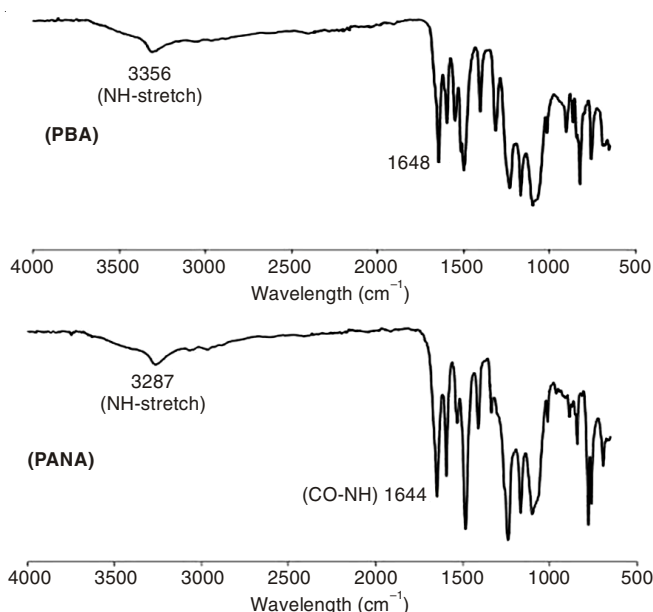
Fig. 1. FTIR of (A-CN) and (A-OH)

Fig. 3. ¹³C NMR of (A-CN) and (A-OH)Fig. 2. ¹H NMR of (A-CN) and (A-OH)

dinitrile (**A-CN**) resonated at a higher field (107.00 ppm) than the other aromatic carbons on account of the anisotropic protecting by the π -electrons of $C\equiv N$. After hydrolysis, the resonance peak of C8 moved to a lower field (124.60 ppm) in view of the absence of an anisotropic field (Fig. 3).

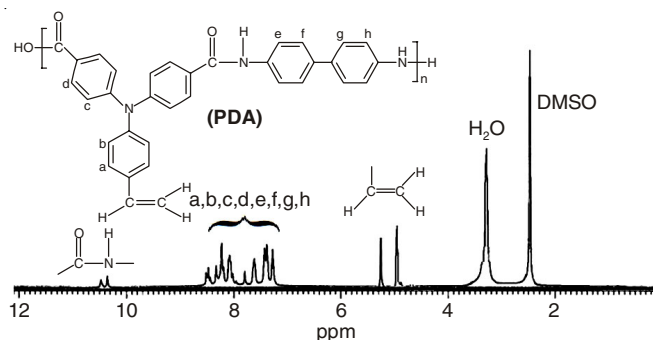
Polymer synthesis: A series of new aromatic poly(amine-amide)s with aryltriphenylamine (ATPA) units were synthesized by the direct polycondensation reactions of the dicarboxylic acid monomer (**A-OH**) with various aromatic diamines, benzidine and anthracene-1,5-diamine using triphenylphosphite (TPP) and pyridine as condensing agents (**Scheme-I**). All the polymerizations proceeded homogeneously throughout the reaction and afforded clear with highly viscous polymer solutions. These polymers precipitated in a tough, fiber-like form when the resulting polymer solutions were slowly poured with stirring into methanol. These poly(amine-amide)s were obtained in almost quantitative yields. All the polymers can be solution-cast into flexible and tough films. Structural features of these poly(amine-amide)s were verified by FTIR and NMR spectroscopy. The characteristic absorption bands observed around 3356 (N-H stretching) and 1648 cm^{-1} ($C=O$ stretching of amide group).

Fig. 4 illustrates a typical FTIR spectra of the poly(amine-amide) (**PBA**) and (**PANA**). ¹H and ¹³C NMR spectra of polyamides in DMSO- d_6 assignments each of proton and carbon

Fig. 4. FTIR of (**PBA**) and (**PANA**)

spectra agree well with the proposed molecular structure of (**PBA**) and (**PANA**). ¹H NMR peaks showed the broad proton peaks of the carboxylic monomer groups were completely absent after polymerization and appearance of singlet peaks at a higher field region at 10.25 ppm which is ascribed to the amide group proton of the resultant poly(amine amide)s (**PDA**) and (**PANA**) (Fig. 5).

