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Synthesis, Characterization of New Polyamides Bearing Triarylamine for Lightemitting Diodes

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Abstract

In this work, new di-acid monomers 4, 4’-di-carboxillic-4”-bromo-2”, 6”-dimethyl triphenylamine (Ma), 4, 4’- di-carboxylic -4”-chloro-2”, 6”-dimethyl triphenylamine (Mb) and 4, 4’- di-carboxylic -2”,4”-dichloro-6”-methyl triphenylamine (Mc) were synthesized by reaction of p-cyanobenzofluride with three different aromatic amines (4-bromo,2,6-dimethyl aniline, 4-chloro,2,6-dimethyl aniline and 2,4 dichloro, 6- methyl aniline) via aromatic nucleophilc substitution method to form three di cyano intermediates 4, 4’-Dicyano-4”-bromo-2”, 6”-dimethyl triphenylamine (Da), 4, 4’-dicyano-4”-chloro-2”, 6”-dimethyl triphenylamine (Db) and 4, 4’-dicyano-2”,4”-dichloro-6”-methyl triphenylamine (Dc) which form final di-carboxylic monomers after alkaline hydrolysis. Finally, these monomers react with two different aromatic di amines, phenylene diamins and benzidine respectively via polycondensation reaction to form final polyamides 4"-bromo-2", 6"-dimethyl-triphenylamine-4, 4'-polyphenylbenzamide (Pa), 4”-chloro-2”,6”-dimethyl- triphenylamine-4,4'-polyphenylbenzamide (Pb), 2”,4”-dichloro-6”-methyl-triphenylamine 4,4'-polyphenylbenzamide (Pc),4"-bromo-2",6"-dimethyl triphenylamine-4,4'- polyphenylbiphenylamide (Pd), 2”,4”-dichloro-6”-methyl-triphenylamine-4,4’-polyphenylamide (Pf). The chemical structure of these polymers characterized by FTIR and NMR techniques. All the results of polyamides showed excellent solubility in most polar solvents to form strong thin films. The polyamides possess a good thermal stability with height glass transition temperatures (Tg). Polyamides in DMSO solvent gave strong photoluminescence PL. Thin casting films of these polyamides in cyclic voltammetry (C.V) on glass base of iridium-tin oxide (ITO) as working electrode in dry CH_3CN solvent contains 0.1 M of tetrabutylantimoneperchlorate (TBAP) as an Electrolyte gave one redox wave.

Keywords: Cyclic voltammetry, polyamides, benzidine, thermal stability, casting.

1. Introduction

Polyamides having triphenyl amine which are characterized by their hole transporting groups, are known in the application of polyamides light emitting (PLEDs). These types of polymers have received great attention because of their important applications in many fields, including screens and lighting points [1,2].

These polyamides are known as low energy ionization, movement activity and easily oxidize to convert to stable radical cations [3-7]. Polyamides with triphenylamine group show electro chromic behavior and mainly used as hole-transport layer in LED devices [8-13]. All aromatic polyamides are resulted as high-performance polymers due to their high thermal and mechanical stabilities and good chemical properties [14,15].

These polymers are recognized as a very rigid because of hydrogen bonding between polymers backbones so when balk group are incorporated between the backbones. This reduces the close packing and interchanges hydrogen bonding which helps to break the rigidity and make the chins in high flexibility [16-18]. The introduction of withdrawing groups improves the oxidation resistance, optical transparency and solubility in organic solvents and lead to decrease the crystallinity behavior, dielectric constant, water absorption and color [19-22].

Polyamides are called conducting polymer, are important part of electrochromic materials and have being developed [23–26]. Electrochromic materials can convert color reversibly by mean of important result of energy saving and sufficient electrochemical potential or redox steps.

2. Materials and methods

2.1. Materials

Sodium hydride (Aldrich, 98%), 4-fluorobenzonitrile (Aldrich, 97.5%), 4-bromo-2,6-dimethylaniline, (Acros, 97%), 4-chloro-2,6-dimethylaniline, (Aldrich, 95%), 2,4-dichloro-6-methylaniline, (Aldrich, 99%), Dimethylsulfoxide (DMSO) (Merck, 98%), Ethanol (Merck, 99.5%), Triphenyl phosphite (Merck, 98%), $CaCl_2$ (Merck, 99%), N-methyl pyrrolidone (NMP) (Aldrich, 99%), phenylene diamine, (Aldrich, 97%), di-phenylene diamine (Aldrich, 98%), potassium hydroxide, (Merck, 99%), Hydrochloric acid, (Fluka, 36.5%).

2.2. Characterization Technique

The spectrum of FT-IR for all new materials was easured by a Spotlight 400 Perkin-Elmer spectrometer. ^{1}H and^{13}C- NMR data are recorded by a JEOL spectrometer. UV–vis absorption and PL spectrum were performed in (10^{-5} M) DMSO on a Cary 60 UV-vis spectrophotometer.

The measurements of X-ray were recorded by Cuka radiation beam (l ¼ 1.541 _A) with Max Flax (CMF) mirror. DSC and TGA were performed on a Perkin Elmer DSC6 instrument under N_2 atmosphere with a scan rate of 20 °C/min and an SDT Q600 thermogravimetric analyzer.

2.3. Synthesis of di-cyanide Intermediates (Da-Dc)

2.3.1. Synthesis of 4, 4'-Dicyano-4"-bromo-2", 6"-dimethyl triphenylamine (Da)

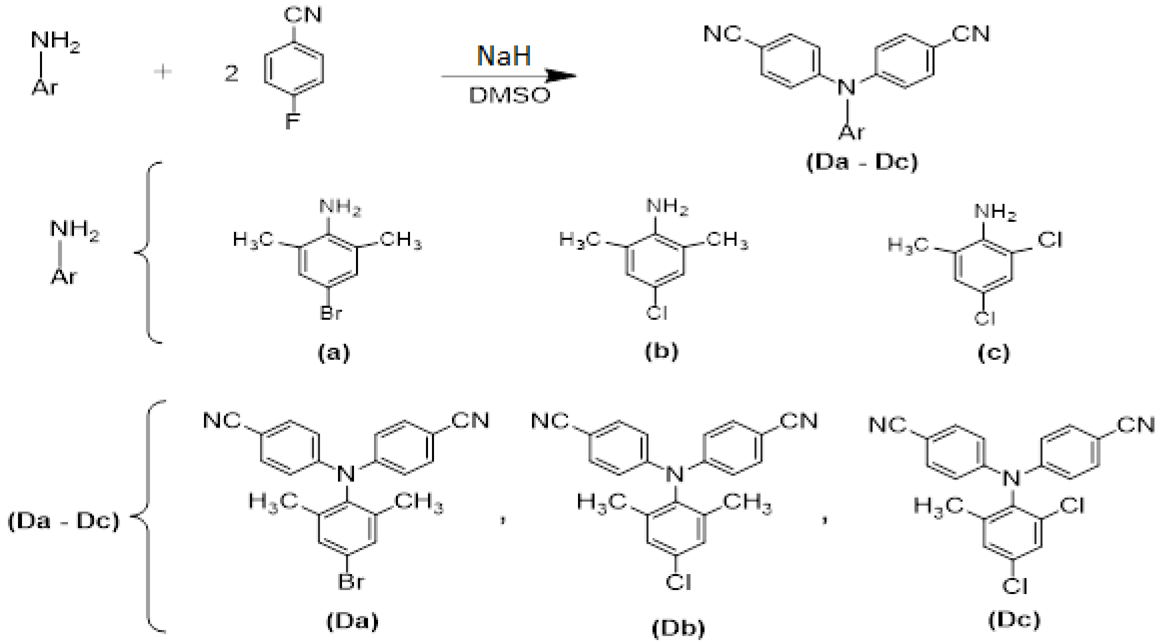
In a round flask with stirrer containing 80 mL of DMSO, added with stirring 2.50 g (0.02 mol) of NaH at a room temperature for half an hour. 4.84 g (0.02 mole) of 4-fluorobenzonitrile, 4.00 g (0.02 mole) of 2,6-dimethyl-4-bromoaniline were added alternately. The stirring mixture was heated at 100 °C for 12 h. After cooling, poured into about 200 mL of cold water. After filtering of the result yellowish precipitate recrystallized from ethanol 3.41 g (yield: 83%), m.p = 151-153 C°. FTIR: 2226.12 Cm^{-1} (CN). HNMR (400 MHz, $CDCl_3$-d1, δ ppm): 7.47-7.54(d, 4H, Ha), 732-7.41 (d, 4H, Hb), 7.19(s, 2H, Hc), 2.17(s, 6H, H_{CH3}). ^{13}CNMR (400 MHz, CDCl3-d1, δ ppm): 150.22 (C5), 142.41(C_4), 137.16 (C_3), 134.52 (C7), 132.08 (C2), 123.14 (C6), 118.62 (C_{CN}), 116.38 (C1), 106.96 (C8), 17.52 (C_{CH3}) **Scheme 1**. By using same method, the compounds (Db) and (Dc) were synthesized:

2.3.2. Synthesis of 4, 4'-dicyano-4"-chloro-2", 6"-dimethyl triphenylamine (Db)

3.41 g (yield: 72 %), m.p = 151-153 C°. FTIR: 2223.61 cm^{-1} (CN). HNMR (400 MHz, CDCl$_3$-d1, δ ppm): 7.46-7.51(d, 4H, Ha), 7.33-7.38 (d, 4H, Hb), 7.21(s, 2H, Hc), 2.12(s, 6H, H_{CH3}). ^{13}CNMR (400 MHz, CDCl3-d1, δ ppm): 150.26 (C5), 141.11(C_4), 136.68 (C3), 133.15 (C7), 130.24 (C2), 128.48 (C1), 124.23(C6), 118.56 (C_{CN}), 107.05 (C8), 17.73 (C_{CH3}).

