Synthesis, Characterization, Effect of Triaryl Ring Substituents Groups on Thermal and Spectral Properties of New Soluble Triphenylamine-Based Aromatic Polyamides

Azhar Kamil Rashid[1,2,*], Rosiya Binti Yahya[1] and Phang Sook Wai[1]

[1]Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia
[2]University of Baghdad, Baghdad, Iraq

*Corresponding author: Fax: +60 79674193; Tel: +60 104259265; E-mail: azhar_almasody@yahoo.co.uk

Three new triphenylamine-containing aromatic diacid monomers, 4,4'-dicarboxy-4''-isopropyl-triphenylamine **(Ma)**, 4,4'-dicarboxy-2'4''-dimethyl-triphenylamine **(Mb,** 4,4'-dicarboxy-4''-ethyltriphenylamine **(Mc)** were successfully synthesized *via* the aromatic nucleophilic fluoro-displacement reaction of 4-fluorobenzonitrile with aniline-derivatives using sodium hydride as the base, followed by alkaline hydrolysis of the dinitrile intermediates **(Ia), (Ib), (Ic)**. A series of poly(amine-amide)s were prepared by the direct phosphorylation polycondensation from the newly synthesized diacid monomers with various aromatic diamines. FTIR, ^{1}H and ^{13}C NMR spectroscopic techniques were used to identify the chemical structures of the dicyano intermediates, the carboxylic acid monomer and the resultant poly(amine-amide)s. These aromatic poly(amine-amide)s were found to be readily soluble in a variety of organic solvents and could afford strong and tough films *via* solution casting. They exhibited excellent thermal stability associated with high glass transition temperatures (T_g = 248.32-290.46 °C) and 10 % weight loss temperatures in excess of 522 °C in nitrogen. In dilute N-methyl pyrrolidone solution, these polymers exhibited a medium to strong photoluminescence in the blue region at (425-443) nm. Cyclic voltammetry of the poly(amine-amide)s films cast onto an ITO-coated glass substrate in dry acetonitrile containing 0.1 M of tetrabutylammonium perchlorate (TBAP) as an electrolyte exhibited one oxidation redox couples (E_{onset}) at (1.30-1.37) V *versus* Ag/AgCl and revealed electrochromic characteristics with a colour change from pale yellow to blue at applied potentials switched between 0.0 and 1.6 V.

Keywords: Hole-transporting materials, Triphenylamine, Emitting layer.

INTRODUCTION

The field of organic light-emitting devices (OLEDs) has attracted considerable interests due to their potential applications in flat panel displays. Materials with hole-transporting capability have been widely used in polymer light-emitting devices. They have relatively high mobility's and low ionization potentials[1-6] and are easily oxidized to form stable radical cations[7]. The use of conjugated polymers in polymer light-emitting devices (PLEDs), has received a great deal of concern in industry because of several appealing advantages and the most efficient devices using PLEDs is architecture with a thin-film multilayer structure consists of a hole-transporting layer, an emitting layer and an electron transporting layer sandwiched between two electrodes[8]. Charge carriers (holes and electrons) are injected separately from anode and cathode, recombine in the emitting layer and thus emit light[9]. Many emitting materials have been designed and used in light-emitting devices. However, high-performance light emitting ones are rare because of the intrinsic wide band-gap required for such materials. Many hole

transporting materials have been tried for light-emission[10]. Most of the hole-transporting materials which contain amine functionalities show lack sufficient emission characteristics due to reductive quenching[11]. Aromatic polyamides are well accepted as high-performance polymeric materials for their excellent mechanical properties, high thermal stability and good chemical resistance[12]. They are also known as difficult processing materials because of high melting or glass transition temperatures and limited solubility in most organic solvents. To overcome these limitations, polymer-structure modification becomes necessary such as introduction of bulky, packing-disruptive groups into the polymer backbone[13-16]. It has been demonstrated that aromatic polyamides containing three-dimensional, propeller-shaped triphenylamine unit had good solubility inorganic solvents while retaining high thermal stability[17-19]. Furthermore, triphenylamine-based polymers are widely used as the hole-transport layer in emitting layer-devices, but they also show interesting electrochromic behaviour[20-25]. The most common method for the preparation of aromatic polyamides is the reaction of diacid compounds

with diamines at high temperatures. The solvents used are polar aprotic solvents like N,N-dimethyl formamide (DMF), N,N-dimethylacetamide (DMAc), N-methyl pyrrolidone (NMP) and HMPA. Salts, such as LiCl, CaCl₂ or a mixture of both, are often used as solubility promoters because the cations interact with the amide groups, diminishing the strength of the interchain hydrogen bonds. The method was developed by Yamazaki *et al.*[26]. In this paper we synthesize new poly(amine-amide)s *via* phosphorylation polycondensation reaction to form newly synthesized monomers. The monomers and polymers characterized structurally by FTIR, ^{1}H and ^{13}C NMR spectroscopic techniques. General properties, thermal, spectral, redox were measured for these poly(amine-amide)s.

EXPERIMENTAL

4-Isopropylaniline (Merck, 99.8 %), 2,4-dimethylaniline (Acros, 98.7), 2-ethylaniline (Merck, 99.5), 4-fluoro-benzonitrile (Acros, 98.7 %), sodium hydride (NaH) (Fluka, 60 %), N,N-dimethylformamide (DMF) (Acros, 99.6 %), potassium hydroxide (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, (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-methyl pyrolidone (NMP) (Fluka, 99.6 %) were used without further purification.

The FT-IR spectrum of the synthesizied compounds were recorded with a Spotlight 400 Perkin Elmer spectrometer. ^{1}H 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 pyrolidone 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 ºC/min with a SDT Q600 thermogravimetric analyser. The thermal decomposition data were recorded at a heating rate of 20 ºC/min under nitrogen atmosphere with a SDT Q600 thermogravimetric analyser (TGA Instrument).