The main peak at the most region at 164.72 ppm is due to the carbon atom in the amide carbonyl group of the polyamide

Fig. 5. ¹H NMR of (**PBA**)

CO-NH of (**PDA**) and (**PANA**). These carbon atoms have higher chemical shifting because of the sp^2 resonance between carbonyl group attached to a highly electronegative nitrogen atom. The peaks of other hydrogen (a-h) and carbon (C_1 - C_{12}) atoms were found in the regions (6.58-7.81), (119.72-151.12) ppm, respectively (Figs. 5 and 6).

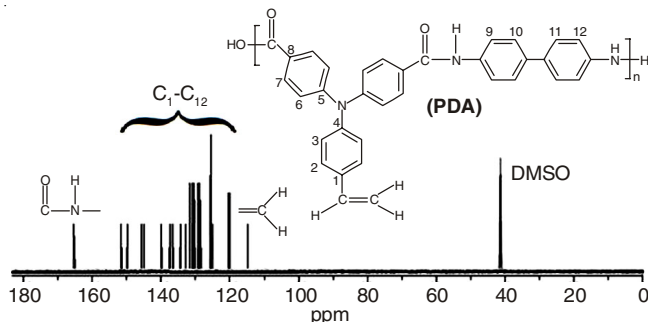


Fig. 6. ^{13}C NMR of (**PBA**)

Polymer properties

Thermal properties: DSC and TGA were utilized to study the thermal properties of all the prepared poly(amine-amide)s. They indicated high glass transition temperatures (T_g) in the range of 271.5-321.4 °C. Fig. 7 indicates DSC of blended poly(amine-amide)s (**PBA**), (**PBB**), (**PBC**), (**PANA**), (**PANB**) and (**PANC**). The T_g values of these poly(amine-amide)s generally decreased with decreasing stiffness of the diamine part. Along these line polymers with phenylene diamine showed higher T_g esteem as a result of higher unbending nature than polymers with anthracene-diamine

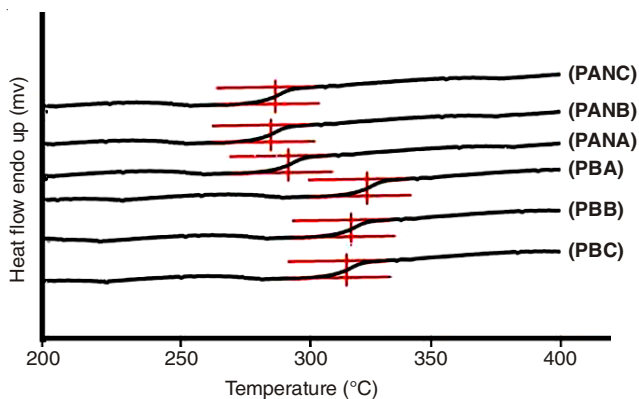


Fig. 7. DSC of synthesized poly(amine-amide)s

Fig. 8 shows the TGA conduct of the synthesized poly(amine-amide)s at a heating rate of 20 °C under nitrogen atmosphere. All the poly(amine-amide)s exhibited great thermal stability with irrelevant weight reduction up to 400 °C with the onset weight loss range (420-580) °C. Poly(amine-amide)s with anthracene-diamine exhibited higher thermal stability contrasted with benzidine diamine because of their high aromatic rings number. The residual weight retention at 800 °C for the resulting polyimides was in the range (22-30) %. The temperature at 10 % weight loss was in the range of (480-600) °C for the poly(amine-amide)s.

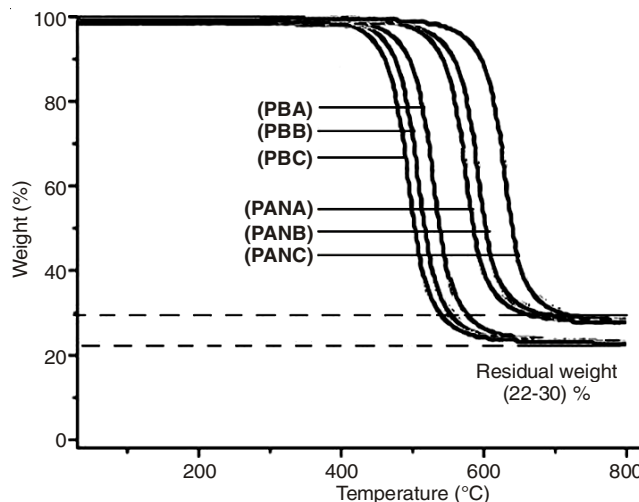


Fig. 8. TGA of synthesized poly(amine-amide)s

Spectral properties: The optical properties of poly(amine-amide)s were investigated by UV-visible spectroscopy. The dilute solutions of these poly(amine-amide)s in N-methyl pyrrolidone exhibited strong UV-visible absorption bands at (338-391) nm assignable to the ($n-\pi^*$) transition resulting from the conjugation between the aromatic rings and nitrogen atoms [21]. Polyamides with anthracene diamine (**PANA**), (**PAAB**) and (**PANC**) have higher UV-visible λ_{abs} max absorption than that with benzidine diamine because they have additional benzene rings so they require less absorbance energy for electronic transition due to extend resonance to high number of benzene rings which causes higher electronic excitation than polyamides with phenylene diamine (**PBA**), (**PBB**) and (**PBC**) having two rings only (Fig. 9).

