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## Study of Spectral, Thermal and Electrochemical Properties of New Thermally Stable Blue Light Emitting Materials Based Aromatic Polyamides

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In this study, new triphenylamine with aromatic diacid monomers, 4,4'-dicarboxy-4"-acetyl-triphenylamine (**AC1**), 4,4'-dicarboxy-4"-ethyl-triphenylamine (**AC2**), 4,4'-dicarboxy-4"-methoxy-triphenylamine (**AC3**) were successfully synthesized by the aromatic nucleophilic displacement reaction of 4-fluorobenzonitrile with three aniline-derivatives using sodium hydride as the base, followed by alkaline hydrolysis of the di-cyanides intermediates (**CY1**, **CY2**, **CY3**). From these di-acids monomers, a series of poly(amine-amide)s were prepared by the phosphorylation poly-condensation reaction with different aromatic diamines. FTIR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic techniques were used to identify the chemical structures of all resultant compounds and poly(amine-amide)s. These aromatic poly(amine-amide)s have a good solubility in several organic solvents and gave strong and tough thin films *via* solution casting. They exhibited excellent thermal stability associated with high glass transition temperatures (*T<sub>g</sub>*). In dilute N-methyl pyrrolidone solution, these polymers exhibited a strong photoluminescence in the blue region. Cyclic voltammetry of the results 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:** Hole-transporting materials, Triphenylamine, Emitting layer.

### INTRODUCTION

Materials with hole-transporting behaviour have been widely used in the polymer light-emitting devices (PLEDs). They are highly interested due to their potential applications in many devices like flat panel displays and lighting sources [1,2]. They have low ionization potentials and relatively high mobility's [3-6] and are easily oxidized to form stable radical cations [7]. The applications of conjugated polymers in polymer light-emitting devices (PLEDs), has received a great deal of concern in industry because of several advantages. Triphenylamine-based polymers are widely used as the hole-transport layer in light emitting devices, but they also show interesting electro chromic behaviour [8-13]. The most efficient devices using PLEDs is designed with a thin-film multilayer structure consists of a hole-transporting layer, the two layers of emitting and an electron transporting are sandwiched between two electrodes [14]. Different charge carriers (holes and electrons) are pushed separately from anode and cathode, recombine in the emitting layer and thus emit light [15]. Most of hole transporting materials, which contain amine functionalities show lack sufficient emission characteristics due to

reductive quenching have been tried for light-emission [16]. It is known that the aromatic polyamides with high melting or glass transition temperatures are high-performance polymeric materials for their excellent mechanical properties, high thermal stability and good chemical resistance [17]. Because of difficult processing and limited solubility in most organic solvents of these polymers, it should be improve these limitations and polymer-structure modification becomes necessary such as introduction of bulky, packing-disruptive groups into the polymer backbone [18,19]. It has been demonstrated that aromatic polyamides containing three-dimensional, propeller-shaped triphenylamine unit had good solubility in organic solvents while retaining high thermal stability [20-22]. The poly(amine-amide)s are always synthesized by the most common method (phosphorylation polycondensation reaction) of diacid compounds with diamines at high temperatures in the polar solvents like N,N-dimethylformamide (DMF) and CaCl<sub>2</sub> Salt as solubility promoters because the cations interact with the amide groups, diminishing the strength of the inter-chain hydrogen bonds. The method was developed by Yamazaki *et al.* [23].

## EXPERIMENTAL

4-Acetyl-aniline (Merck, 99.7 %), 4-ethyl-aniline (Acros, 98.7), 4-methoxyaniline (Merck, 99.8), 4-fluorobenzonitrile (Acros, 98.7 %), sodium hydride (NaH) (Fluka, 60 %), N,N-dimethylformamide (DMF) (Acros, 99.6 %), potassium hydroxide (KOH) (Fluka, 99.8 %), ethanol (Merck, 99.7 %), acetic acid (Merck, 98 %), hydrochloric acid (Merck, 36 %), dimethyl sulfoxide- $d_6$ , (DMSO- $d_6$ ) (Merck, 99.8 %), chloroform-D1, ( $CDCl_3$ ) (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 (NMP) (Fluka, 99.6 %) were used without further purification.

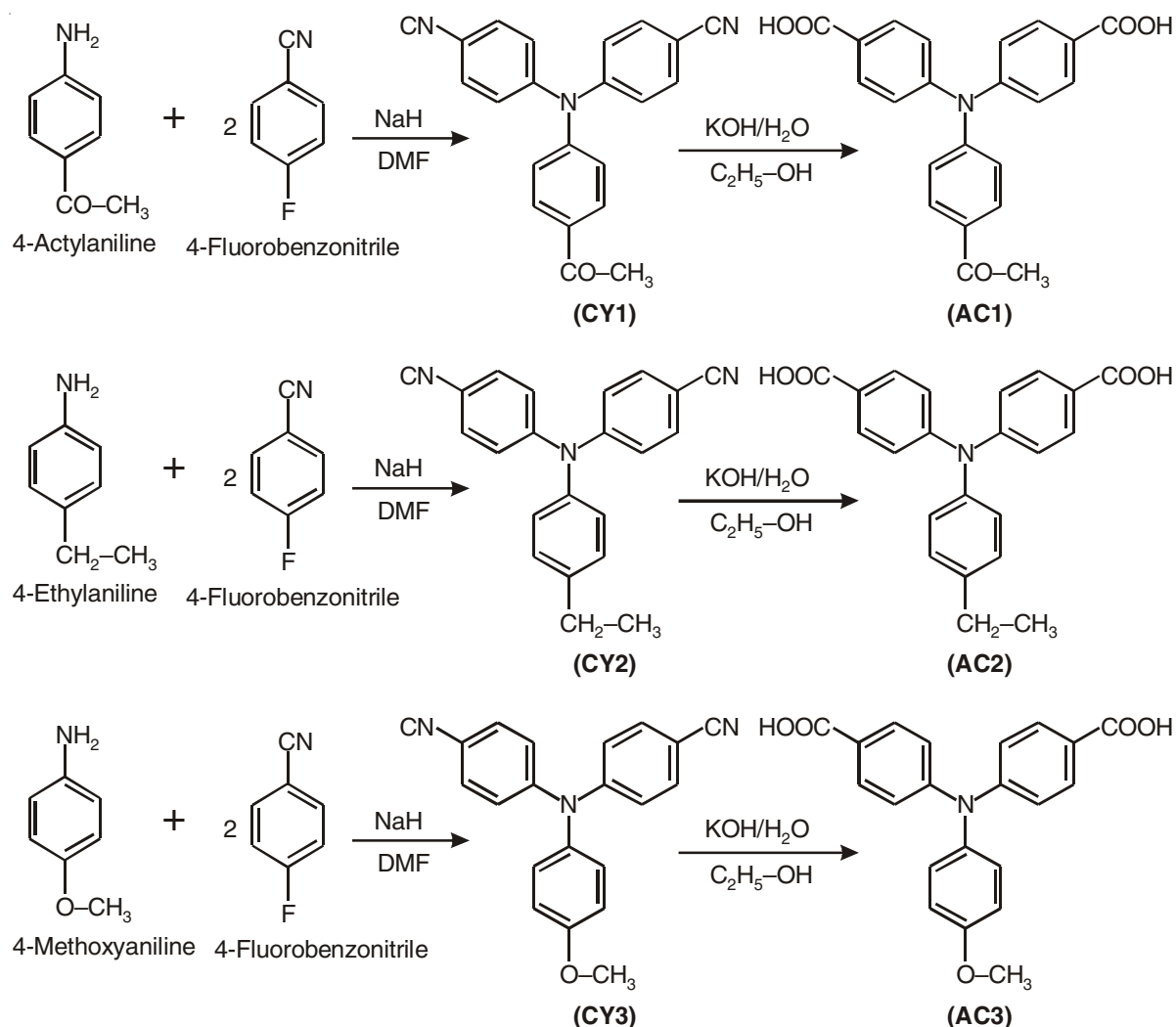
The FT-IR spectrum of the synthesized compounds was recorded with a Spotlight 400 Perkin Elmer spectrometer.  $^1H$  NMR (400 MHz) and  $^{13}C$  NMR (100 MHz) measurements were performed with a JEOL spectrometer. UV-visible absorption and photoluminescence spectra were recorded in N-methyl pyrrolidone 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 (**AC1**, **AC2** and **AC3**) have synthesized *via* the aromatic nucleophilic displacement reaction of 4-fluorobenzonitrile with three aniline-derivatives to produce three cyanides intermediates (**CY1**, **CY2**, **CY3**) as follow:

**Synthesis of 4,4'-dicyano-4''-acetyltriphenylamine (**CY1**):** 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, 2.70 g (0.02 mol) of 4-acetyl aniline 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 [20,24]. The products were filtered and recrystallized from ethanol to give pale yellowish solid. In same procedure other intermediates (**CY2**, **CY3**) were synthesized (**Scheme-I**).

**Synthesis of 4,4'-dicarboxy-4''-acetyltriphenylamine (**AC1**):** A mixture of 15.5 g of KOH and 6.74 g (0.02 mol) of dinitrile compound (**CY1**) in 60 mL of ethanol and 60 mL of distilled water was stirred at about 100 °C until no further



Scheme-I: Synthesis routes of monomers

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 dil. HCl to around 3. The yellowish precipitate formed was collected by filtration, washed with water. Recrystallization from acetic acid gave pale yellow crystals. By using procedure other monomers (**AC2**, **AC3**) were synthesized (**Scheme-I**).

#### Spectral characteristics data

**4,4'-Dicyano-4''-acetyltriphenylamine (CY1):** 4.04 g (yield: 60 %), m.p. = (188-190) °C. FTIR: 2218 cm<sup>-1</sup> (CN); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>-d<sub>1</sub>, δ ppm): 7.78-8.12 (d, 2H, H<sub>a</sub>), 7.41-7.76 (d, 4H, H<sub>d</sub>), 7.07-7.23 (d, 4H, H<sub>c</sub>), 6.91-7.07 (d, 2H, H<sub>b</sub>), 2.55 (s, 3H, H<sub>CH<sub>3</sub></sub>). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>-d, δ ppm): 150 (C<sub>4,5</sub>), 108.43 (C<sub>8</sub>), 118.74 (CN), 125.54 (C<sub>6</sub>), 126.02 (C<sub>2</sub>), 128.21 (C<sub>3</sub>), 132.38 (C<sub>7</sub>), 133.61 (C<sub>1</sub>), 24.73 (CH<sub>3</sub>).

**4,4'-Dicyano-4''-ethyl triphenylamine (CY2):** 2.31 g (yield: 71.5 %), m.p. = 167-170 °C. FTIR: 2221 cm<sup>-1</sup> (CN), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>-d<sub>1</sub>, δ ppm): 7.35-7.57 (d, 4H, H<sub>a</sub>), 6.89-7.13 (d, 2H, H<sub>a</sub>), 6.71-6.86 (d, 4H, H<sub>c</sub>), 6.43-7.71 (d, 2H, H<sub>b</sub>), 2.47-2.72 (m, 3H, H<sub>CH<sub>2</sub></sub>), 1.26 (t, 3H, H<sub>CH<sub>3</sub></sub>). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>-d<sub>1</sub>, δ ppm): 150.22 (C<sub>5</sub>), 143.41 (C<sub>4</sub>), 142.68 (C<sub>1</sub>), 132.91 (C<sub>7</sub>), 128.11 (C<sub>2</sub>), 127.09 (C<sub>3</sub>), 123.11 (C<sub>6</sub>), 118.12 (CN), 108.19 (C<sub>8</sub>), 28.60 (C<sub>CH<sub>2</sub></sub>), 14.52 (C<sub>CH<sub>3</sub></sub>).

**4,4'-Dicyano-4''-methoxytriphenylamine (CY3):** 2.80 g (yield: 77.5 %), m.p. = 178-181 °C. FTIR: 2219 cm<sup>-1</sup> (CN). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>-d<sub>1</sub>, δ ppm): 7.28-7.63 (d, 4H, H<sub>a</sub>), 6.71-6.93 (d, 4H, H<sub>c</sub>), 6.61-6.53 (d, 2H, H<sub>a</sub>), 2.37-2.62 (d, 2H, H<sub>b</sub>), 3.82 (s, 3H, H<sub>CH<sub>3</sub></sub>). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>-d<sub>1</sub>, δ ppm): 157.48 (C<sub>1</sub>), 150.14 (C<sub>5</sub>), 138.31 (C<sub>4</sub>), 134.04 (C<sub>7</sub>), 131.87 (C<sub>3</sub>), 123.58 (C<sub>6</sub>), 118.06 (CN), 116.33 (C<sub>2</sub>), 108.54 (C<sub>8</sub>), 58.73 (C<sub>CH<sub>3</sub></sub>).