Monomer synthesis: The monomers (Ma-Mc) have synthesized *via* the route as explained in the **Scheme-I**.
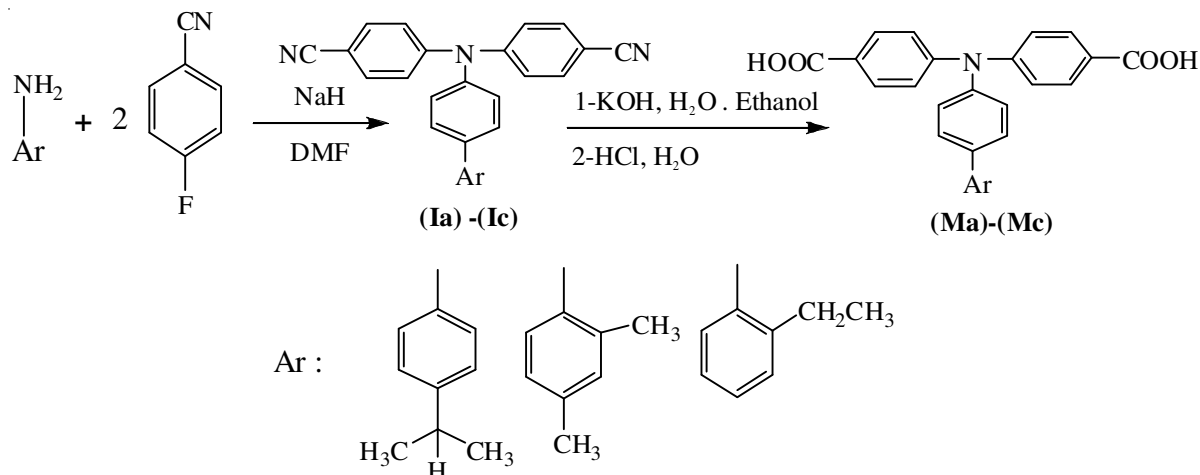
Synthesis of 4,4'-dicyano-4"-isopropyltriphenylamine (Ia): A mixture of 1.40 g (0.02 mol) of sodium hydride and 80 mL of DMF was stirred at room temperature for 0.5 h. To the mixture, 2.70 g (0.02 mol) of 4-isopropylaniline and 4.84 g (0.02 mol) of 4-fluorobenzonitrile were added in sequence. The mixture was heated with stirring at 120 ºC for 24 h under nitrogen and then precipitated into 150 mL of cold water[27,28]. The products were filtered and recrystallized from ethanol to give pale yellowish solid 3.43 g (yield: 51 %), m.p. =(185-188) ºC. FTIR: 2211.4 cm⁻¹ (C≡N). ^{1}H NMR (400 MHz, CDCl₃-d, δ ppm):7, 42 (d, 4H, H_d), 7.15 (d, 2H, Ha), 7.03 (d, 4H, Hc), 6.97(d, 2H, H_b), 2.85 (m, 1H, H_CH), 1.20.(d, 6H, H_CH3). ^{13}C NMR (400 MHz, CDCl₃-d, δ ppm):150.20 (C₅), 147.47(C₄), 105.38(C₈), 118.92(CN), , 122.54(C₆), 126.93(C₂), 128.21(C₃), 133.40(C₇), 142.38(C₁),. 33.62(C_CH), 23.84(C_CH3).

4,4'-Dicarboxy-4"-isopropyltriphenylamine (Ma): A mixture of 15.5 g of potassium hydroxide and 6.74 g (0.02 mol) of the dinitrile compound (**1**) in 60 mL of ethanol and 60 mL of distilled water was stirred at 100 ºC until no further ammonia was generated. The time taken to reach this stage was *ca.* 24 h. The solution was cooled and the pH value was adjusted by dilute HCl to near 3. The yellowish precipitate formed was collected by filtration, washed thoroughly with water. Recrystallization from acetic acid gave pale yellow crystals 6.0 g (80 % yield); m.p. = 268-270 ºC. FTIR: 1681 cm⁻¹ (C=O), 2987 cm⁻¹ (O-H). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 7.99 (d, 4H, H_d),7.28(d, 2H, H_a),7.07(d, 2H, (H_b), 7.00 (d, 4H, H_C), 2.88 (m, 1H, H_CH), 1.21 (d, 6H, H_CH3), 12.70 (br, 2H, COOH).^{13}C NMR (400MHz,DMSO-d_6, δ ppm):166.83 (COOH), 150.44 (C₅), 145.82 (C₄), 143.22 (C₁), 130.97 (C₇), 128.01 (C₃),124.42 (C₂) 126.56 (C₈), 121.86 (C₆), 23.81 (CH), 23.81 (CH₃).

4,4'-Dicyano-4"-2,4-dimethylaniline(Ib): The synthesis of this compound was the same to that for **Ia.** The product was filtered and recrystallized from ethanol to give pale yellowish solid 2.31 g (yield: 71.5 %), m.p. = 146-148 ºC. FTIR: 2222.4 cm⁻¹(CN). ^{1}H NMR (400 MHz, CDCl₃-d_1, δ ppm): 7.71-7.69 (d, 4H, H_e), 7.53-7.49 (m, 1H, Ha), 7.13-7.09 (m, 5H, H_b,d), 7.05-7.03(m, 1H, Hc), 2.12 (s, 3H, H_CH3"), 1.29-1.23(m, 3H, H_CH3'). ^{13}C NMR (400 MHz, CDCl₃-d_1, δ ppm): 150.22(C₇), 143.41(C₃), 138.68(C₁), 136.91 (C₆), 135.22 (C₉), 134.06(C₂), 121.81(C₄), 120.51(C₈), 119.19 (C₅), 118.60 (C_CN), 108.36(C₁₀).

Scheme-I: Synthesis routes of monomers

4,4'-Dicarboxy-4''-2,4-dimethyltriphenylamine (Mb): The synthesis of this compound was the same that for **Ma**. The pale yellow crystals 3.40 g (94.18 % yield); m.p = 276-278 °C. FTIR: 1683 cm^{-1} (C=O), 2710-3321 cm^{-1} (O-H). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm):12.81(s, 2H, H$_{COOH}$), 7.98(d, 4H, H$_e$), 7.84-7.80(m, 1H, H$_a$), 7.14-7.12(d, 4H, H$_d$), 7.02-7.00(d, 1H, H$_b$), 6.96-6.94(d, 1H, H$_c$), 2.06(s, 3H, H$_{CH3''}$), 1.20(s, 3H, H$_{CH3'}$). ^{13}C NMR (400 MHz, DMSO-d_6, δ ppm): 166.88(C$_{COOH}$), 149.86(C$_7$), 143.47(C$_3$), 132.00(C$_9$), 131.11(C$_1$), 129.00(C$_2$), 128.02(C$_6$), 122.04(C$_4$), 126.76(C$_{10}$) 120.29 (C$_5$), 118.98(C$_8$), 33.15(C$_{CH3''}$), 23.99(C$_{CH3'}$).

4,4'-Dicyano-4''-2-ethylaniline (Ic): The synthesis of this compound was the same to that for **Ia**. The product was filtered and recrystallized from ethanol to give pale yellowish solid 2.80 g (yield: 77.5%), m.p. = 110-112 °. FTIR: 2219 cm^{-1} (CN). ^{1}H NMR (400 MHz, CDCl$_3$-d_1, δ ppm): 7.62-7.60(d, 4H, H$_f$), 7.43-7.31(m, 3H, H$_{a,b,c}$), 7.17-7.09 (dd, 5H, H$_{e,d}$), 2.39-2.32 (q, 2H, H$_{CH2}$), 0.99-0.96 (t, 3H, H$_{CH3}$), ^{13}C NMR (400 MHz, CDCl$_3$-d_1, δ ppm): 150.48(C$_7$), 142.97(C$_6$), 135.38-135.31 (C$_{1,5}$), 134.04 (C$_9$), 131.34(C$_2$), 130.59(C$_3$), 129.06(C$_4$), 122.33(C$_8$) 120.54(C$_{CN}$), 105.51(C$_{10}$), 24.46(C$_{CH2}$), 13.86 (C$_{CH3}$).