2.3.3. Synthesis of 4, 4'-dicyano-2",4"-dichloro-6"-methyl triphenylamine (Dc)

3.80 g (yield: 80 %), m.p= 163-165 C°. FTIR: 2225.11 cm^{-1}, (CN). HNMR (400 MHz, CDCl$_3$-d1, δ ppm): 7.43-7.48(d, 4H, Ha), 7.32-7.38 (d, 4H, Hb), 7.16(s, 1H, Hc), 2.16(s, 3H, H_{CH3}). ^{13}CNMR (400 MHz, CDCl$_3$-d1, δ ppm): 150.26 (C7), 141.79 (C4), 137.91(C5), 133.13 (C9), 132.87 (C3), 131.23 (C6), 130.04 (C1), 128.23 (C2), 122.79 (C8), 118.52 (C_{CN}), 107.08 (C10), 16.98 (C_{CH3}).



Scheme 1: The synthesis routes of di-cyanide intermediates **(Da-Dc).**

2.4. Synthesis of di-carboxylic monomers (Ma-Mc)

2.4.1. Synthesis of 4, 4'-di-carboxillic-4"-bromo-2", 6"-dimethyl triphenylamine (Ma)

A mixture of 3.00 g (0.02 moles) of di-cyanide intermediate **(Da)** and 7.00 g of KOH in 80 mL distilled water and 80 mL ethanol was stirred at 120°C until all ammonia is finished. After the solution became cool, the pH value was regulated to about 3 by dilute HCl. The collected yellowish precipitate was filtration and washed via water and Recrystallized from acetic acid to give crystals in yellowish color (3.7 g, 86% yields): mp = 266-167°C. FTIR: 1678.04 cm^{-1} (C=O), 2800-3421 cm^{-1} (O-H). HNMR (400 MHz, DMSO-d6, δ ppm): 12.37-12.78 (br, 2H, H_{COOH}). 7.83 -7.91 (d, 4H, Ha), 7. 68-7.77 (d, 2H, Hb), 7.59 (s, 2H, Hc), 2.17 (s, 6H, H_{CH3}). ^{13}CNMR

(400 MHz, DMSO-d6, δ ppm): 166.72 (C_{COOH}), 152.04 (C5), 142.84(C_4), 137.22 (C_3), 131.68 (C7), 131.11 (C2), 124.86 (C6), 124.52 (C8), 115.28 (C1), 17.61(C_{CH3}).

Other monomers **(Mb)** and **(Mc)** were synthesized in the same procedure:

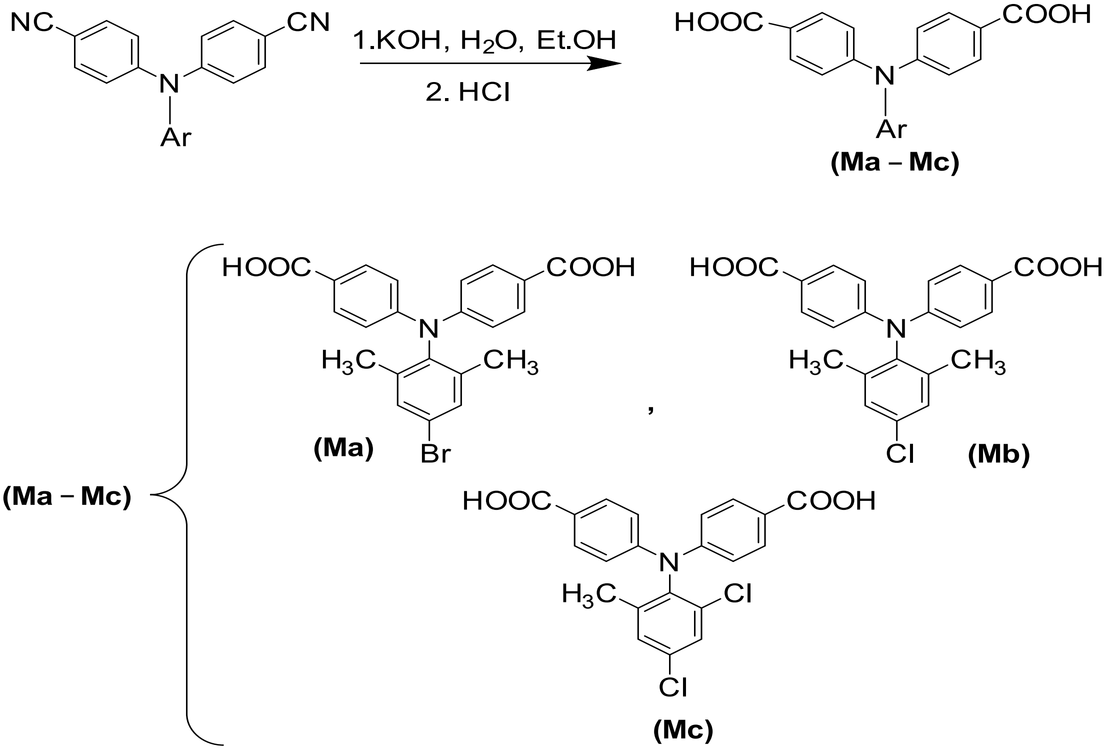
2.4.2. Synthesis of 4, 4'- di-carboxylic -4"-chloro-2", 6"-dimethyl triphenylamine (Mb)

3.40 g (80 % yields), m.p = 265-168 C°. FTIR: 1676.11 cm^{-1} (C=O), 2900-3540cm^{-1} (O-H). HNMR (400 MHz, DMSO-d6, δ ppm): 12.48-12.76 (br, 2H, H_{COOH}), 7.82-7.91(d, 4H, Ha), 7.32-7.42 (d, 4H, Hb), 7.21 (s, 2H, Hc), 2.13 (s, 6H, H_{CH3}). ^{13}CNMR (400 MHz, DMSO-d6, δ ppm): 168.51 (C_{COOH}), 151.12 (C5), 141.76 (C_4), 136.31 (C_3), 131.54 (C7), 130.08 (C2), 124.90 (C6), 124.62 (C8), 128.20 (C1), 17.71 (C_{CH3}).

2.4.3. Synthesis of 4, 4'- di-carboxylic -2",4"-dichloro-6"-methyl triphenylamine (Mc)

3.40 g (83 % yields): m.p = 257-258 C°. FTIR: 1678.23 cm^{-1} (C=O), 2650-3550cm^{-1} (O-H). HNMR (400 MHz, DMSO-d6, δ ppm): 12.47-12.86 (br, 2H, H_{COOH}), 8. 15-8.44(d, 4H, Ha), 7.47 (s, 1H, Hc), 7.35-7.43 (d, 4H, Hb), 7.31(s, 1H, Hd), 2.12 (s, 3H, H_{CH3}). ^{13}CNMR (400 MHz, DMSO-d6, δ ppm): 168.87 (C_{COOH}), 151.21 (C7), 140.63(C_4), 138.51 (C_5), 132.90 (C3), 131.30 (C6), 131.88 (C9), 13.412 (C1), 128.30 (C2), 124.93 (C8), 124.60 (C10), 16.83(C_{CH3}).

Scheme -1 shows the routes of synthesis



Scheme 2: the synthesis routes of di-carboxylic monomers **(Ma-Mc).**

2.5. Synthesis of polyamides (Pa-Pc)

2.5.1. Synthesis of (Pa)

The stirring mixture of 0.37 g (0.03 mole) of p-phenylenediamine,1.50 g (0.03 mole) of the monomer **(Ma)**, 4.0 mL of (TPP), 0.5 g of calcium chloride, 4.5 mL of (NMP) and 1.5 mL of pyridine was heated at 80°C for 4 h. The collected of high viscosity polymer was poured slowly in 100 mL of stirring cold water which formed stringy precipitate collected after filtration, washed by hot water and dried in thermal oven for 24 h [27]. (65 % yield). The FTIR spectrum band of amide group was at 3312.25 (N-H stretching), and 1648.07 cm^{-1} (amide carbonyl). HNMR (400 MHz, DMSO-d6, δ ppm): 10.24 (s, 1H, H_{NH-CO}), 7.86-7.98 (d, 2H, H_c), 7.72 (s, 4H, Hd), 7.18 (s, 2H, Ha), 7.23-7.34 (d, 4H, Hb), 2.19(s, 6H, H_{CH3}). ^{13}CNMR (400 MHz, DMSO-d6, δ ppm): 164.63 (C_{CONH-}), 151.12 (C_5), 143.62 (C4), 131.71 (C9), 131.23 (C7), 127.84 (C3), 124.62 (C2), 125.20 (C8), 119.04 (6), 116.30 (C_{10}), 115.56(C1), 17.67(C_{CH3}).