**4,4'-Dicarboxy-4''-isopropyltriphenyl-amine (AC1):** 6.4 g (85 % yields): m.p. = 275-277 °C. FTIR: 1681 cm<sup>-1</sup> (C=O), 2987 cm<sup>-1</sup> (O-H). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ ppm): 12.61-12.89 (s, 2H, C<sub>COOH</sub>), 7.65-7.97 (d, 4H, H<sub>d</sub>), 7.56-7.84 (d, 2H, H<sub>a</sub>), 6.70-6.98 (d, 4H, H<sub>c</sub>), 6.58-6.91 (d, 2H, H<sub>b</sub>), 2.55 (s, 3H, H<sub>CH<sub>3</sub></sub>). <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ ppm): 197.22 (C<sub>CO-CH<sub>3</sub></sub>), 168.81 (C<sub>COOH</sub>), 151.47 (C<sub>5</sub>), 150.46 (C<sub>4</sub>), 135.16 (C<sub>1</sub>), 131.76 (C<sub>7</sub>), 129.13 (C<sub>2</sub>), 124.68 (C<sub>6</sub>), 124.64 (C<sub>8</sub>), 124.92 (C<sub>3</sub>), 26.61 (C<sub>CH<sub>3</sub></sub>).

**4,4'-Dicarboxy-4''-ethyltriphenylamine (AC2):** 3.40 g (94.18 % yields): m.p. = 276-278 °C. FTIR: 1683 cm<sup>-1</sup> (C=O), 2710-3321 cm<sup>-1</sup> (O-H). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ ppm): 12.52-12.91 (s, 2H, C<sub>COOH</sub>), 7.67-7.98 (d, 4H, H<sub>d</sub>), 6.91-7.21 (d, 2H, H<sub>a</sub>), 6.71-6.97 (d, 4H, H<sub>c</sub>), 6.46-6.75 (d, 2H, H<sub>b</sub>), 2.45-2.74 (t, 2H, H<sub>CH<sub>2</sub></sub>), 1.11-1.41 (d, 3H, H<sub>CH<sub>3</sub></sub>). <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ ppm): 168.81 (C<sub>COOH</sub>), 151.44 (C<sub>5</sub>), 143.42 (C<sub>4</sub>), 142.18 (C<sub>1</sub>), 131.88 (C<sub>7</sub>), 128.11 (C<sub>2</sub>), 127.42 (C<sub>3</sub>), 124.76 (C<sub>6</sub>), 124.64 (C<sub>8</sub>), 28.22 (C<sub>CH<sub>2</sub></sub>), 14.61 (C<sub>CH<sub>3</sub></sub>).

**4,4'-Dicarboxy-4''-methoxytriphenylamine (AC3):** 3.40 g (94.2 % yield): m.p. = 273-275 °C. FTIR: 1680 cm<sup>-1</sup> (C=O), 2713-3332 cm<sup>-1</sup> (O-H). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ ppm): 12.76 (s, 2H, H<sub>COOH</sub>), 7.68-7.97 (d, 4H, H<sub>d</sub>), 6.60-6.98 (d, 4H, H<sub>c</sub>), 6.58-6.89 (d, 2H, H<sub>a</sub>), 6.37-6.77 (d, 2H, H<sub>b</sub>), 3.83 (s, 3H, H<sub>CH<sub>3</sub></sub>). <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ ppm): 168.83 (C<sub>COOH</sub>), 157.23 (C<sub>1</sub>), 150.23 (C<sub>5</sub>), 138.31 (C<sub>4</sub>), 132.11 (C<sub>3</sub>), 131.20 (C<sub>7</sub>), 124.91 (C<sub>6</sub>), 115.34 (C<sub>2</sub>), 55.82 (C<sub>CH<sub>3</sub></sub>). **Scheme-I** shows the routes of synthesis.

**Synthesis of poly(amine-amide) (PA1):** The poly(amine-amide) (**PA1**) was synthesized as follow: A mixture of 1.12 g (0.03 mol) of the dicarboxylic acid monomer (**AC1**), 0.32 g (0.03 mol) of *p*-phenylenediamine, 0.5 g of calcium chloride, 4.5 mL of triphenyl phosphite (TPP), 1.5 mL of pyridine and 4.5 mL of N-methyl-2-pyrrolidone (NMP) 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 (**Scheme-II**). The other poly(amine-amide)s (**PA2**, **PA3**) were prepared by above same procedure.

**Synthesis of poly(amine-amide) (PAB1):** This polymer (**PAB1**) was synthesized by the same method, which described in synthesis of **PA1** but used benzidine instead of *p*-phenylene diamine.