4,4'-Dicarboxy-4''-2-ethyltriphenylamine (Mc): The synthesis of this compound was the same that for **Ma**. The pale yellow crystals 3.40 g (94.2 % yield); m.p = 273-275 °C. FTIR: 1680 cm^{-1} (C=O), 2713-3332 cm^{-1} (O-H). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 12.76(s, 2H, H$_{COOH}$), 7.83-7.81(d, 4H, H$_f$), 7.42-7.31 (m, 3H, H$_{a,b,c}$), 7.15-7.13 (d, 5H, H$_{e,d}$), 2.34-2.28 (q, 2H, H$_{CH2}$), 0.96-0.91 (t, 3H, H$_{CH3}$). ^{13}C NMR (400 MHz, DMSO-d_6, δ ppm): 166.81 (C$_{COOH}$), 150.86(C$_7$), 143.25(C$_6$), 131.20(C$_1$)131.03(C$_5$), 132.18(C$_9$), 128.50(C$_2$), 128.34(C$_3$), 128.17(C$_4$), 126.33(C$_{10}$), 122.16(C$_8$) 23.15(C$_{CH3}$), 13.23 (C$_{CH3}$).
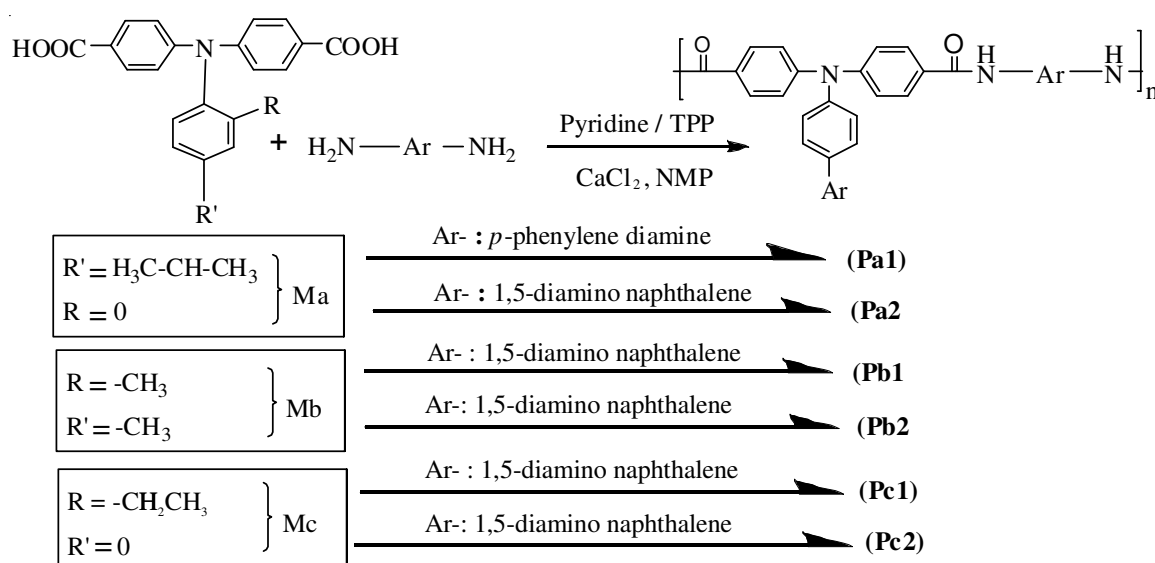
Polymer synthesis

Synthesis of poly(amine-amide) (Pa1): The polymers (**Pa1-Pc1, Pa2-Pc2**) have synthesized *via* the routes as explained in the **Scheme-II**. The synthesis of poly(amine-amide) (**Pa1**)

is used as an example to illustrate the general synthetic routes. The typical procedure is as follows. A mixture of 1.14 g (3 mmol) of the dicarboxylic acid monomer (**Ma**), 0.324 g (3 mmol) of *p*-phenylenediamine, 0.4 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. The inherent viscosity of the obtained poly-(amine-amide) was 0.62 dL/g, measured at a concentration of 0.5 g/dL in dimethyl acetamide. The IR spectrum exhibited characteristic amide absorption bands at 3309.39 (N-H stretching) and 1644 cm^{-1} (amide carbonyl). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 10.25 (S, 1H, H$_{NH-CO}$), 8.05 (d, 4H, H$_d$) 7.75 (s, 4H, H$_e$), 7.39 (d, 2H, H$_a$), 7.20 (d, 4H, H$_c$), 6.59 (d, 2H, H$_b$), 3.19 (m, 1H, H$_{CH}$) 2.07 (s, 6H, H$_{CH3}$). ^{13}C NMR (400 MHz, DMSO-d_6, δ ppm): 166.74 (NHCO), 150.44 (C$_5$), 145.82 (C$_4$), 143.22 (C$_1$), 131.83 (C$_9$), 130.97 (C$_7$), 128.23 (C$_3$), 124.12(C$_2$), 126.12(C$_8$), 121.76C$_6$), 120.02 (C$_{10}$), 32.91 (C$_{CH}$), 23.81 (C$_{CH3}$). The other poly(amine-amide)s were prepared by analogous procedure.

Synthesis of poly(amine-amide) (Pb1): The polymer **Pb1** was synthesized by the same method as described in synthesis of **Pa1**. The obtained poly(amine-amide) was 0.66 dL/g, measured at a concentration of 0.5 g/dL in DMAc. The IR spectrum 3304 cm^{-1} (N-H stretching) and 1644 cm^{-1} (amide carbonyl). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 10.26 (s, 1H, H$_{NHCO}$), 8.05-7.90 (d, 5H, H$_e$), 7.74 (s, 4H, H$_f$), 7.20 (s, 4H, H$_{a,b,d}$), 6.74 (s, 1H, H$_b$), 6.74-6.56 (s, 1H, H$_c$), 1.97(s, 3H, H$_{CH3''}$) 1.21(s, 3H, H$_{CH3'}$). ^{13}C NMR (400 MHz, DMSO-d_6, δ ppm): 166.89 (C$_{CO-NH}$), 149.97 (C$_7$), 142.89 (C$_3$), 131.91(C$_9$), 131.21(C$_1$), 129.04(C$_2$), 128.34(C$_6$), 126.45(C$_{10}$), 125.22(C$_{11}$), 123.17(C$_4$), 120.17(C$_5$), 118.12(C$_8$), 117.23(C$_{12}$), 33.45(C$_{CH3''}$).

Synthesis of poly(amine-amide) (Pc1): The polymer **Pb1** was synthesized by the same method as described in synthesis of **Pa1**. The obtained poly(amine-amide) was 0.63 dL/g,

Scheme-II: Synthetic routes of the polymers

measured at a concentration of 0.5 g/dL in dimethyl acetamide. The IR spectrum 3314 cm^{-1} (N-H stretching) and 1644 cm^{-1} (amide carbonyl). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm):10.23(S, 1H, H$_{NHCO}$), 7.98-7.83 (S, 1H, H$_{f,a}$), 7.40-7.34 (S, 1H, H$_{g,c}$), 7.13-6.73 (S, 1H, H$_{b,e,d}$), 2.06(S, 1H, H$_{CH2}$), 0.93(S, 1H, H$_{CH_3}$) ^{13}C NMR (400 MHz, DMSO-d_6, δ ppm): 166.82 (C$_{CO-NH}$), 150.12 (C$_7$), 142.89(C$_6$), 131.20 (C$_1$), 131.03(C$_5$), 131.91(C$_9$), 129.17(C$_2$), 128.89(C$_3$), 127.16(C$_4$), 126.12(C$_{10}$), 125.32(C$_{11}$), 122.23(C$_8$), 121.18(C$_{12}$), 26.45(C$_{CH2}$), 13.43(C$_{CH_3}$).