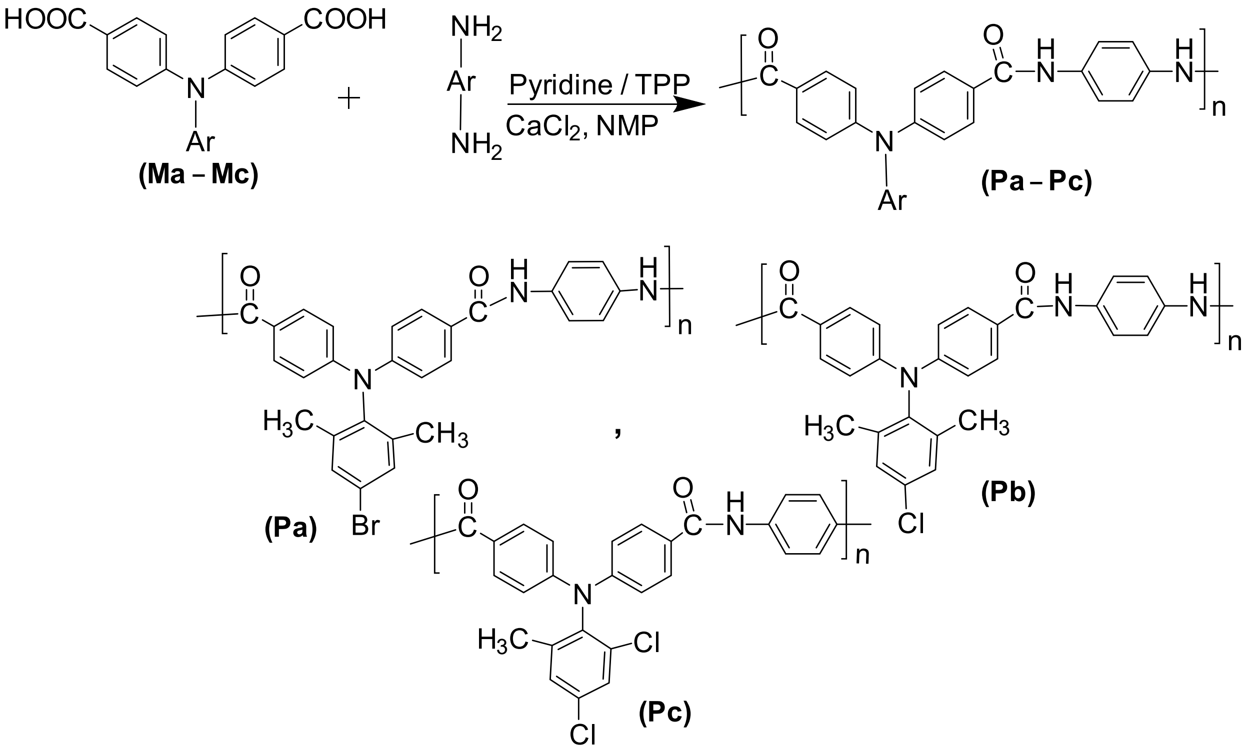
By using same above method, other polyamides **(Pb)** and **(Pc)** were prepared.

2.5.2. Synthesis of (Pb)

The collected polyamide, (61 % yield), IR spectrum 3310.12 cm^{-1} (N-H stretching) and 1644.51 cm^{-1} (amide carbonyl).

2.5.3. Synthesis of (Pc)

The obtained polyamide, (65 % yield), IR spectrum 3310.45 cm^{-1} (N-H stretching) and 1645.46 cm^{-1}(amide carbonyl). **Scheme 3** shows the synthesis routs of **(Pa-Pc).**



Scheme 3: The synthesis routes of polyamides **(Pa-Pc).**

2.6. Synthesis of polyamides (Pd-Pf)

These polyamides synthesized by same above method but using di-phenylene diamine instead of phenylene diamine **Scheme 4.**

2.6.1. Synthesis of (Pd)

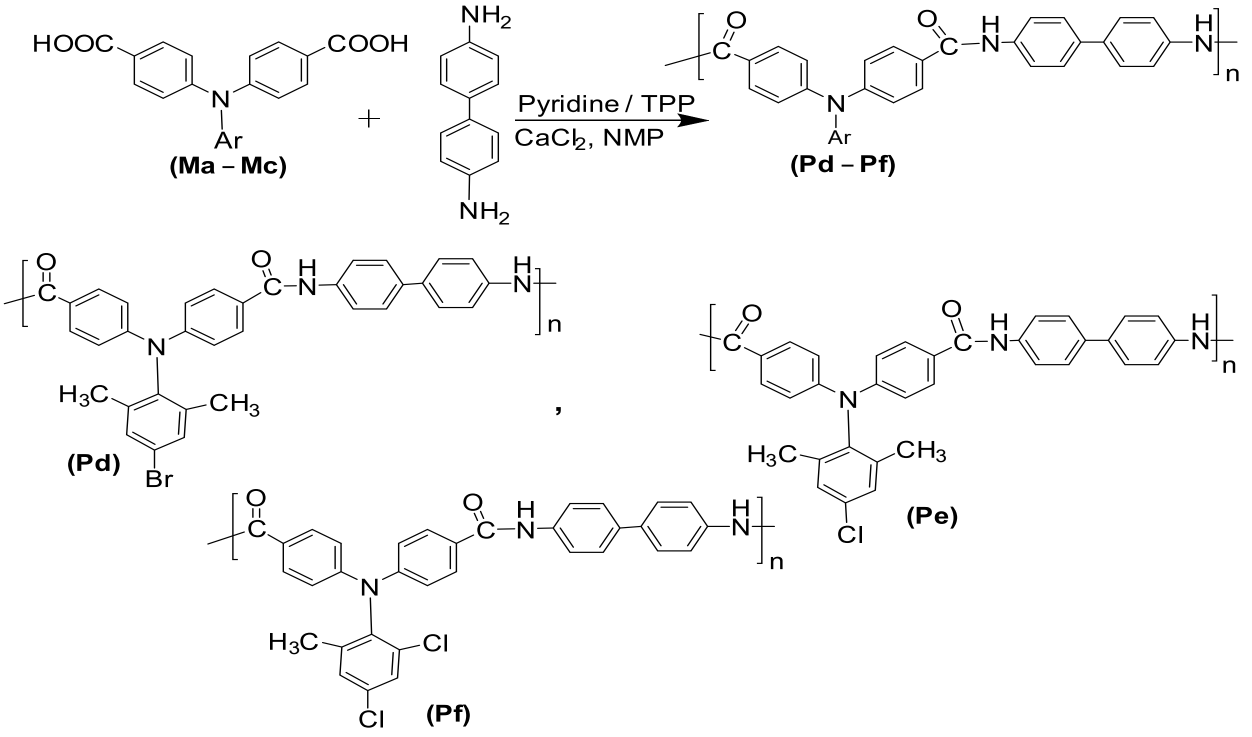
The obtained polyamide, (56 % yield), IR spectrum 3311.34 cm^{-1} (N-H stretching) and 1647.56 cm^{-1} (amide carbonyl). HNMR (400 MHz, DMSO-d6, δ ppm): 10.25 (s, 1H, H_{NH-CO}), 7.84-7.78 (d, 4H, H_c), 7.73-7.66 (d, 4H, Hd), 7.71-7.57 (d, 2H, He), 7.27-7.31 (d, 4H, Hb), 7.183 (d, 2H, Ha), 2.19(s, 6H, H_{CH3}). ^{13}CNMR (400 MHz, DMSO-d6, δ ppm): 164.73 (C_{CONH-}), 150.89 (C_5), 143.78 (C4), 138.08(C12), 131.59 (C9), 130.28 (C7), 127.74 (C11), 125.29 (C3), 124.74 (C2), 124. 58(C8), 119.06 (6), 116.30 (C_{10}), 115.56(C1), 17.67(C_{CH3}).

2.6.2. Synthesis of (Pe)

The obtained polyamide, (54 % yield), IR spectrum 3312.45 cm^{-1} (N-H stretching) and 1648.37 cm^{-1} (amide carbonyl).

2.6.3. Synthesis of (Pf)

The obtained polyamide, (68 % yield), IR spectrum 3310.46 cm^{-1} (N-H stretching) and 1647.38 cm^{-1} (amide carbonyl).