#### Spectral characteristics data

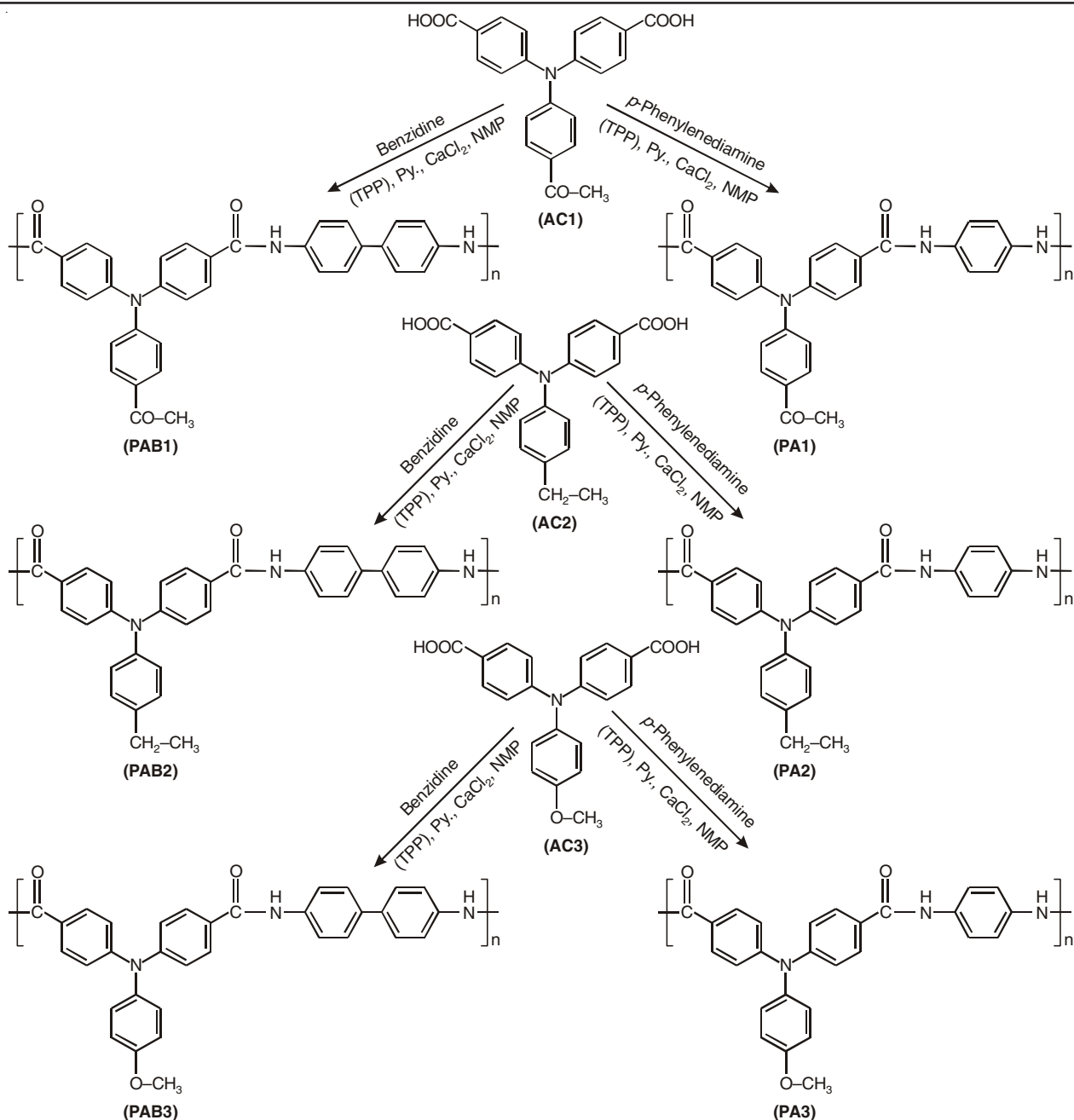
**Poly(amine-amide) (PA1):** The IR spectrum exhibited characteristic amide absorption bands at 3321 (N-H stretching) and 1645 cm<sup>-1</sup> (amide carbonyl). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ ppm): 10.25 (s, 1H, H<sub>NH-CO</sub>), 7.55-7.84 (d, 4H, H<sub>d</sub>), 7.28-7.58 (d, 2H, H<sub>c</sub>), 7.54-7.86 (d, 2H, H<sub>a</sub>), 6.59-7.89 (d, 4H, H<sub>c</sub>), 6.59-7.88 (d, 2H, H<sub>b</sub>), 2.52 (s, 3H, H<sub>CH<sub>3</sub></sub>). <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ ppm): 196.97 (C<sub>CO-CH<sub>3</sub></sub>), 168.84 (C<sub>CO-</sub>), 164.77 (C<sub>CO-NH</sub>), 151.14 (C<sub>5</sub>), 150.32 (C<sub>4</sub>), 135.42 (C<sub>1</sub>), 131.23 (C<sub>7</sub>), 129.77 (C<sub>2</sub>), 128.63 (C<sub>9</sub>), 124.94 (C<sub>3,6</sub>), 122.42 (C<sub>11</sub>), 116.56 (C<sub>12</sub>), 26.61 (C<sub>CH<sub>3</sub></sub>).

**Poly(amine-amide) (PA2):** Infrared spectrum shows bands at 3314 cm<sup>-1</sup> (N-H stretching) and 1644 cm<sup>-1</sup> (amide carbonyl). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ ppm): 10.25 (s, 1H, H<sub>NH-CO</sub>), 7.68-7.97 (d, 4H, H<sub>d</sub>), 7.25-7.44 (d, 2H, H<sub>e</sub>), 6.91-7.16 (d, 2H, H<sub>a</sub>), 6.70-6.98 (d, 4H, H<sub>c</sub>), 6.46-6.78 (d, 2H, H<sub>f</sub>), 6.35-6.66 (d, 2H, H<sub>b</sub>), 2.62 (q, 3H, H<sub>CH<sub>3</sub></sub>). <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ ppm): 168.81 (C<sub>CO-</sub>), 164.76 (C<sub>CO-NH</sub>), 151.21 (C<sub>5</sub>), 146.34 (C<sub>4</sub>), 144.06 (C<sub>13</sub>), 134.43 (C<sub>1</sub>), 131.24.

**Poly(amine-amide) (PA3):** Infrared spectrum shows bands at 3304 cm<sup>-1</sup> (N-H stretching) and 1644 cm<sup>-1</sup> (amide carbonyl). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ ppm): 10.25 (s, 1H, H<sub>NH-CO</sub>), 7.68-7.97 (d, 4H, H<sub>d</sub>), 7.25-7.44 (d, 2H, H<sub>e</sub>), 6.59-6.89 (d, 2H, H<sub>a</sub>), 6.70-6.98 (d, 4H, H<sub>c</sub>), 6.46-6.78 (d, 2H, H<sub>f</sub>), 6.38-6.68 (d, 2H, H<sub>b</sub>), 3.82 (s, 3H, H<sub>CH<sub>3</sub></sub>). <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ ppm): 168.81 (C<sub>CO-</sub>), 164.79 (C<sub>CO-NH</sub>), 151.11 (C<sub>5</sub>), 144.06 (C<sub>13</sub>), 136.21 (C<sub>4</sub>), 132.24 (C<sub>3</sub>), 131.34 (C<sub>7</sub>), 128.65 (C<sub>9</sub>), 124.92 (C<sub>6</sub>), 124.67 (C<sub>8</sub>), 122.42 (C<sub>11</sub>), 116.52 (C<sub>12</sub>), 115.23 (C<sub>1</sub>), 55.82 (C<sub>CH<sub>3</sub></sub>).