Synthesis of poly(amine-amide) (Pa2): This polymer **Pa2** was synthesized by the same method as described in synthesis of **Pa1** but used 1,5-diamine naphthalene instead of *p*-phenylene diamine.The inherent viscosity of the obtained poly(amine-amide) was 0.75 dL/g, measured at a concentration of 0.5 g/dL in DMAc. The IR spectrum exhibited characteristic amide absorption bands at 3364 cm^{-1} (N-H stretching) and 1647 cm^{-1} (amide carbonyl). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 10.42 (s, 1H, H$_{NH-CO}$), 7.99-7.97(d, 2H, H$_g$), 7.84-7.82(d, 4H, H$_d$), 7.50(s, 2H, H$_f$), 7.37-7.35(d, 2H, H$_a$), 7.29-7.27(d, 2H, H$_e$), 7.15-7.13(d, 4H, H$_c$), 7.03-7.01(d, 2H, H$_b$), 1.92-1.84(m, 1H, H$_{CH}$), 1.21-1.19(d, 6H, H$_{CH_3}$). ^{13}C NMR(400 MHz, DMSO-d_6, δ ppm): 166.56 (C$_{CONH}$), 150.47(C$_5$), 145.68 (C$_4$), 143.46(C$_1$), 131.76(C$_9$), 130.36(C$_7$), 128.33(C$_3$), 127.40(C$_2$), 126.11(C$_8$),125.98(C$_{13}$), 125.68(C$_{11}$), 121.86(C$_6$), 110.77(C$_{12}$), 104.24(C$_{10}$), 32.82(C$_{CH}$), 23.87(C$_{CH_3}$).

Synthesis of poly(amine-amide) (Pb2): This polymer was synthesized by the same method ass describd in synthesis of **Pa1** but used 1,5-diamine naphthalene instead of *p*-phenylene diamine.The inherent viscosity of the obtained poly(amine-amide) was 0.67 dL/g, measured at a concentration of 0.5 g/dL in DMAc. The IR spectrum exhibited characteristic amide absorption bands at 3364 cm^{-1} (N-H stretching) and 1648 cm^{-1} (amide carbonyl). ^{1}H NMR (400MHz, DMSO-d_6, δ ppm): 10.46 (s, 1H, H$_{NH-CO}$),8.14 (s, 6H, H$_{e,h}$), 7.94-7.88(d, 2H, H$_g$), 7.55-7.24(d, 2H, H$_f$),7.20-7.06(d, 6H, H$_{a,b,d}$), 6.68-6.64 (d, 2H, H$_c$), 1.98-1.76(s, 3H, H$_{CH_3''}$), 1.23-0.92(s, 3H, H$_{CH_3'}$). ^{13}C NMR (400 MHz, DMSO-d_6, δ ppm): 166.86 (C$_{CONH}$), 150.54(C$_7$), 143.73(C$_3$), 132.71(C$_{11}$), 131.75(C$_9$), 131.12(C$_1$), 130.76 (C$_2$), 128.58(C$_6$), 126.67(C$_{10}$), 125.87(C$_{15}$), 124.77(C$_{13}$), 122.57(C$_4$),121.82(C$_5$). 118.82(C$_8$), 110.23(C$_{14}$), 107.63(C$_{12}$), 33.07(C$_{CH_3''}$), 23.65(C$_{CH_3'}$).

Synthesis of poly(amine-amide) (Pc2): This polymer **Pc2** was synthesized by the same method as described in synthesis of **Pa1** but used 1,5-diamine naphthalene instead of *p*-phenylene diamine.The inherent viscosity of the obtained poly(amine-amide) was 0.81 dL/g, measured at a concentration of 0.5 g/dL in DMAc. The IR spectrum exhibited characteristic amide absorption bands at 3357 cm^{-1} (N-H stretching) and 1648 cm^{-1} (amide carbonyl). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 10.43(s, 1H, H$_{NHCO}$), 8.12-8.08(s, 7H, H$_{f,a,i}$), 7.88-7.86 (d, 2H, H$_h$), 7.64-7.50 (d, 2H, H$_{g,c}$), 7.19-7.00(d, 5H, H$_{e,d}$), 6.66-6.64 (d, 1H, H$_b$), 2.06 (q, 1H, H$_{CH_2}$), 0.97 (t, 1H, H$_{CH_3}$).^{13}C NMR (400 MHz, DMSO-d_6, δ ppm): 165.92 (C$_{CONH}$), 150.24 (C$_7$), 142.56(C$_6$), 132.05(C$_5$), 131.85(C$_1$), 131.24(C$_{11}$), 130.86(C$_9$), 131.12(C$_2$), 130.76(C$_3$), 128.58(C$_4$), 126.56(C$_{10}$), 124.06(C$_{15}$), 121.77(C$_{13}$), 118.57(C$_8$), 110.32(C$_{14}$). 106.81(C$_{12}$), 26.43(C$_{CH_2}$), 13.63 (C$_{CH_3}$).

Monomer synthesis: The new aromatic dicarboxylic acid having 4-isopropyl substituted triphenylamine unit, 4,4'-dicarboxy-4"-isopropyltriphenylamine **(Ma)**, was synthesized by the amination reaction of 4-isopropylaniline with 4-fluoro-benzonitrile, followed by the alkaline hydrolysis of the intermediate dicyano compound **(Ia)**. According to the synthetic routes outlined in **Scheme-I**. FT IR, ^{1}H and ^{13}C NMR spectroscopic techniques were used to identify the chemical structures of the intermediate dicyano compounds **(Ia)** and the dicarboxylic acid monomer **(Ma)**.The FTIR spectra of compound **Ia** gave a cyano group characteristic band at 2221 cm^{-1} (C≡N stretching). After hydrolysis, the cyano group absorption beak disappeared and the carboxylic acid group showed a typical carbonyl absorption band at 1678 cm^{-1} (C=O stretching) together with the appearance of broad bands around 3400-2700 cm^{-1} (O-H stretching) (Fig. 1).
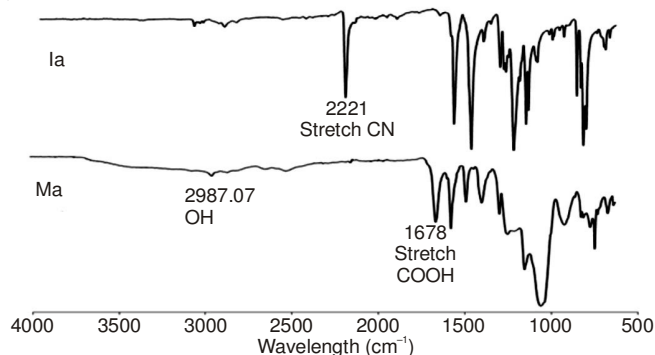