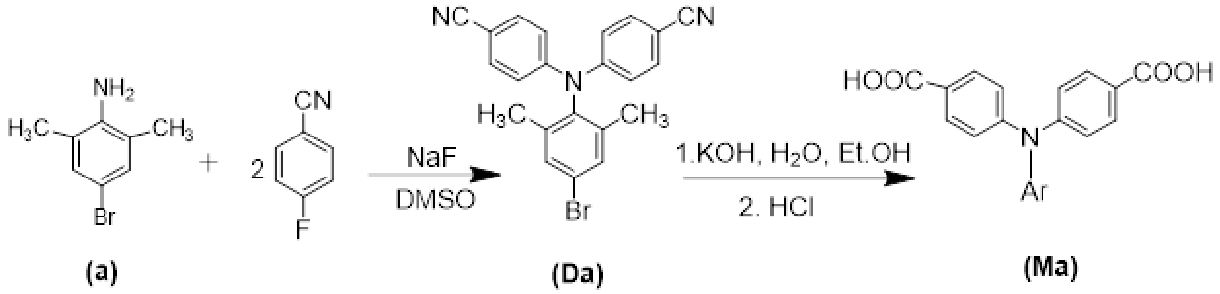


Scheme 4: The steps synthesis of polyamides **(Pd-Pf).**

3. Result and Discussion

3.1. Monomer synthesis

The new aromatic dicarboxylic acids with substituted triphenylamine group **(Ma-Mc),** were prepared via the reaction of aromatic amines **(a-c)** with p-fluorobenzocyanide in strong base NaH using a polar solvent DMSO by amination reaction technique to form dicayno product as intermediate **(Da-Dc)** which hydrolysis to form the final product. In this work, 2,6-dimethyl-4-bromoaniline **(a)** is used as an example for the expression of this synthesis. 4,4'-dicarboxy-4"-4-bromotriphenylamine **(Ma)** was synthesized via reaction of 2,6-dimethyl -4-bromoaniline and 4-fluorobenzonitrile. The dicyano intermediate **(Da)** formed **(Ma)** after hydrolysis as monomer **Scheme 5.**



Scheme 5: The synthesis steps of (**Da)** and (**Ma).**

The chemical characterization of the intermediate di-cyanides **(Da-Dc)** and the monomers **(Ma-Mc)** were confirmed by FTIR technique. Compounds **(Da-Dc)** gave a characteristic band at around (2222- 2226) cm^{-1} (C≡N stretching). The di-carboxylic acid groups which appeared after the hydrolysis of the di-syano groups, showed absorption band at around (1676-1678) cm^{-1} (C=O stretching) with the broad bands around (2800-3428) cm^{-1} (O-H stretching) **(Figure 1).**

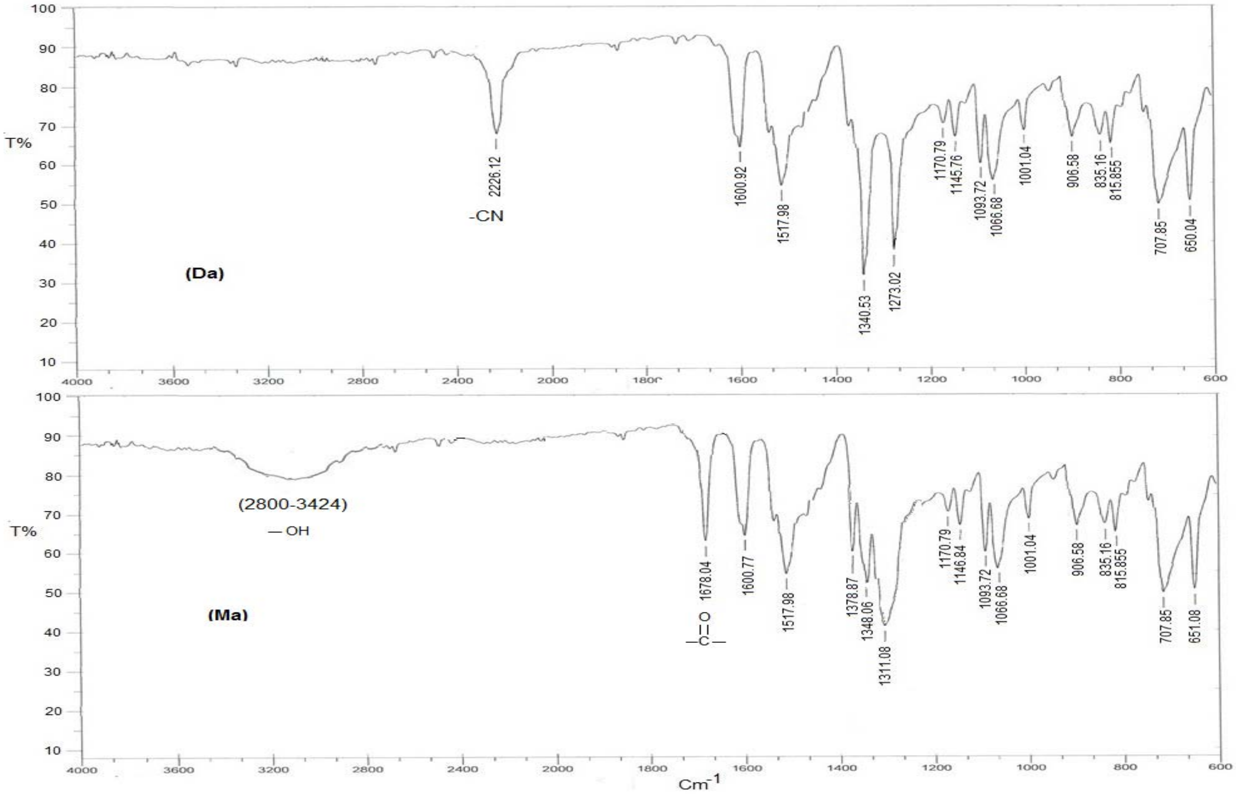


Figure 1: FTIR spectra of compounds **(Da)** before and **(Ma)** after hydrolysis.

The ^{1}H and ^{12}C-NMR spectrum are used to confirmed the structures of **(Da)** and **(Ma), Figure 2**. big sharp doublet peaks at 7.47-7.54(d, 4H, Ha) and 732-7.41 (d, 4H, Hb) were resulted from four phenylene protons (a) and (b) respectively. Two singlet peaks at 7.19 (s, 2H, Hc) and 2.17(s, 6H, H$_{CH3}$) are assigned to proton of (Hc) and three protons of the methyl group (CH$_3$) respectively.

The ^{13}C NMR spectra as shown in **Figure 2.** showed the two mains peaks of carbon atoms at 134.52 (C7) and 123.14 (C6) respectively. One peak at 118.62 (C$_{CN}$) for two cyano groups. Peaks at 116.38 (C$_1$), 137.16 (C$_3$) and 142.41(C$_4$) are assigned to the three single carbon atoms 1, 3 and 4 respectively. Other peaks at 150.22 (C5), 132.08 (C2) and 106.96 (C8) are assigned to these doublet C atoms. 17.52 (C$_{CH3}$) are resulting from doublet carbon atoms of CH$_3$ group.

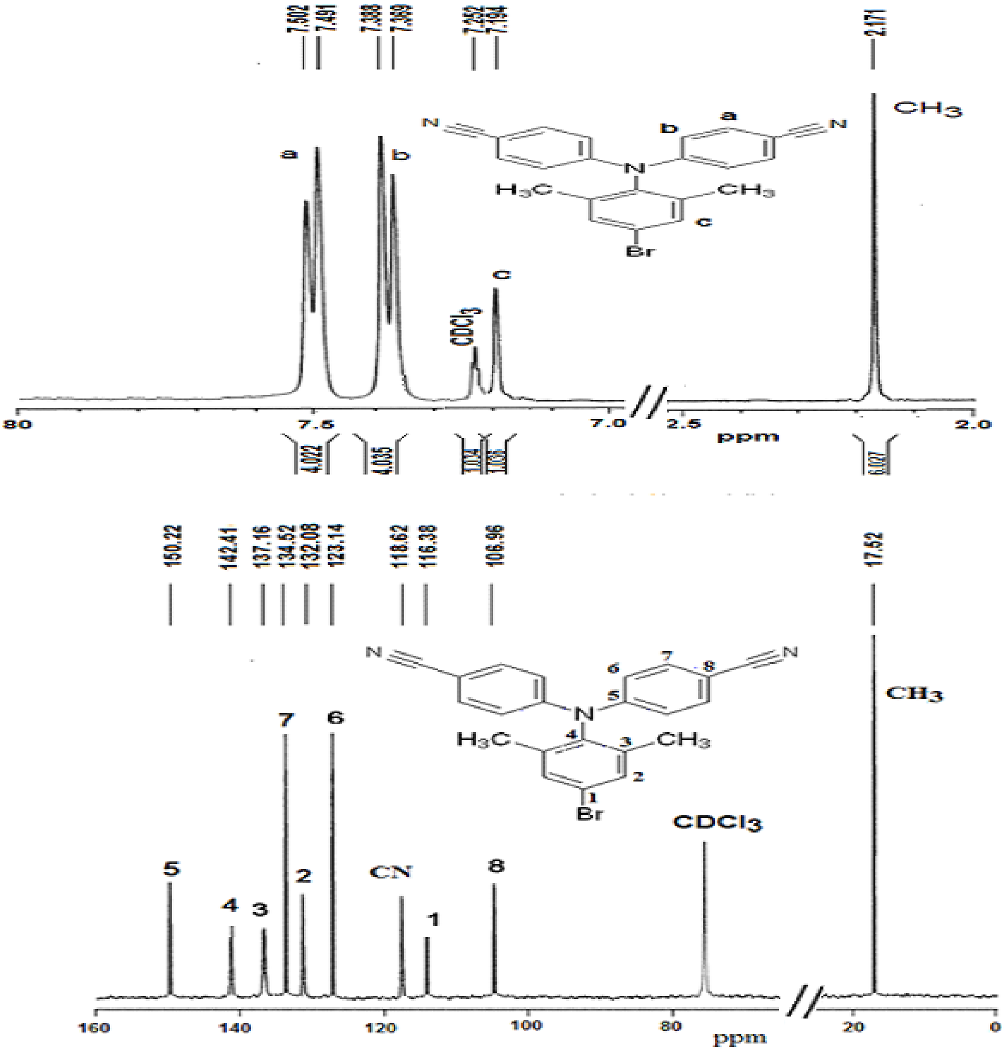


Figure 2: ^{1}H and ^{13}C NMR spectrum of compound (**Da).**

Figure 3. shows the proton of carboxylic group appeared as a very broad singlet peak and hardly observable resulting from the substitution of carboxylic group hydrogen atoms by deuterium of DMSO solvent and H-bonding formation, also the disappearance of the cyano carbon at 118.62 ppm and appearance of the carboxylic peak at 166.72 ppm.