**Poly(amine-amide) (PAB1):** The IR spectrum exhibited characteristic amide absorption bands at 3364 cm<sup>-1</sup> (N-H stretching) and 1647 cm<sup>-1</sup> (amide carbonyl). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ ppm): 10.25 (s, 1H, H<sub>NH-CO</sub>), 7.38-8.18 (d, 12H, H<sub>e,d,f,a,g</sub>), 6.58-6.88 (d, 8H, H<sub>c,b,h</sub>), 2.56 (s, 3H, H<sub>CH<sub>3</sub></sub>). <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ ppm): 197.00 (C<sub>CO-CH<sub>3</sub></sub>), 164.76 (C<sub>CONH</sub>), 151.47 (C<sub>5</sub>), 150.68 (C<sub>4</sub>), 144.56 (C<sub>17</sub>), 139.38 (C<sub>13</sub>), 136.84 (C<sub>10</sub>), 135.46 (C<sub>1</sub>), 133.86 (C<sub>14</sub>), 131.23 (C<sub>7</sub>), 129.70 (C<sub>2</sub>), 128.71 (C<sub>15</sub>), 128.68 (C<sub>9</sub>), 128.11 (C<sub>12</sub>), 124.91 (C<sub>3,6</sub>), 124.62 (C<sub>8</sub>), 119.81 (C<sub>16</sub>), 124.71 (C<sub>11</sub>), 26.63 (C<sub>CH<sub>3</sub></sub>).

**Poly(amine-amide) (PAB2):** The IR spectrum exhibited characteristic amide absorption bands at 3364 cm<sup>-1</sup> (N-H stretching) and 1648 cm<sup>-1</sup> (amide carbonyl). <sup>1</sup>H NMR (400 MHz,



Scheme-II: Synthesis routes of monomers

DMSO-*d*<sub>6</sub>,  $\delta$  ppm): 10.26 (s, 1H, H<sub>NH-CO</sub>), 7.64-7.96 (d, 4H, H<sub>d</sub>), 7.24-7.54 (d, 4H, H<sub>e</sub>), 6.85-7.14 (d, 2H, H<sub>a</sub>), 6.70-6.98 (d, 4H, H<sub>c</sub>), 6.44-6.44 (d, 2H, H<sub>b</sub>), 2.63 (q, 2H, H<sub>CH3</sub>), 1.25 (t, 3H, H<sub>CH3</sub>). <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  ppm): 164.76 (C<sub>CONH</sub>), 151.11 (C<sub>5</sub>), 144.54 (C<sub>17</sub>), 143.12 (C<sub>4</sub>), 142.72 (C<sub>1</sub>), 139.41 (C<sub>13</sub>), 136.83 (C<sub>10</sub>), 131.22 (C<sub>7</sub>), 128.71 (C<sub>2,9,15</sub>), 128.11 (C<sub>3,12</sub>), 124.92 (C<sub>6,8</sub>), 119.73 (C<sub>11,16</sub>), 28.23 (C<sub>CH2</sub>), 14.52 (C<sub>CH3</sub>).

**Poly(amine-amide) (PAB3):** The IR spectrum exhibited characteristic amide absorption bands at 3357 cm<sup>-1</sup> (N-H stretching) and 1648 cm<sup>-1</sup> (amide carbonyl). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  ppm): 10.25 (s, 1H, H<sub>NHCO</sub>), 7.52-8.03 (d, 8H, H<sub>e,d,f</sub>), 6.60-6.98 (d, 6H, H<sub>c,a</sub>), 7.31-7.68 (d, 2H, H<sub>g</sub>), 6.38-6.73 (d, 4H, H<sub>b,b</sub>), 3.84 (s, 1H, H<sub>CH3</sub>). <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  ppm): 164.72 (C<sub>CONH</sub>), 157.75 (C<sub>1</sub>), 151.14 (C<sub>5</sub>), 144.52 (C<sub>17</sub>), 139.41 (C<sub>13</sub>), 138.22 (C<sub>4</sub>), 136.81 (C<sub>10</sub>), 133.82 (C<sub>14</sub>), 132.21 (C<sub>3</sub>), 131.24 (C<sub>7</sub>), 128.11 (C<sub>12</sub>), 125.13 (C<sub>6</sub>),

124.62 (C<sub>8</sub>), 119.76 (C<sub>11,16</sub>), 115.22 (C<sub>2</sub>), 128.76 (C<sub>15</sub>), 55.83 (C<sub>CH3</sub>).

## RESULTS AND DISCUSSION

**Monomer synthesis:** New substituted aromatic dicarboxylic monomers with triphenylamine units, 4,4'-dicarboxy-4''-acetyl triphenylamine (AC1), 4,4'-dicarboxy-4''-ethyl triphenylamine (AC2) and 4,4'-dicarboxy-4''-methoxy triphenylamine (AC3) were synthesized by the aromatic nucleophilic substitution reaction of aromatic diamines with 4-fluorobenzonitrile, followed by the alkaline hydrolysis of intermediate dicyano compound (CY1), (CY2) and (CY3). The chemical structures of intermediate dicyano compounds (CY)s and the dicarboxylic acid monomer (AC)s were characterized by FTIR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic techniques. The FTIR spectra of compounds (CY)s gave a cyano group characteristic band at 2218

$\text{cm}^{-1}$  ( $\text{C}\equiv\text{N}$  stretching). The cyano group absorption peak disappeared after hydrolysis and carboxylic acid group showed a typical carbonyl absorption band at  $1678\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  stretching) together with the appearance of broad bands around  $3400\text{--}2700\text{ cm}^{-1}$  ( $\text{O-H}$  stretching) (Fig. 1).

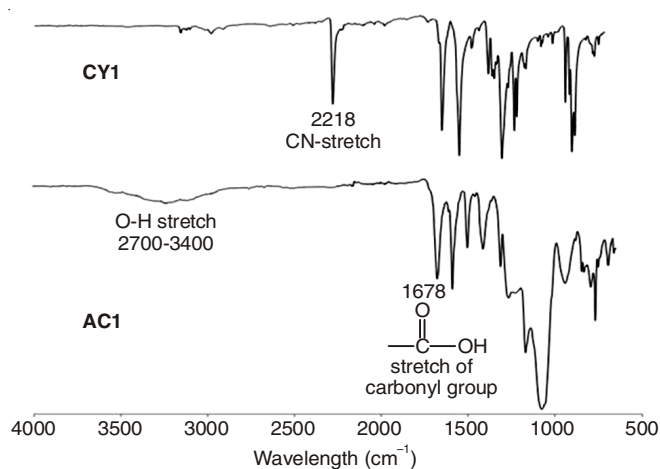


Fig. 1. FTIR of **CY1** and **AC1**

Structures of compounds (**CY**s) and (**AC**s) were also confirmed by high-resolution NMR spectra. **CY1** shows  $^1\text{H}$  NMR spectrum of two big doublet peaks at 7.41–7.76 (d, 4H,  $\text{H}_d$ ) of four protons ( $\text{H}_d$ ) and 7.07–7.23 (d, 4H,  $\text{H}_c$ ) of four protons ( $\text{H}_c$ ). Doublet peaks at 6.91–7.07 (d, 2H,  $\text{H}_b$ ) and 7.78–8.12 (d, 2H,  $\text{H}_a$ ) due to two phenylene protons ( $\text{H}_b$ ) and ( $\text{H}_a$ ) respectively.