Fig. 1. FTIR spectrum of compounds **(Ia)**, **(Ma)**

Structures of compounds **Ia** and **Ma** were also confirmed by high-resolution NMR spectra (Figs. 2 and 3). In ^{1}H NMR spectrum (Fig. 2), a two big doublet peaks at 7.42 (d, 4H, H$_d$), 7.03 (d, 4H, H$_c$), due to four phenylene protons(d) and (c), respectively. Doublet peak at 7.15 (d, 2H, Ha) due to two protons of (a). Doublet peak at 6.97(d,2H, H$_b$) for two protons of (b). Multiplet peak of proton (-CH-). Doublet peak of six protons for (2CH$_3$). Fig. 3 exhibits very broad singlet peak due to proton of carboxylic group which is hardly observed because replacement hydrogen atoms of (COOH) by deuterium of DMSO solvent and formation of H-bonding. The ^{13}C NMR spectra (Figs. 4 and 5) confirmed that the chemical shifting of C-atoms and that the cyano groups were completely converted into the carboxylic acid groups by the disappearance of the resonance peak for the cyano carbon at 105.42 ppm and by the appearance of the carboxylic peak at 166.8 ppm.
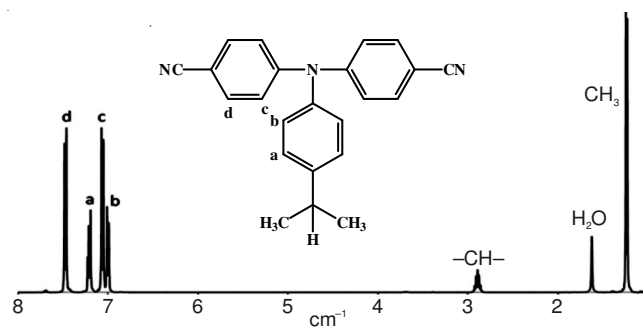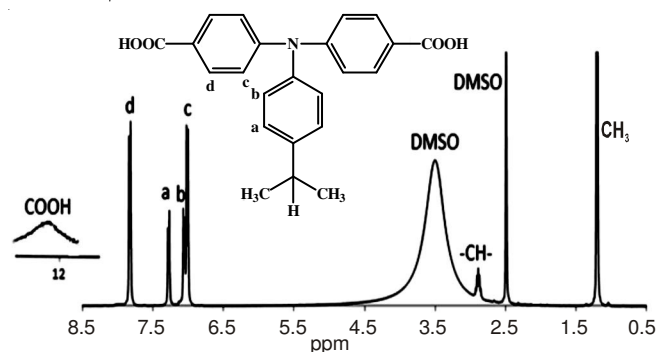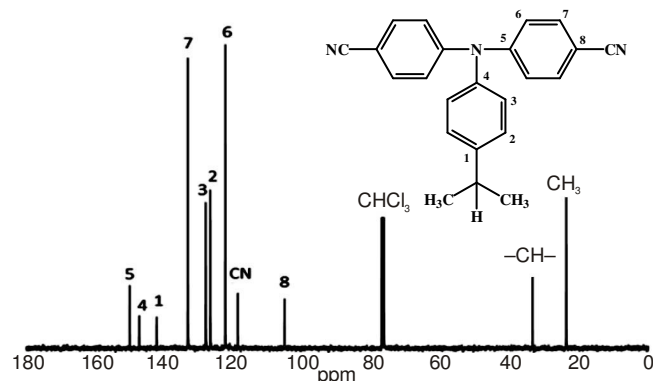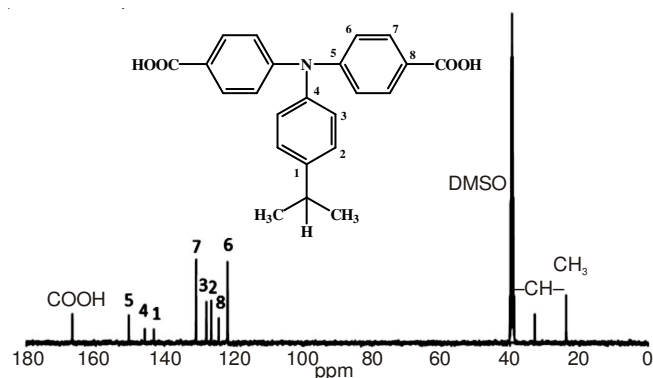

Fig. 2. ^{1}H NMR spectrum of compound **(Ia)** in CDCl$_3$-D1

Fig. 3. ¹H NMR spectrum of compound (Ma) in CDCl₃-D1

Fig. 4. ¹³C NMR spectrum of compound (Ia) in CDCl₃-D1

Fig. 5. ¹³C NMR spectrum of compound (Ma) in DMSO-d_6

TABLE-1 POLYMER CODES		
	Polymer diamine	Monomer code
pa1	1	**Ma**
pb1	1	**Mb**
pc1	1	**Mc**
pa2	2	**Ma**
pb2	2	**Mb**
pc2	2	**Mc**

Other important evidence of this change is the shifting of the carbon resonance signals of C_8 adjacent to the cyano or carboxyl group. The C_8 of dinitrile (**Ia**) resonated at a higher field (105.4 ppm) than the other aromatic carbons because of the anisotropic shielding by the π-electrons of Ca≡N. After hydrolysis, the resonance peak of C_8 shifted to a lower field (126.56 ppm) because of the lack of an anisotropic field.

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 (**Ma**) with various aromatic diamines, *p*-phenyl-enediamine, 1,5-diamino naphthalene using triphenylphosphite (TPP) and pyridine as condensing agents (**Scheme-II**). All the polymerizations proceeded homogeneously throughout the reaction and afforded clear, 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, with η_{Cinh} values in the range of 0.62-0.81 dL/g (Table-2). 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 spectro-scopy. The characteristic absorption bands observed around 3309.39 (N-H stretching) and 1644 cm⁻¹ (C=O stretching of amide group). Fig. 6 illustrates a typical FTIR spectrum of the representative poly(amine-amide) (**pa1**). Typical set of ¹H and ¹³C NMR spectra of polyamide in DMSO-d_6. Assignments of each proton and the spectra agree well with the proposed molecular structure of **pa1**.
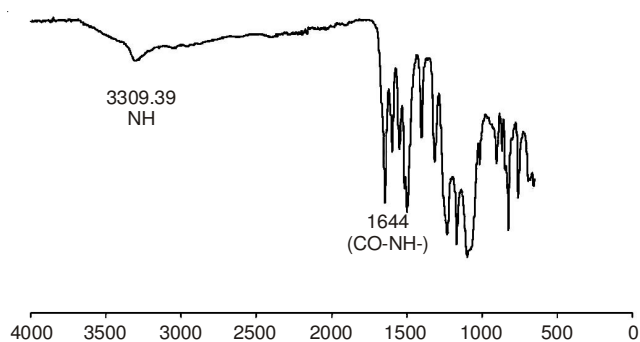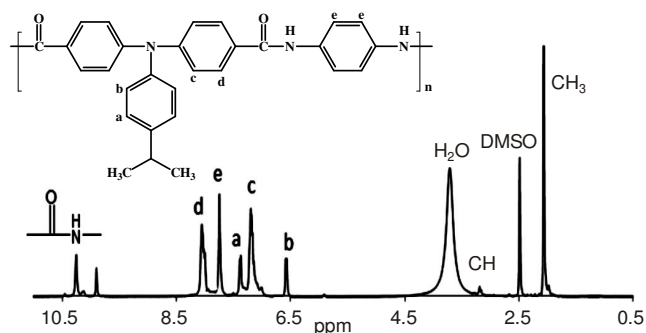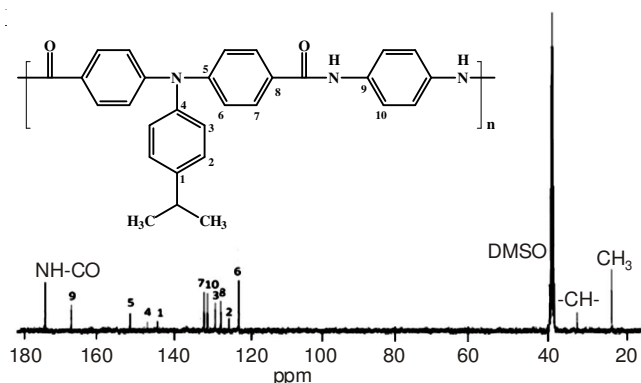