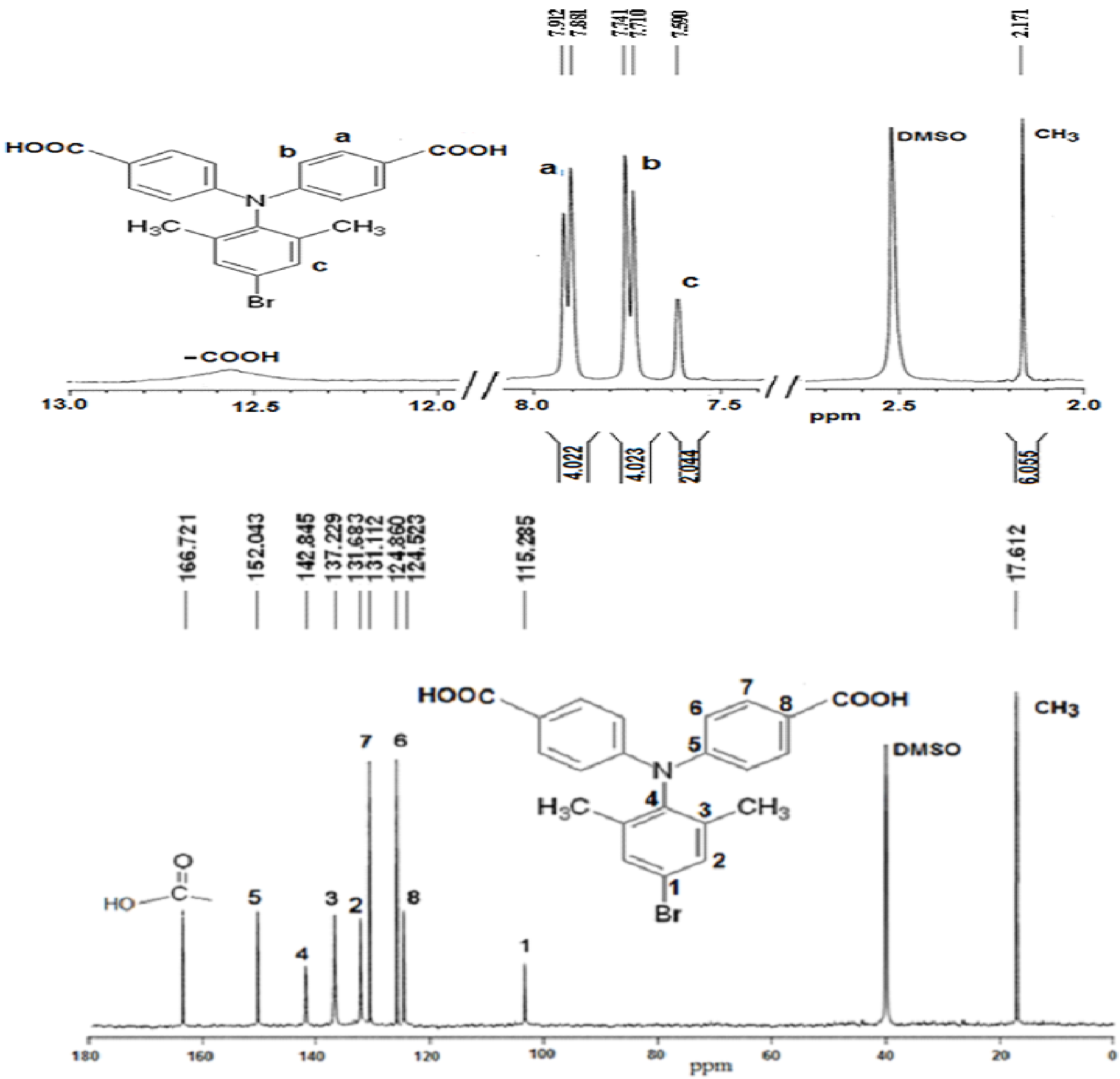


Figure 3: ^{1}H and ^{13}C NMR spectrum of (**Ma).**

3.2. Polyamides Synthesis

All the new aromatic polyamides bearing triphenyl amine (TPA) group are synthesized via polycondensation technique. The reaction of synthesized dicarboxylic acid monomers with two types of aromatic diamines (p-phenylenediamine and benzidine in the presence of pyridine and triphenylphosphite (TPP) as promote condensation reaction and $CaCl_2$ addition to decrease the hydrogen bonding in the polyamide chains. This leads to increase the solubility of these polyamides. The structural form of the synthesized (**Pa-Pf)** were confirmed by FTIR spectra which exhibited absorption bands around (3310- 3313) cm^{-1} (N-H stretching) and (1644- 1648) cm^{-1} (C=O stretching of amide group) as shown in **Figure 4.**

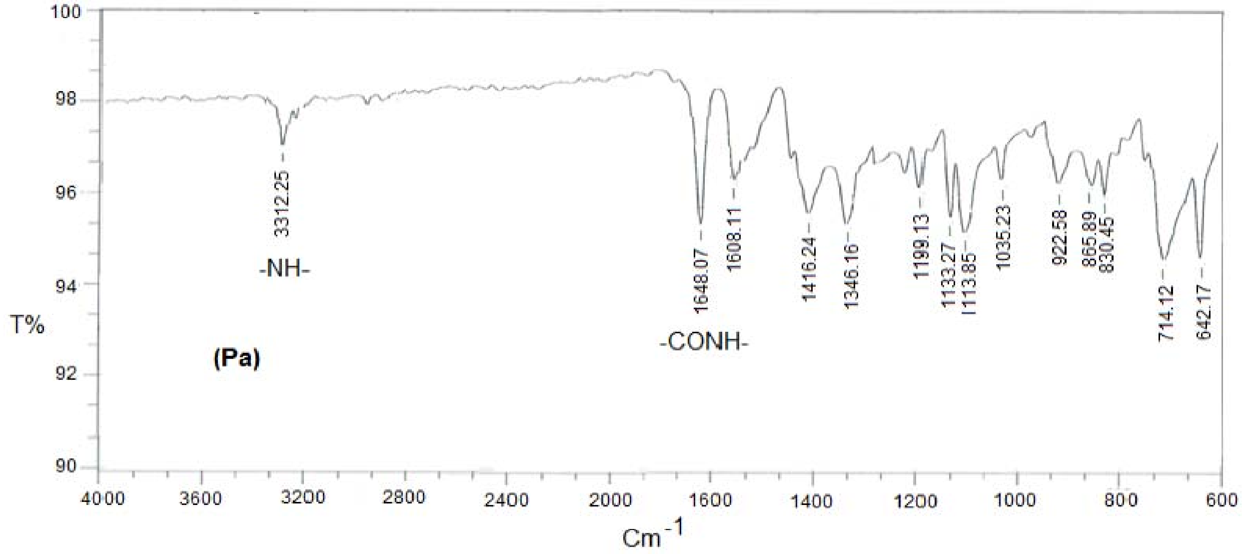


Figure 4: FTIR of the synthesized polyamides **(Pa).**

The ^{1}H NMR spectrum of **(Pa)** showed that the broad peaks of COOH proton groups appeared at 12.37-12.78. The ppm is disappeared with appearance of singlet peak at 10.21-10.28 after polymerization is assigned to the **(Pa)** amide group protons. The doublet peaks at 7.23-7.36 ppm and 7.86-7.98 ppm are resulting from the four protons **b** and **c** in the triphenylamine group respectively. Singlet peak in the region 7.72 ppm is assign to four equivalent protons d of the phenylene diamine groups. Singlet peak in the region 7.45 is resulting from 2 protons **a** in the ring of triphenylamine group **Figure 5**.

The figure also shows the ^{13}C NMR spectra of the polyamide (**Pa**), the main peak at 164.63 ppm is attributed to the carbonyl carbon atom of the polyamide. This carbon atom is with bigger chemical shifting resulting from the carbonyl group resonance with attached to a nitrogen atom with highly electronegative. ^{13}C NMR peaks are assigned to the carbon atoms 1, 3, and 4 of the first ring of the TPA at the regions **115.56 (C1), (131.23) C3** and **143.62 (C4)** respectively. The second ring has other peaks at the regions **127.84 (C2), 151.12 (C_5), 1119.04(6), 131.71 (C7)** and **124.62 (C8).** Tow peaks assigned to the two equivalent carbon atoms 9 at the region 131.71 and of four carbon atoms 10 at the region 116.30 in the phenylene diamine ring group. One peak for tow carbon atoms of the methyl groups at the region 17.61.