**AC1** exhibits broad hardly observed singlet peak due to the proton of carboxylic group 12.61–12.89 (br, 2H,  $\text{H}_{\text{COOH}}$ ) because of replacement hydrogen atoms of ( $\text{COOH}$ ) by deuterium of DMSO solvent and formation of H-bonding.

Two doublet peaks at 7.65–7.97 (d, 4H,  $\text{H}_d$ ) and 7.56–7.84 (d, 2H,  $\text{H}_a$ ) are due to ( $\text{H}_a$ ) and ( $\text{H}_d$ ) protons. Two doublet peaks at 6.70–6.98 (d, 4H,  $\text{H}_c$ ) and 6.58–6.91 (d, 2H, ( $\text{H}_b$ ) are due to ( $\text{H}_c$ ) and ( $\text{H}_b$ ) protons. Singlet peak at 2.55 (s, 3H,  $\text{H}_{\text{CH}_3}$ ) due to three protons of methyl group (Fig. 2).

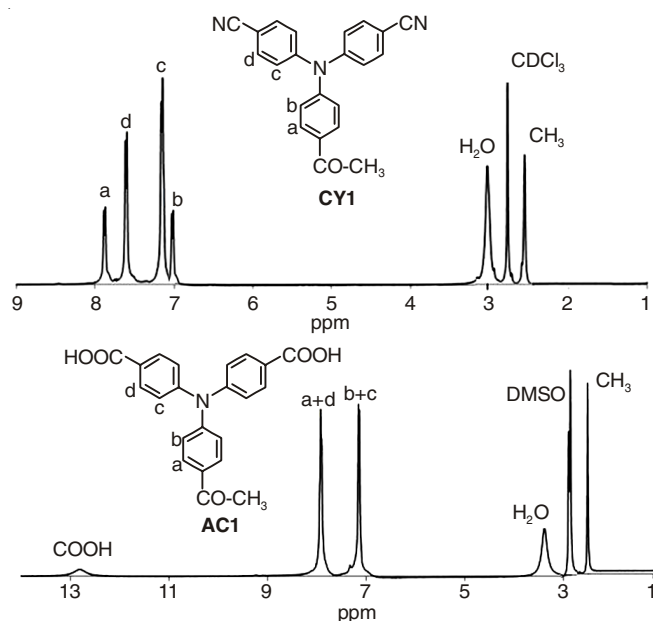


Fig. 2.  $^1\text{H}$  NMR of **CY1** and **AC1**

The difference of the chemical shifting in the  $^{13}\text{C}$  NMR spectra of C-atoms of the cyano and carboxylic groups confirmed that the cyano group was completely converted into the carboxylic acid group. The  $^{13}\text{C}$  NMR showed that the disappearance of the resonance peak for the cyano carbon at 118.74 ppm and the appearance of the carboxylic peak at 168.81 ppm was other evidence of that conversion. Other important evidence of this change is the shifting of the carbon resonance signals of  $\text{C}_8$  adjacent to the cyano or carboxyl group. The  $\text{C}_8$  of dinitrile (**CY1**) resonated at a higher field (108.43 ppm) than the other aromatic carbons because of the anisotropic shielding by the  $\pi$ -electrons of  $\text{C}\equiv\text{N}$ . After hydrolysis, the resonance peak of  $\text{C}_8$  shifted to a lower field (124.64 ppm) because of the lack of an anisotropic field (Fig. 3).

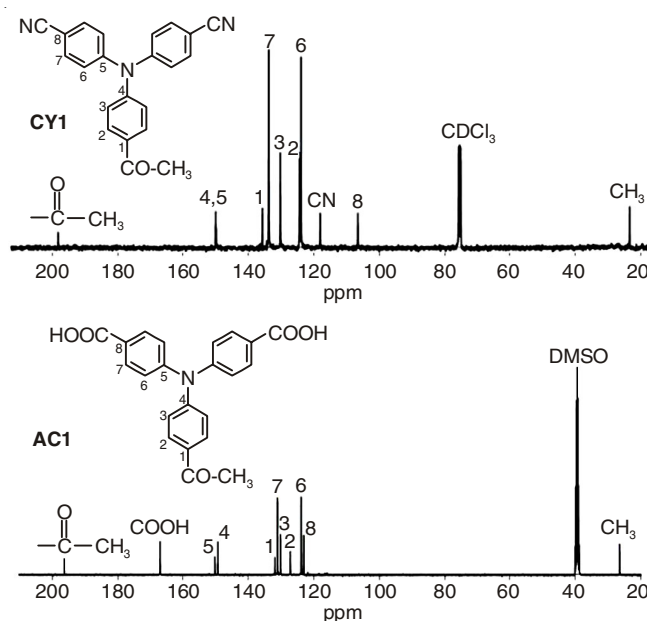


Fig. 3.  $^{13}\text{C}$  NMR of **CY1** and **AC1**

**Polymer synthesis:** A series of new aromatic poly(amine-amide)s with aryltriphenylamine (ATPA) units were prepared by the direct polycondensation reactions of the dicarboxylic acid monomer (**AC1**) with various aromatic diamines, *p*-phenylenediamine, benzidine using triphenylphosphite (TPP) and pyridine as condensing agents (**Scheme-II**). All the polymerizations proceeded homogeneously throughout the reaction and afforded 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  $3321\text{ cm}^{-1}$  ( $\text{N-H}$  stretching) and  $1645\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  stretching of amide group).