Fig. 6. FTIR spectrum of poly(amine-amide) (pa1)

Fig. 7. ¹H NMR of compound poly(amine-amide) (pa1)

Fig. 8. ¹³C NMR of poly(amine-amide) (Pa1) in DMSO-d_6

TABLE-2
SOLUBILITY OF AROMATIC POLYAMIDES

Polymer code	η inh[b] (dl/g)	Solvents[a]						
		NMP	DMAc	DMF	DMSO	*m*-Cresol	THF	CHCl$_3$
pal1	0.62	++	++	++	++	–	–	–
pb1	0.66	++	++	++	++	–	–	–
pcl1	0.63	++	++	++	++	–	–	–
pa2	0.75	++	++	++	++	+	–	–
pb2	0.67	++	++	++	++	+	–	–
pc2	0.81	++	++	++	++	+	–	–

[a]Solubility: ++, soluble at room temperature, +: soluble on heating, -, insoluble even on heating. [b]Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 ºC.

Also, the monomer **Ma** reacts with 1,5-diamino naphthalene to form polyamide with more solubility in the polar solvent. This polymer characterized by FTIR, ^{1}H and ^{13}C NMR as shown in Figs. 9-11.
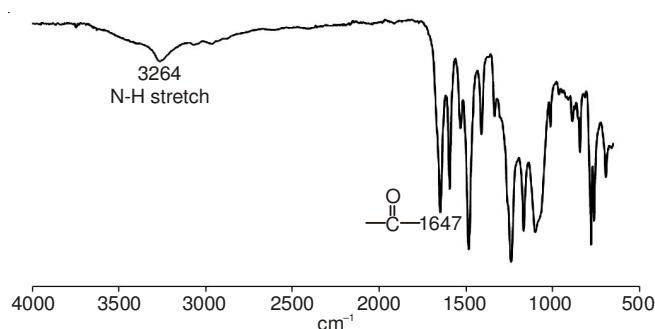

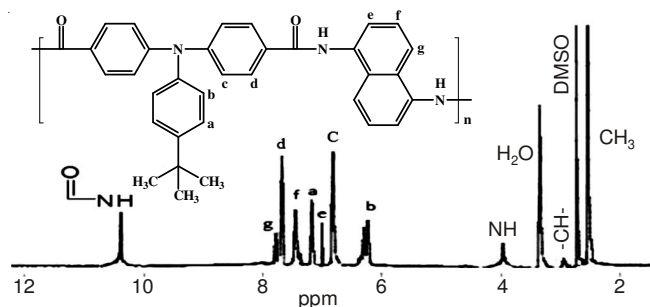Fig. 9. FTIR spectrum of poly(amine-amide) **(pa2)**

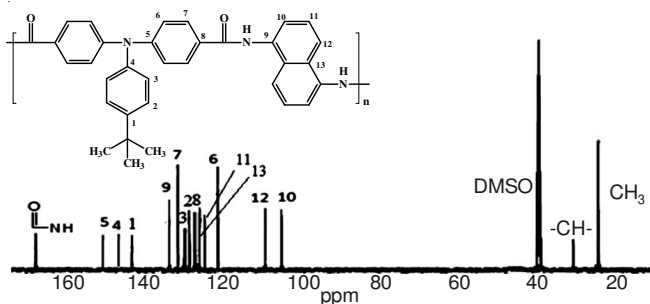Fig. 10. ^{1}H NMR of compound poly(amine-amide) **(pa2)**

Fig. 11. ^{13}C NMR of poly(amine-amide) **(Pa2)**

Polymer properties

Solubility: The qualitative solubility properties of poly-(amine-amide)s in several organic solvents at 10 % (w/v) are also summarized in Table-2. All the polymers exhibited excellent solubility in polar organic solvents such as NMP and DMAc. The enhanced solubility can be attributed to the presence of introduced triphenylamine unit. Polymers **(pa2)**, **(pb2)**, **(pc2)** have more solubility than others because the more bulky pendent naphthalene group chromophores in the repeating unit leading to increase in free volume in the polymer chains to allow more solvent to come in. Further more, polymers **(pb2)**-**(pc2)** are more flexibility. The excellent solubility makes these polymers convenient to process into articles by spin-coating.

Thermal properties: DSC thermograms of all the poly(amine-amide)sare as shown in Fig. 12. The thermal behaviour data of these polymers are summarized in Table-3. They showed high glass transition temperatures T_g in the range of (289.60-248.32) ºC. The T_g values of these poly(amine-amide)s generally decreased with decreasing stiffness of the diamine component. So polymers with phenylene diamine exhibited high T_g value due to more rigidity than of polymers with 1,5-diamine.The lowest $T_g$value of poly(amine-amide)s can be explained in terms of the flexibility and low rotation barrier of its diamine moiety. Poly(amine-amide) **(pb1)** exhibited the highest T_g value (289.60 ºC) in this series polymers because of the presence of rigid phenylene diamine and methyl groups segment in the main chain.
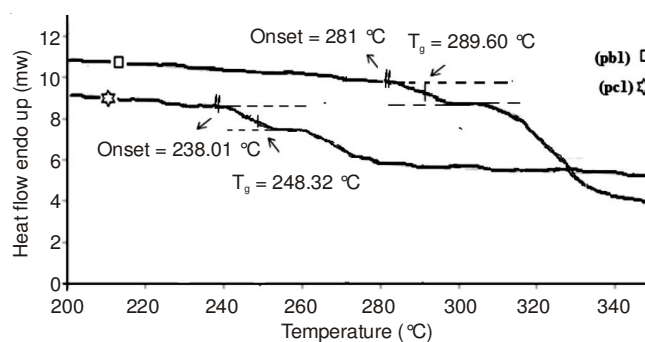

Fig. 12. DSC of poly(amine-amide)s **(pa1)**, **(pc1)**

Fig. 13 shows the TGA curves of poly(amine-amide) **(pa1)**. The decomposition temperatures (T_d) at 5 and 10 % weight losses in nitrogen atmosphere are given in Table-3. All the poly(amine-amide)s exhibited good thermal stability with insignificant weight loss up to 300 ºC in nitrogenand the 5 % weight-loss temperatures in nitrogen were recorded in the range of (410-460 ºC) and (451-522 ºC) for 10 % weight. Due to their high aromatic content, these polymers revealed high char yields in nitrogen, more than 60 % at 800 ºC.