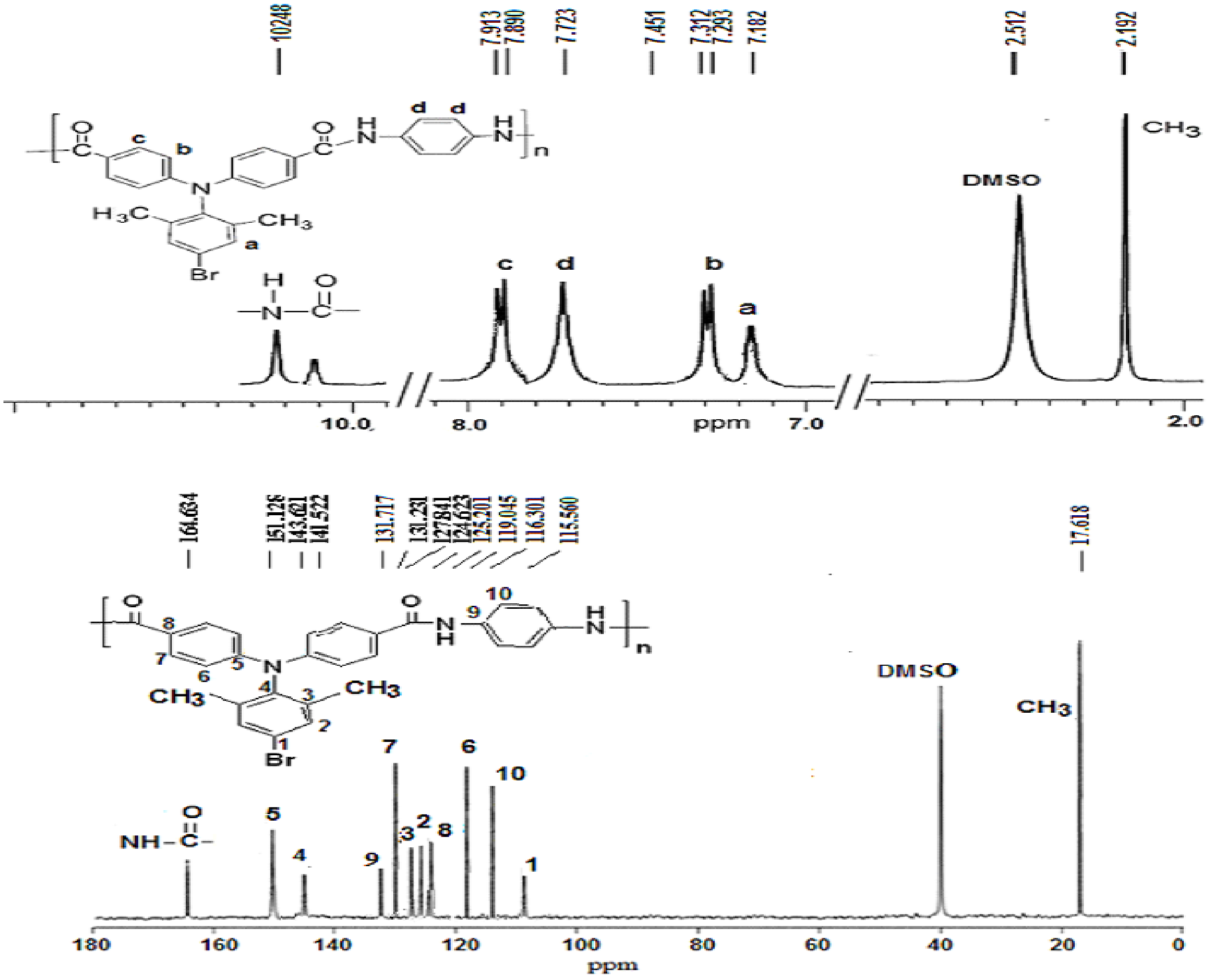


Figure 5: ^{1}H and ^{13}C NMR spectrum of the polyamide (**Pa).**

3.3. Properties of the synthesized polyamides

3.3.1. Thermal properties of the polyamides

The thermal behaviors of all polyamides were checked via DSC and TGA technique. DSC measurements are investigated with ACAN rate of 20 ºC /min in N_2. They gave high (Tg) in the average of (245.5 - 278.8) °C. **Figures 6** shows the (Tg) values of all polyamides (**Pa) - (Pd)** and (**Pe) - (Pf)** respectively. In general, if the diamine component in the polyamides decreases leads to decrease the stiffness and the (Tg) values. Polyamides with phenylene diamine showed high Tg value resulting from increasing of chain rigidity compared with polyamides with diphenylene diamines. It is agreeing with the values of glass transitions (Tg) of the polyamides (**Pa), (Pb)** and (**Pc)** with the rigged chain which have higher (Tg) than other polyamide **(Pd), (Pe)** and **(Pf)** with lower stiffness chain because of their flexible diamine diphenylene component.

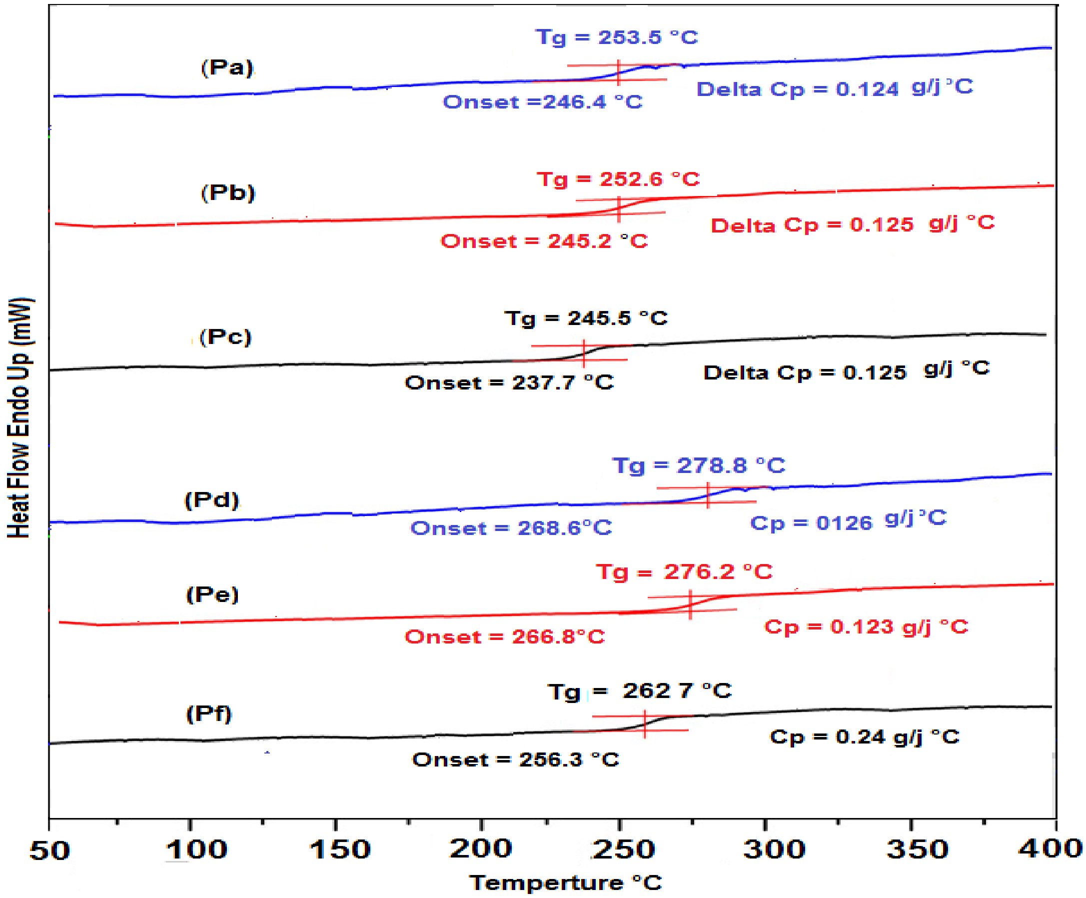


Figure 6: DSC of **(Pa), (Pb)** and **(Pc)**.

The thermal decomposition behavior of the synthesized poly (amine amide) is evaluated by TGA analysis with a heating rate of 20 °C /min in nitrogen atmosphere. The lowest onset temperature in which the polyamides started to decompose was 305.6 °C up to 365 °C for samples. Polyamides **(Pd), (Pe)** and **(Pf)** revealed onset degradation temperature (T^d) at the range (305-330) °C because of their flexible chain comparison with the rigid chain polyamides **(Pa), (Pb)** and **(Pc)** which showed higher onset (T^d) at the range (335-362) °C. The 10% weight loss temperatures (T^d10%) were investigated in the range of (380-420) °C for the flexible polyamides and (442-466) °C for rigid polyamides. The synthesized polyamides exhibited residual yields about (43-54) % at 800°C, **Figure 7.** and **Table 1.** shows the thermal data of the polyamides.