Fig. 4 illustrates a typical FTIR spectrum of the representative poly(amine-amide) (**PA1**) and (**PAB1**). Typical set of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of polyamide in  $\text{DMSO-}d_6$ . Assignments of each proton and the spectra agree well with the proposed molecular structure of **PA1** and **PAB1**.  $^1\text{H}$  NMR peaks showed

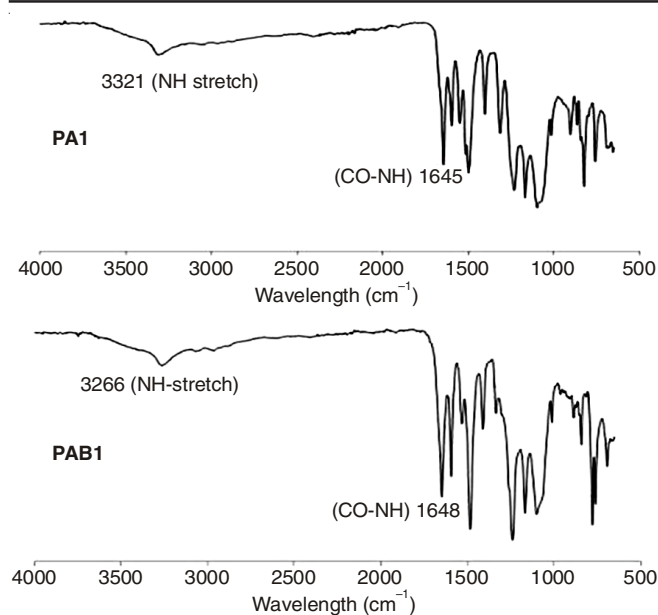


Fig. 4. FTIR of PA1 and PAB1

the disappearance of the broad proton peaks of the carboxylic monomer groups after polymerization and appearance of singlet peaks at a higher field region at 10.25 ppm ascribed to the amide group proton of the resultant poly(amine amide)s (PA1 and PAB1).

$^{13}\text{C}$  NMR shows the main peak at 164.77 ppm is due to the carbon atom in the amide carbonyl group of polyamide CO-NH of PA1 and PAB1. These carbon atoms have higher chemical shifting because of  $sp^2$  resonance between carbonyl group attached to a highly electronegative nitrogen atom. Any of polyamides have the higher chemical shifting at about 197 ppm of carbonyl group  $-\text{CO}-\text{CH}_3$  due to the resonance between acyl groups with phenyl ring.

**Thermal properties:** DSC and TGA were used to investigate the thermal properties of all the synthesized poly(amine-amide)s, the thermal behaviour data of these poly(amine-amide)s are summarized in Table-1. They showed high glass transition temperatures ( $T_g$ ) in the range of 241.5–287.6 °C as determined by DSC. Fig. 5 shows DSC of synthesized poly(amine-amide) (PA1, PA2, PA3, PAB1, PAB2 and PAB3). The  $T_g$  values of these poly(amine-amide)s generally decreased with decreasing stiffness of the diamine component. Therefore polymers with phenylene diamine exhibited higher  $T_g$  value due to higher rigidity than polymers with benzidine-diamine.

TABLE-1 THERMAL BEHAVIOUR OF POLY(AMINE-AMIDE)S				
Polymer	Onset $T_g$ (°C)	$T_g$ (°C)	Wt. loss 10 % Temp. (°C)	Char. (%)
PA1	262.5	273.4	461	17
PA2	231.5	241.5	460	11
PA3	250.0	256.7	410	10
PAB1	276.5	287.6	521	21
PAB2	255.5	257.3	490	22
PAB3	262.5	272.4	470	18

Fig. 6 shows the TGA curves of synthesized poly(amine-amide)s. The thermal degradation behaviour of poly(amine amide)s at a heating rate of 20 °C in nitrogen atmosphere has

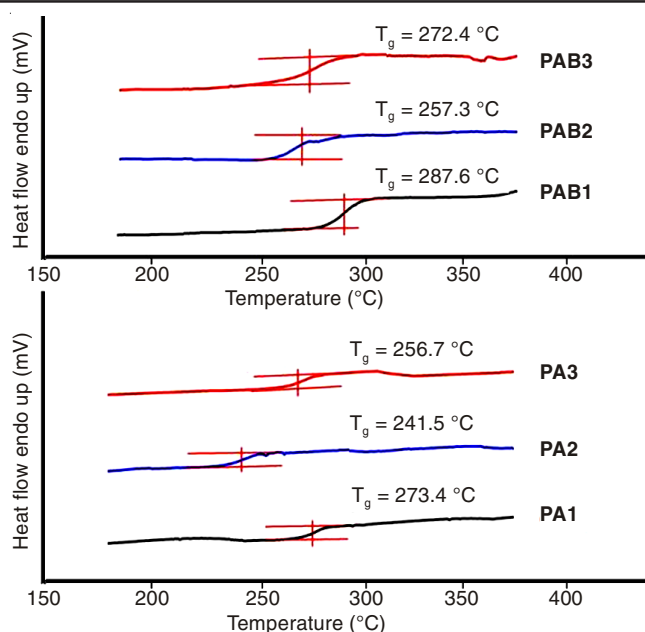


Fig. 5. DSC of synthesized poly(amine-amide)s

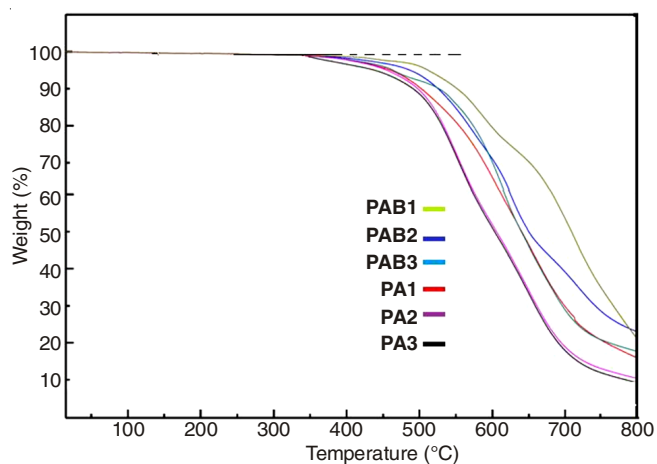


Fig. 6. TGA of synthesized poly(amine-amide)s

been investigated by TGA analysis. All the poly(amine-amide)s exhibited good thermal stability with insignificant weight loss up to 400 °C with the onset weight loss range (348–380) °C. Poly(amine-amide)s with benzidine-diamine exhibited higher thermal stability compared to phenylene diamine due to their high aromatic content. The residual weight retention at 800 °C for the resulting polyimides was in the range (10–23) %. The temperature at 10 % weight loss was in the range of (410–521) °C for the 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 NMP exhibited strong UV-visible absorption bands at (351–398) nm assignable to the ( $n-\pi^*$ ) transition resulting from the conjugation between the aromatic rings and nitrogen atoms and transition from the characteristic ( $\pi-\pi^*$ ) transitions of aromatic rings [25]. Polyamides with benzidine diamine (PAB1, PAB2 and PAB3) have lower UV-visible  $\lambda_{\text{abs}}$  max absorption than that with phenylene diamine because they have ( $n-\pi^*$ ) electronic transitions and more ( $\pi-\pi^*$ ) transitions from additional benzene ring so they require more absorbance energy for transition than polyamides with phenylene diamine (PA1, PA2) and PA3 (Fig. 7).