Spectral properties: The optical properties of poly-(amine-amide)s were investigated by UV-visible and photo-

TABLE-3

Polymer code (ºC)	Onset[a] (ºC)	T_b^b (ºC)	Onset[c] (ºC)	T^d 5 % (ºC)	T^d 10 % (ºC)	Peak (%)	Char.[e]
(pb1)	265.45	283.32	383.76	460	522	444.04	63
(pc1)	281.00	289.60	364.84	410	480	443.72	65
(pa1)	230.01	248.32	367.37	400	475	437.20	67
(pa2)	243.32	260.00	357.04	400	475	421.22	61
(pb2)	246.92	265.45	361.43	430	472	411.04	65
(pc2)	238.30	248.32	370.21	420	451	405.23	65

a: onset temp,recorded by DSC. b: The midpoint temperature of baseline shift on the subsequent DSC trace (from 30-350 ºC at heating rate 20 ºC/min) was defined as T_g. C: onset temp. Recorded by TGA. T_d: Decomposition temperature at which a 5% or 10% weight loss was recorded by TGA at a heating rate of 20 ºC/min. Peak: The midpoint temperature of baseline shift on the subsequent TGA trace (from 50-800 ºC at heating rate 20 ºC/min) was defined as peak(ºC). e: Residual weight percentages at 800 ºC under nitrogen flow.
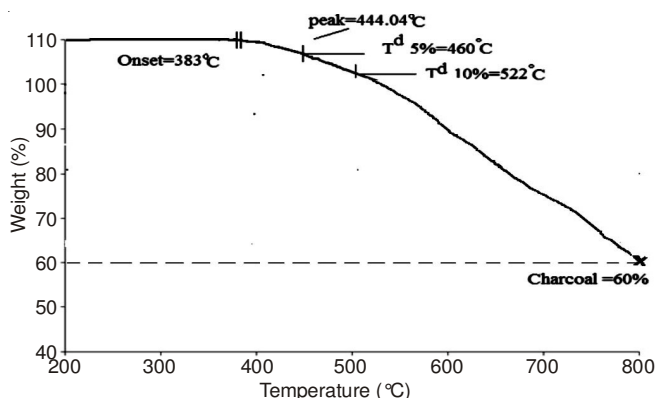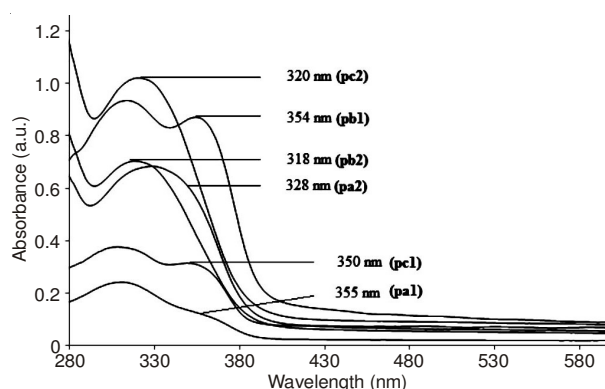

Fig. 13. TGA of Poly(amin-amide) (pa1)

Fig. 14. UV-visible absorption spectra of poly(amine-amide)s in concentration (10^{-5} M) in NMP

luminescence spectroscopy. The results are summarized in Table-4. The dilute solutions of these poly(amine-amide)s in NMP exhibited strong UV-VIS absorption bands at (318-355) nm, assignable to the (n-π*) transition resulting from the conjugation between the aromatic rings and nitrogen atoms and transition from the characteristic (π-π*) transitions of naphthalene chromophore[29]. Their spectra in NMP solution showed photoluminescence emission maxima bands around (425-443) nm in the blue region. Figs. 14 and 15 shows the UV-visible absorption and photoluminescence spectra for poly(amine-amide)s. Fig. 16 showed the strong fluorescence emissions inthe blue region which can be explained from the decreased intra- and intermolecular electronic interactions. The bulky, crank effective in decreasing charge transfer formation within or between polymer chains through steric hindrance. The UV-visible transmittance spectra of these poly(amine-amide)s films and cut-off wavelengths (absorption edge λ_o) in the range of (412-430) nm are also indicated in Fig. 16.

Electrochemical properties: The redox behaviour of poly-(amine-amide)s was investigated by cyclic voltammetry for

Fig. 15. UV-visible photoluminescence emission of poly(amine-amide)s in concentration (10^{-5} M) in NMP

TABLE-4

Polymer code	$\lambda_{abs,max}$ (nm)[a]	λ_{abs} (nm)[a]	Onset (nm)[b]	$\lambda_{PL}\lambda_o$ (nm)[c]
(pa1)	355(352)	422(420)	431	427
(pb1)	354(356)	436(438)	439	420
(pc1)	350(350)	418(417)	425	418
(pa2)	328(327)	427(422)	438	410
(pb2)	318(319)	423(419)	443	405
(pc2)	320(321)	421(423)	427	414

a: UV-VIS absorption measurements in NMP (1×10^{-5} M) at room temperature. Values in the parentheses were measured in polymer film. b: PL spectra measurements in NMP (1×10^{-5} M). c: the cutoff wavelengths (λ_o) from the transmission.

Fig. 16. UV-visible transmittance spectra of poly(amine-amide)s with a concentration (10^{-5} M) in NMP

TABLE-5

Polymer code	E_{onset}/V(*vs*. Ag/AgCl) in CH_3CN (nm)	λ_{abs}, onset HOMO[a] (eV)	LUMO[b] (eV)	HOMO-LUMO gap[c] (eV)
pa1	1.35	422(420) 5.74	2.79	2.95
pb1	1.31	436(438) 5.70	2.87	2.83
pc1	1.27	418(417) 5.66	2.69	2.97
pa2	1.37	421(423) 5.76	2.83	2.93
pb2	1.34	423(419) 5.73	2.78	2.95
pc2	1.30	27(422) 5.69	2.76	2.93

a: The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV). b: LUMO = HOMO – gap. c: Energy gap data were calculated of thin film by the equation: Energy gap = $1240/\lambda_{onset}$ of polymer film.