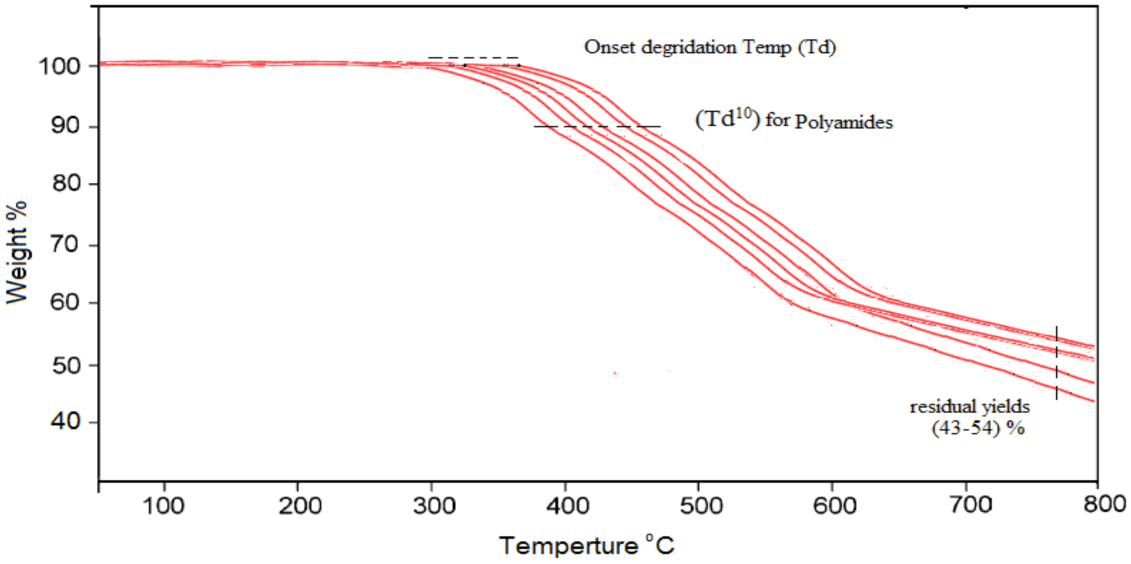


Figure 7: UV-vis absorption of the polyamides in 10^{-5} DMSO.

Table 1: Thermal data of the polymides.

Polyamide codes	**(Tg) Onset (°C)** a	**(Td) Onset (°C)** b	**(Tg) (°C)** c	**(Td) 10% (°C)** d	**Residual yields (%)** e
(Pa)	246.4	362	353.5	466	54
(Pb)	245.2	352	352.6	458	52
(Pc)	137.7	335	245.5	442	47
(Pd)	268.6	330	278.8	420	51
(Pe)	266.8	315	276.2	412	50
(Pf)	256.3	305	262.7	380	43

a: onset temp.

b: onset temp. of baseline shifts of DSC trace.

c: Onset temperature of the decomposition polymer

d: Decomposition temp. of 10% weight loss

e: Residual weight percent.

3.3.2. Optical Properties

UV-Vis and photoluminescence spectroscopy (PL) techniques have been used to calculate the optical behavior of the polyamides. All data are listed in **Table 3-2**.

Polyamide Solutions in concentrations of 10^{-5}M in (DMSO) gave intensive UV-Vis absorption bands in an average of (301.4–364.3) nm resulting from the (n-π*) transitions assignable to the nitrogen atoms conjugation with aromatic rings in (TPA) units and (π-π*) transitions in the diamine phenylene rings chromophore and triphenylamine [28]. Polyamides **(Pd), (Pe)** and **(Pf)** gave lower UV-Vis λabs max absorption compared with **(Pa)**, **(Pb)** and **(Pc)** because they have extra (π-π*) transitions of further diphenylene with (n-π*) electronic transitions so they need excess absorbance energy for transition than polyamides with phenylene diamine which require low absorption energy **Figure 8**.

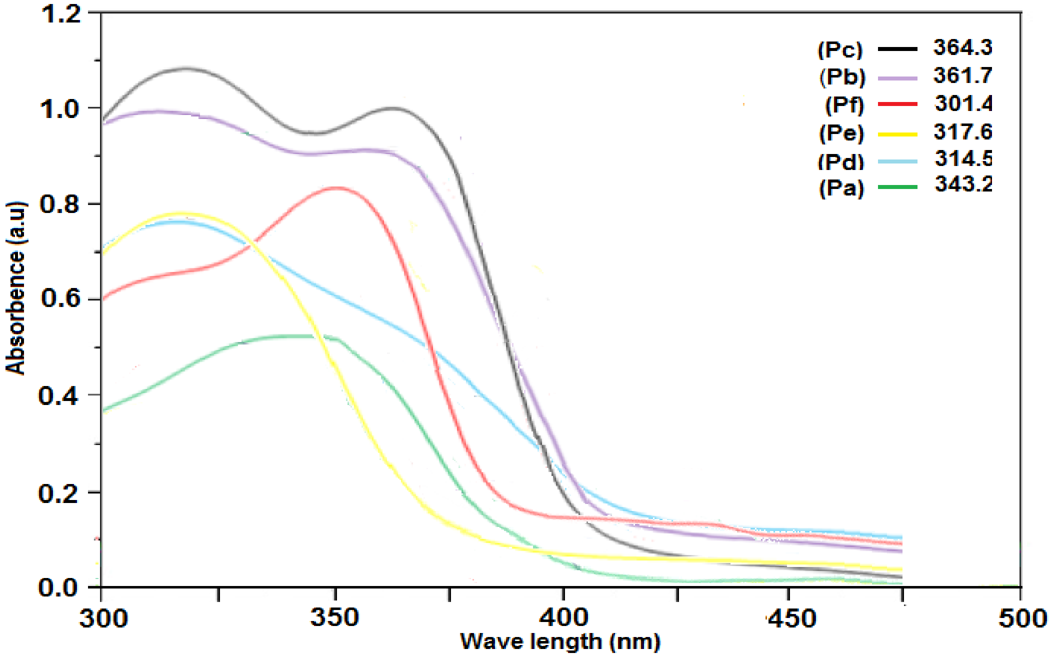


Figure 8: UV-vis absorption of polyamieds in 10^{-5} DMSO.

Solution of polyamides in DMSO gave PL emission bands in the blue region at the average (438 – 462) nm (**Figure 9**). PL spectra is assignable from the low inter and intra molecular electronic interactions. The large triphenyl unit led to decrease the charge transfer formation within or between polymer chains by steric hindrance. Polyamides **(Pa)**, **(Pb)** and **(Pc)** have convergent and higher λPL values rather than in polyamides **(Pd), (Pe)** and **(Pf)** diphenylene diamine in which increase the excitation of π-electrons which leads to decrease the λPL. **Table 2** shows optical behaviors data of the polyamides.

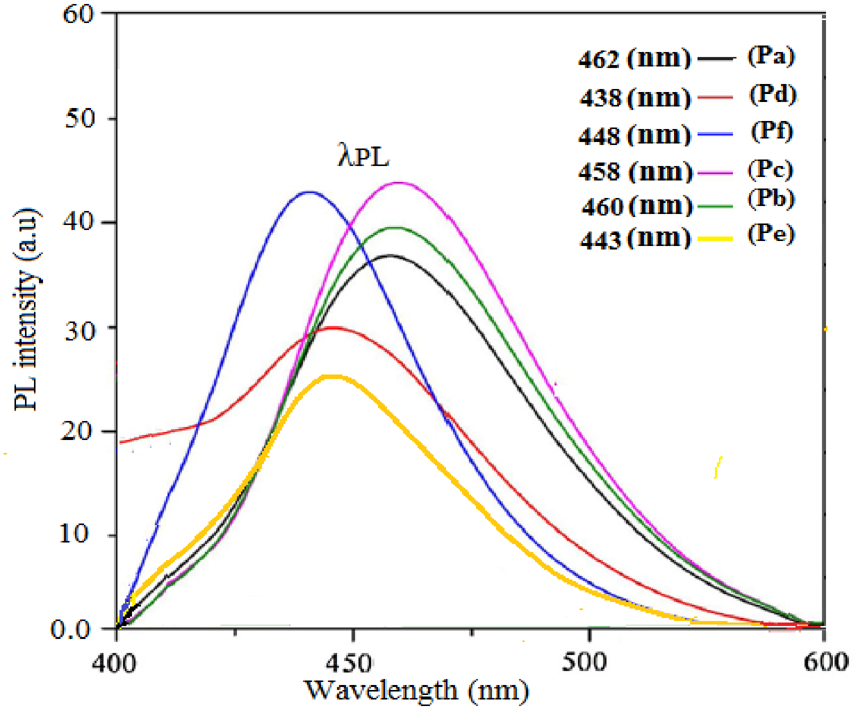


Figure 9: Photoluminescence of the polyamides in 10^{-5} DMSO.

Table 2: Optical properties all polyamides.

Polyamide codes	λabs Onset (nm)a	λabs max (nm)a	λPL (nm)b
(Pa)	406	343.2	462
(Pb)	410	361.7	460
(Pc)	404	364.3	458
(Pd)	406	314.5	438
(Pe)	393	317.6	443
(Pf)	398	301.4	448

3.3.4. Electrochemical Properties

Cyclic voltammetry (CV) was used to verify the redox properties of synthesized polyamides. The method supports on synthetic a working electrode as anode by coating a special glass plate containing (TiO) by a thin layer of the polyamide. This electrode is a part of the electrolytic cell with external cathode electrode Ag/AgCl. The used electrolyte in this proccese is dry CH_3CN contains 0.1 M of tetrabutylammonium perchlorate (Bu4NH4ClO$_4$).

Figure 11. shows a typical cyclic voltammetry curve for the synthesized polyamides **(Pa)-(Pf).** All polyamides showed the half-wave at oxidation potential in the range E1/2 = (1.13-1.28) V with scan rate at 0.2 V/s to remove two unpaired electrons from the nitrogen atom at each repeating triarylamine unit to form stable polymide^{2+} [29].

By change the potential scans between 0.0 - 1.51 V lead to conversion the pale yellowish color to the blue (**Figure 11.** HOMO and LUMO) energy levels of the compatible polyamides is calculated from the oxidation half-wave potential E1/2 and the onset absorption wavelength of the UV-Vis absorption (λabs onset) of the solution [30]. The result data are listed in **Table 3**. The external ferrocene/ferrocenium (Fc/Fc+) redox standard E1/2 was 0.41 V vs Ag/AgCl in CH3CN and the HOMO energy for the Fc/Fc+ standard was 4.80 eV.