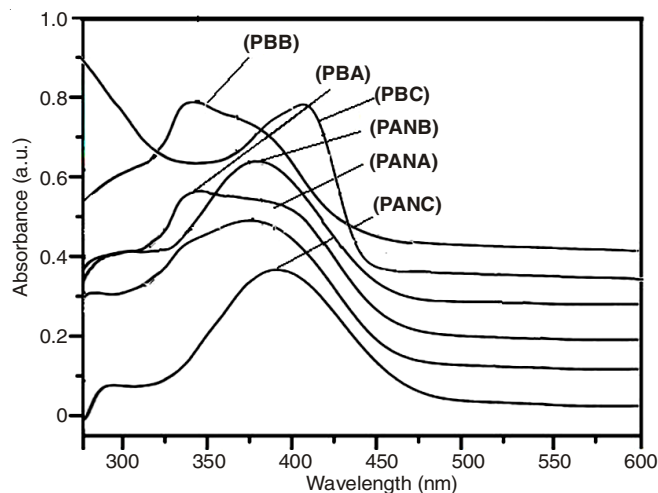
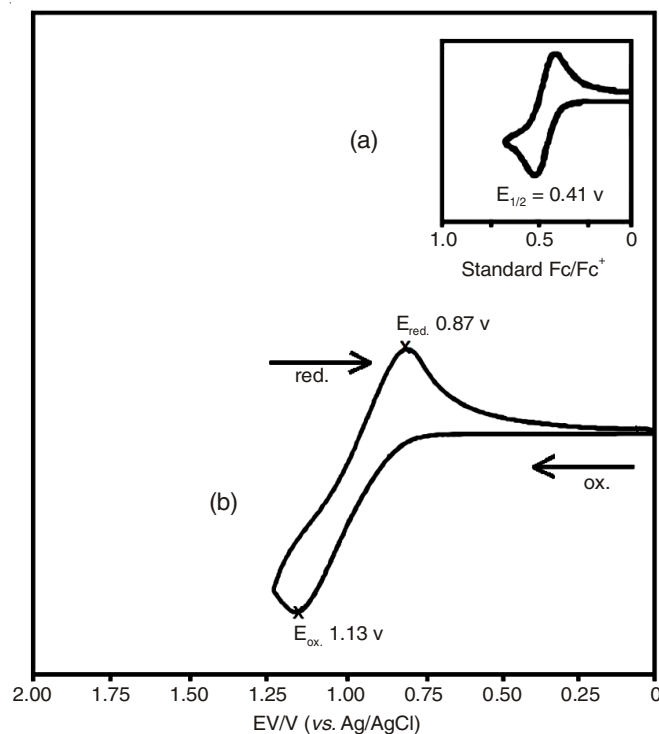


Fig. 9. UV-visible absorption of synthesized poly(amine-amide)s

Electrochemical properties: The redox behaviour of the synthesized poly(amine-amide)s was calculated by cyclic voltammetry for the cast film of the sample polymer on an ITO-coated glass substrate as working electrode in dry acetonitrile containing 0.1 M of tetrabutylammonium perchlorate as an electrolyte under nitrogen atmosphere to determine the energy levels of the highest occupied molecular orbital HOMO and the lowest unoccupied molecular orbital (LUMO). All the poly(amine-amide)s showed an reversible oxidation process.