the cast film on an ITO-coated glass substrate as working electrode in dry acetonitrile containing 0.1 M of tetrabutyl-ammonium perchlorate as an electrolyte, under nitrogen atmosphere. All the poly(amine-amide)s showed an reversible oxidation process. Fig. 17 shows the typical cyclic voltammogram for poly(amine-amide) **(pa1)** recorded at scanning rate of 0.1 V/s. One reversible oxidation redox couple with half- wave at $E_{1/2}$ = 1.35 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 poly-amide **(pa1)** exhibited good reversibility of electrochromic characteristics by continuous five scans between 0.0-1.60 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-VIS absorption of thin films[30] and the results are listed in Table-5. The external ferrocene/ferrocenium (Fc/Fc+) redox standard E_{onset} is 0.41 V *versus* Ag/AgCl in CH_3CN and the HOMO energy for the Fc/Fc + standard is 4.80 eV with respect to the zero vacuum level. Therefore, the HOMO energy for **(pa1)** has been evaluated to be 5.74 EV as follows: $E_{1/2}$ (onset)= $(E_{PC} + E_{pa})/2$ where pc and pa are potentials of cathode and anode, respectively.

$$E_{1/2}(onset) = (1.48 +1.23)/2 = 1.35 \text{ V}$$
$$E_{HOMO} = [E_{1/2}(onset) \% E_{1/2}(ref.) + 4.8] \text{ eV}$$
$$E_{HOMO} = [1.35 \% 0.41 + 4.8] = 5.74 \text{ eV}$$
$$Gap = 1240/\lambda_{onset} = 1240/420 = 2.95 \text{ eV}$$
$$HOMO – LUMO = GAP$$
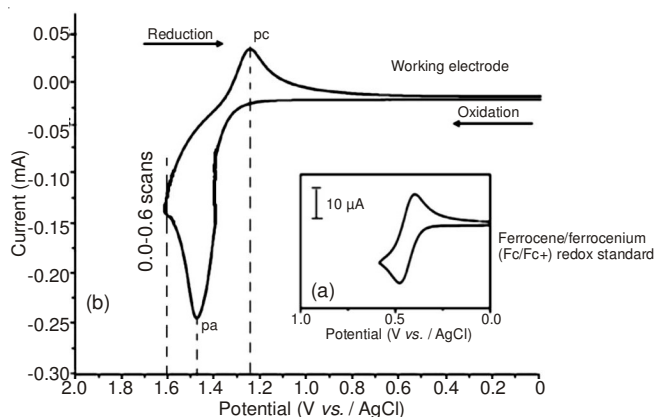$$LUMO = 5.74 \% 2.95 = 2.79 \text{ eV}$$

Fig. 17. Cyclic voltammograms of (a) ferrocene as reference and (b) the cast film of poly(amine-amide) **(pa1)** on the indium-tin oxide(ITO)-coated glass substrate in CH_3CN containing 0.1 M TBAP, with a scan rate of 0.1 V/s

Conclusion

A series of new poly(amine-amide)s bearing derived-triphenylamine units in the polymer main chain have been successfully prepared from a newly synthesized aromatic derived triphenylamine dicarboxylic acid, 4,4'-dicarboxy-4"-triphenylamine with two different aromatic diamines by phosphorylation polyamidation technique. All the poly(amine-amide)s were amorphous with high T_g and 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.

REFERENCES

1. C.W. Tang and S.A. Van Slyke, *Appl. Phys. Lett.*, **51**, 913 (1987).
2. C.W. Tang, S.A. Van Slyke and C.H. Chen, *J. Appl. Phys.*, **85**, 3610 (1989).
3. C. Adachi, K. Nagai and N. Tamoto, *Appl. Phys. Lett.*, **66**, 2679 (1995).
4. Y. Shirota, *J. Mater. Chem.*, **10**, 1 (2000).
5. M. Yang and Q. Zhang, *J. Mater. Sci.*, **39**, 3777 (2004).
6. A.P. Kulkarni, C.J. Tonzola, A. Babel and S.A. Jenekhe, *Chem. Mater.*, **16**, 4556 (2004).
7. M. Thelakkat, J. Hagen, D. Haarer and H.-W. Schmidt, *Synth. Met.*, **102**, 1125 (1999).
8. N.C.M. Greenham, S.C. Moratti, D.D.C. Bradley, R.H. Friend and A.B. Holmes, *Nature*, **365**, 628 (1993).
9. M. Strukelj, F. Papadimitrakopoulos, T.M. Miller and L.J. Rothberg, *Science*, **267**, **5206**, 1969 (1995).
10. U.B. Mitschke and P. Bäuerle, *J. Mater. Chem.*, **10**, 1471 (2000).
11. E.N. Ueta, H. Nakano and Y. Shirota, *Chem. Lett.*, **12**, 2397 (1994).
12. H.H. Yang, Aromatic High-Strength Fibers, Wiley (1989).
13. Y. Imai, *High Perform. Polym.*, **7**, 337 (1995).
14. Y. Imai, *React. Funct. Polym.*, **30**, 3 (1996).
15. G.-S. Liou and S.-H. Hsiao, *J. Polym. Sci. A: Polym. Chem.*, **40**, 1781 (2002).
16. S.H. Hsiao, C.-W. Chen and G.-S. Liou, *J. Polym. Sci. A: Polym. Chem.*, **42**, 3302 (2004).
17. Y. Oishi, H. Takado, M. Yoneyama, M.-A. Kakimoto and Y. Imai, *J. Polym. Sci. A: Part A: Polym. Chem.*, **28**, 1763 (1990).
18. G.-S. Liou, S.-H. Hsiao, M. Ishida, M. Kakimoto and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, **40**, 2810 (2002).
19. G.-S. Liou and S.-H. Hsiao, *J. Polym. Sci. Part A: Polym. Chem.*, **41**, 94 (2003).
20. K. Ogino, A. Kanegae, R. Yamaguchi, H. Sato and J. Kurjata, *Macromol. Rapid Commun.*, **20**, 103 (1999).
21. M.-Y. Chou, M.- Leung, Y.O. Su, C.L. Chiang, C.-C. Lin, J.-H. Liu, C.-K. Kuo and C.-Y. Mou, *Chem. Mater.*, **16**, 654 (2001).
22. S.-H. Cheng, S.-H. Hsiao, T.-H. Su and G.-S. Liou, *Macromolecules*, **38**, 307 (2005).
23. S.-H. Hsiao, Y.-M. Chang, H.-W. Chen and G.-S. Liou, *J. Polym. Sci. A: Polym. Chem.*, **44**, 4579 (2006).
24. S. Beaupre, J. Dumas and M. Leclerc, *Chem. Mater.*, **18**, 4011 (2006).
25. K. Choi, S.J. Yoo, Y.-E. Sung and R. Zentel, *Chem. Mater.*, **18**, 5823 (2006).
26. N. Yamazaki, F. Higashi and J. Kawabata, *J. Polym. Sci. Polym. Chem.*, **12**, 2149 (1974).
27. G.-S. Liou, N.-K. Huang and Y.-L. Yang, *J. Polym. Sci. Part A: Polym. Chem.*, **44**, 4095 (2006).
28. Y. Oishi, K. Mori, H. Hirahara, Y. Fujimura and K. Miya, Japan Patent, 11-255723 (1999).
29. R. Martínez-Máñez and F. Sancenón, *Chem. Rev.*, **103**, 4419 (2003).
30. D.M. de Leeuw, M.M.J. Simenon, A.R. Brown and R.E.F. Einerhand, *Synth. Met.*, **87**, 53 (1997).