Energy gab **(Eg)** can be calculated by the equation:

Eg = 1242/ λabs, onset (1)

Where **1242** is a constant, λabs onset is the onset wavelength which can be calculated by intersection of two tangents on the absorption edges as shown in **Figure 10.**

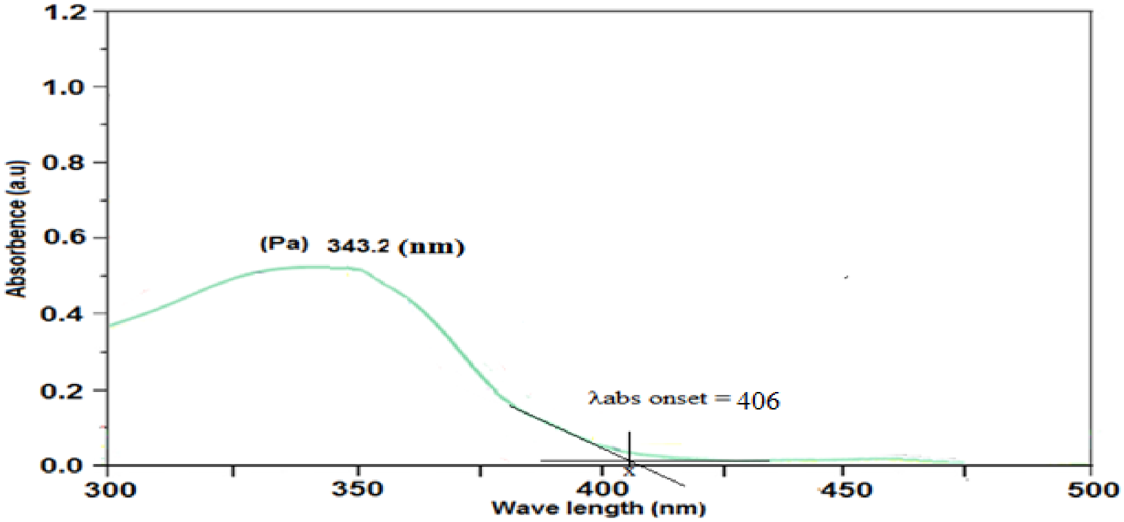


Figure 10: Uv-Vis absorption spectrum of polyamide **(Pa)** in (10^{-5} M) DMSO.

Therefore, the HOMO energy for **(Pa)** can be calculated as follows:

E_{HOMO} = [E1/2 ─ E1/2(ref.) +4.8] eV (2)

Where E1/2 is the oxidation half-wave potential which can be determined from the relation:

E1/2 = (Ered + Eox) /2 (3)

Where **Ered** and **Eox** are the potentials of cathode and anode respectively

E1/2 (ref.) is the external standard oxidation energy of ferrocene/ferrocenium ion couple under the same experimental conditions. Its value is 0.41 V versus Ag/AgCl in CH3CN.

From application of above equations on the synthesized polyamide **(Pa)** as following:

E1/2 = (Ered + Eox) /2

E1/2 = 1.12 V + 1.36 V / 2 =1.24V

E_{HOMO} = [E1/2 - E1/2(ref.) +4.8] eV = [1.24 V - 0.41 V + 4.8] eV

E_{HOMO} = 5.63 eV

E_{gap} = 1240/λabs.onset = 1240/406 = 3.05 eV

E_{HOMO} - Egap = E_{LUMO}

E_{LUMO} = 5.63─3.05 = 2.58 Ev

By using same method, the same data calculated for other polyamides as shown in the **Table 3**.

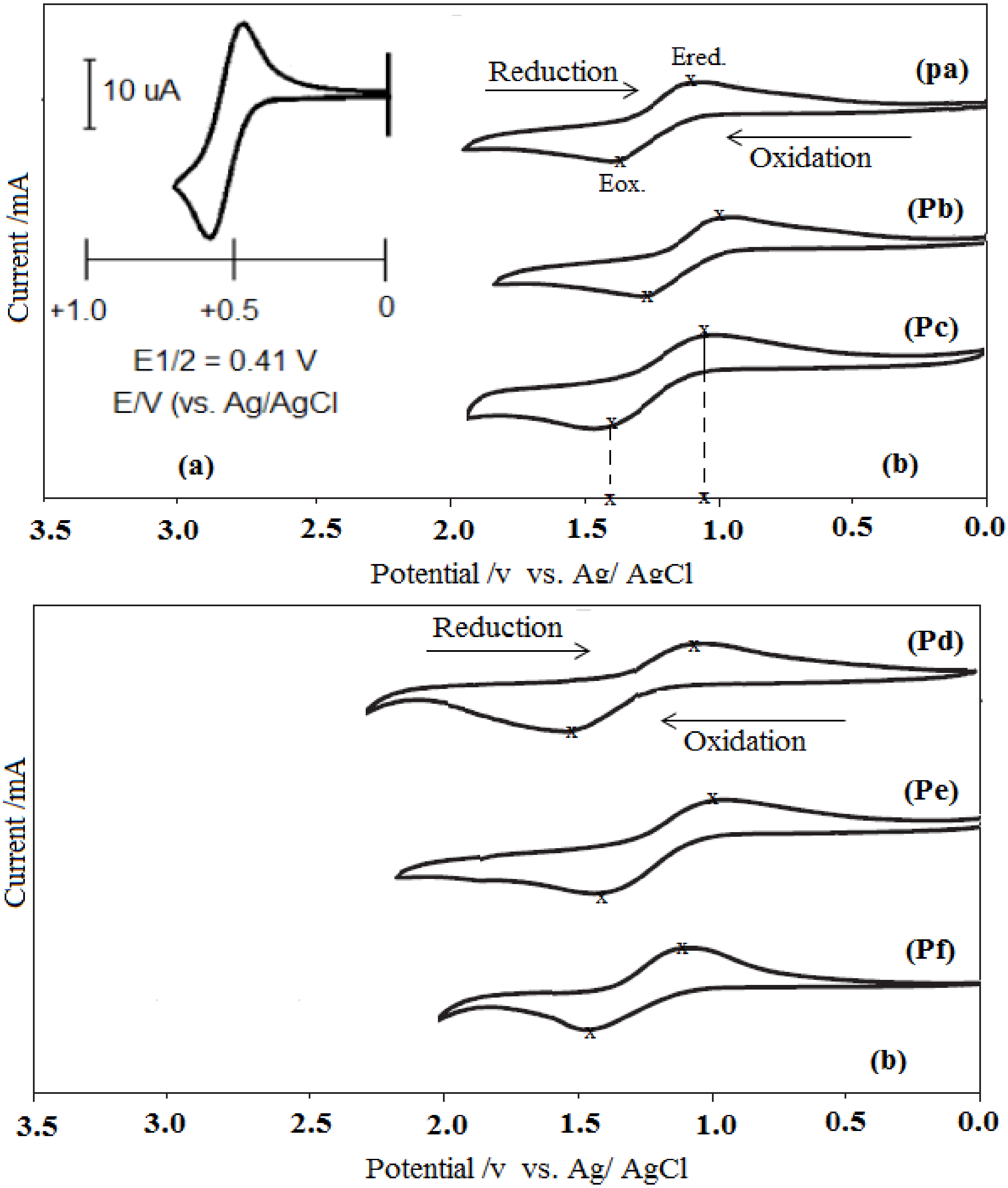


Figure 11: (C.V) of (a) Ferrocene as reference and (b) the cast film of polyamides.

Table 3: electrochemistry data for all the synthesized polyamides.

Polymer codes	E1/2 V vs.Ag/AgCl	λabs, onset (nm)	E_{Homo} a (eV)	E_{Lumo} b (eV)	E_{Homo}-E_{Lumo} c gap (eV)
(Pa)	1.24	406	5.63	2.58	3.05
(Pb)	1.13	410	5.52	2.50	3.02
(Pc)	1.24	404	5.63	2.56	3.07
(Pd)	1.27	406	5.66	2.61	3.05
(Pe)	1.24	393	5.63	2.48	3.15
(Pf)	1.28	398	5.61	2.50	3.11

a: HOMO energy levels were calculated from (C.V) which
referenced to ferrocene/ferrocenum couple (4.8 eV).

b: E_{Lumo} =E_{Homo} – Egap.

c: Energy gap data

4. Conclusion

New amorphous polyamides having triarylamine group in their backbone structure have been successfully synthesized from the reaction of aromatic dicarboxylic acid with aromatic diamines. All these polymers were characterized by excellent thermal properties such as glass transition (Tg) was in the range (245.5-278.8) °C, its thermal stability was also very high. Polyamides with mono phenylene diamine showed a high Tg value due to its high hardness of single phenylene amine compared with than di phenylene diamine with lower stiffness and rigidity. The optical properties (Uv-Vis) and photoluminance spectroscopy were analyzed for the solutions of all polyamides in concentration10^{-5} M in DMSO which showed strong UV-Vis absorption at the ranges (301.4 - 364.3) nm and PL emission ranges at about (438-462) nm. All polyamides showed halve oxidative wave at a scan rate of 0.2 V / s to convert the original yellowish color to the blue.

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