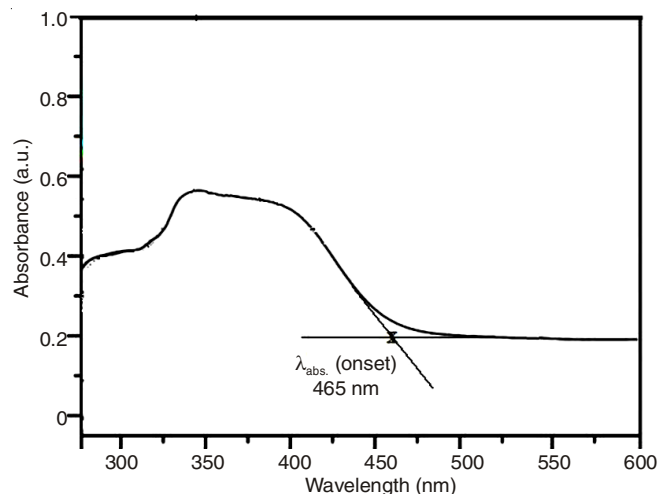
Fig. 10 shows the typical cyclic voltammogram for **(PBA)** recorded at scanning rate of 0.25 V/s. One reversible oxidation redox couple with half-wave at $E_{1/2}$ (onset) = 0.94 V (vs. Ag/Ag/Cl) in the oxidative scan was observed. Because of electrochemical stability of the films and good adhesion between the polymer and ITO substrate, the polyamide (**PBA**) exhibited good reversibility of electrochromic characteristics by continuous five scans between 0.0-1.25 V changing colour from original pale yellowish to blue. The energy of the HOMO and LUMO levels of the corresponding poly(amine-amide)s can be determined from the oxidation onset (E_{onset}) and the onset absorption wavelength of the UV-visible absorption of thin films [22] (Fig. 11) and the results are listed in Table-1. The external ferrocene/ferrocenium (Fc/Fc^+) redox standard E_{onset} is 0.41 V vs. Ag/AgCl in CH_3CN and the HOMO energy for Fc/Fc^+ standard is 4.80 eV with respect to the zero vacuum level. Therefore, HOMO energy for (**PBA**) has been evaluated to be 5.41 V as follows:

$$E_{\text{gap}} = \frac{1241}{\lambda_{\text{abs. (onset)}}} = \frac{1241}{465} = 2.67 \text{ eV}$$

Fig. 10. Cyclic voltammogram for (**PBA**)TABLE-1
ELECTROCHEMICAL PROPERTIES
OF POLY(AMINE-AMIDE)S

Polyamides (onset)	$\lambda_{\text{abs. (onset)}}$ nm vs. Ag/AgCl	$E_{1/2}$ (onset) (eV)	E_{HOMO} (onset) (eV)	E_{gap} (eV)	E_{LUMO} (onset) (eV)
(PBA)	465	0.99	5.38	2.67	2.71
(PBB)	481	1.01	5.40	2.58	2.82
(PBC)	468	0.99	5.38	2.65	2.73
(PANA)	486	1.04	5.43	2.55	2.83
(PANB)	471	1.05	5.44	2.63	2.81
(PANC)	478	1.07	5.46	2.59	2.87

where E_g is Energy gap and 1242 is a constant, $\lambda_{\text{abs. onset}}$ is the onset wavelength which can be calculated by intersection of two tangents on the absorption edges as shown in Fig. 11.

Fig. 11. UV-visible absorption spectrum of polyamide (**PBA**) film

$E_{1/2}$ (onset) = $(E_{\text{pc}} + E_{\text{pa}})/2$ where pc and pa are potential of cathode and anode respectively.

$$E_{1/2}(\text{onset}) = \frac{(1.12 + 0.86)}{2} = 0.99 \text{ eV}$$

$$E_{\text{HOMO}}(\text{onset}) = E_{1/2} - E_{1/2 \text{ ref.}} + 4.8 \text{ eV}$$

$$E_{\text{HOMO}}(\text{onset}) = 0.99 - 0.41 + 4.8 = 5.38 \text{ eV}$$

$$E_{\text{LUMO}}(\text{onset}) = E_{\text{HOMO}}(\text{onset}) - E_{\text{gap}} \text{ eV}$$

$$E_{\text{LUMO}}(\text{onset}) = 5.38 \text{ eV} - 2.67 \text{ eV} = 2.71 \text{ eV.}$$

Conclusion

In this paper, new poly(amine-amide)s with derived-triphenylamine units in the main polymeric chain have been successfully synthesized from the new synthesized aromatic derived triphenylamine dicarboxylic acid (**A-OH**), (**B-OH**) and (**C-OH**) with two different aromatic diamines by phosphorylation polyamidation reaction. All the poly(amine-amide)s were characterized and the thermal, spectral and electrochemistry behaviour are reported. They exhibited good thermal stability and helpful redox stability. Both solution and film polymers exhibited blue photoluminescence. Thus, these novel polyamides with triphenylamine may find applications in electroluminescent devices as hole-transporting or blue-light-emitting polymeric materials.

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