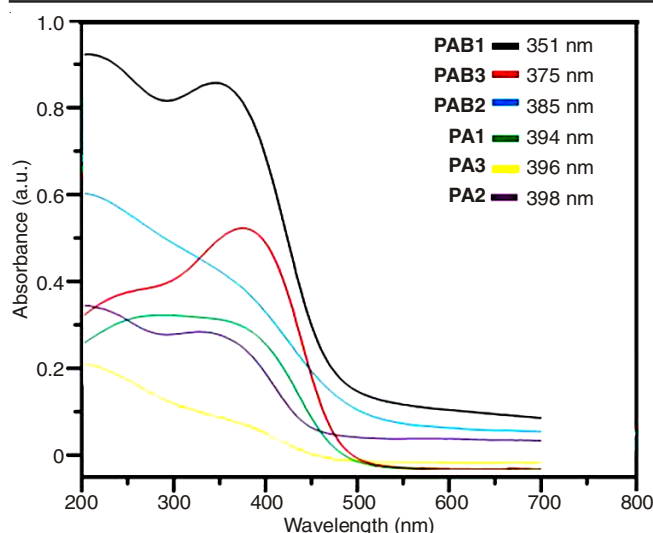
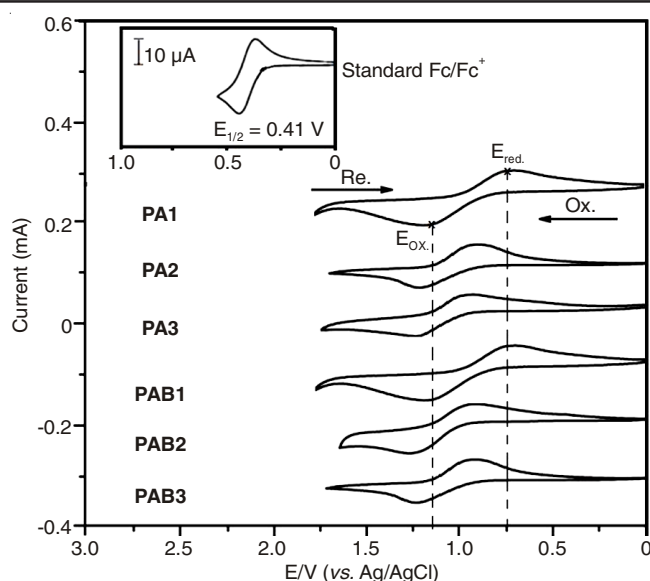


Fig. 7. UV-visible absorption of synthesized poly(amine-amide)s

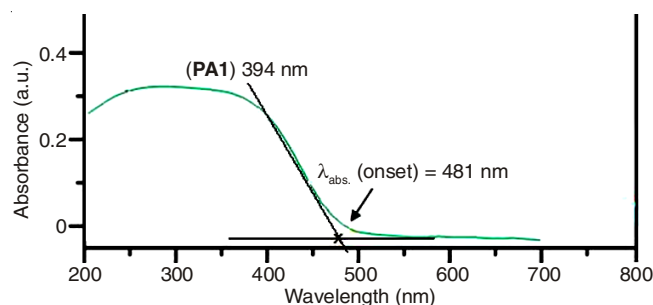
**Electrochemical properties:** The redox behaviour of the synthesized conjugated poly(amine-amide)s was investigated by cyclic voltammetry for the cast film of the sample polymer on an ITO-coated glass substrate as working electrode in dry acetonitrile containing 0.1 M of tetrabutylammonium perchlorate 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 a reversible oxidation process. Fig. 8 shows the typical cyclic voltammogram for **PA1** 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 (**PA1**) exhibited good reversibility of electrochromic characteristics by continuous seven scans between 0.0-1.75 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 ( $E_{\text{onset}}$ ) and the onset absorption wavelength of the UV-visible absorption of thin films [26] (Table-2). The external ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox standard  $E_{\text{onset}}$  is 0.41 V *vs.* Ag/Ag/Cl in CH<sub>3</sub>CN and the HOMO energy for the Fc/Fc<sup>+</sup> standard is 4.80 eV with respect to the zero vacuum level. Therefore, the HOMO energy for **PA1** has been evaluated to be 5.41 V as follows:

$$E_{\text{gap}} = \frac{1241}{\lambda_{\text{abs. (onset)}}} = \frac{1241}{481} = 0.94 \text{ eV}$$

Polymer	$\lambda_{\text{abs. onset}}$ (nm)	$E_{1/2}$ onset <i>vs.</i> Ag/Ag/Cl	$E_{\text{HOMO}}$ onset (eV)	$E_{\text{gap}}$ onset (eV)	$E_{\text{LUMO}}$ onset (eV)
<b>PA1</b>	418	0.94	5.41	2.58	2.83
<b>PA2</b>	452	0.99	5.38	2.74	2.64
<b>PA3</b>	483	1.02	5.41	2.56	2.85
<b>PAB1</b>	481	0.98	5.37	2.58	2.79
<b>PAB2</b>	510	1.05	5.44	2.43	3.01
<b>PAB3</b>	492	1.06	5.44	2.52	2.92

Fig. 8. Cyclic voltammogram for **PA1**

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. 9.

Fig. 9. UV-visible absorption spectrum of polyamide (**PA1**) film

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

$$E_{1/2}(\text{onset}) = \frac{(1.13 + 0.75)}{2} = 0.94 \text{ eV}$$

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

$$E_{\text{HOMO}}(\text{onset}) = 0.94 - 0.41 + 4.8 = 5.41 \text{ eV}$$

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

$$E_{\text{LUMO}}(\text{onset}) = 5.41 \text{ eV} - 0.94 \text{ eV} = 2.83 \text{ eV}$$

## Conclusion

In this paper, new poly(amine-amide)s with derived-triphenylamine units in the polymer main chain have been successfully prepared from a newly synthesized aromatic derived triphenylamine dicarboxylic acid (**AC1**, **AC2**, **AC3**) with two different aromatic diamines by phosphorylation polyamidation reaction. All the poly(amine-amide)s were characterized using thermal, spectral and electrochemistry behaviour properties. They exhibited excellent thermal stability and useful redox stability. These polymers exhibited blue photoluminescence both in film and in solution. Thus, these novel triphenylamine-containing polyamides may find applications in electroluminescent devices as hole-transporting or blue-light-emitting polymeric materials.

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