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New N-triaryl-substituted polyamides materials as light Emitters for semiconductors applications

Kawther Ayad Obead **Azhar Kamil Rashid**

Department of Chemistry, College of Education for Pure sciences Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq.

kawtyher70@yahoo.com azhar_almasody@yahoo.co.uk

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Abstract

In this work, new di-acid monomers 4, 4’-di-carboxillic-2”-chloro-4”- nitro triphenylamine (Di-CO2H-1), 4, 4’- di-carboxylic -2”,4”,6”-trichloro-triphenylamine (Di-CO2H-2) were synthesized by reaction of p-cyanobenzofluride with two aromatic amines (2-chloro 4-nitro aniline and 2,4,6-trichloro aniline by aromatic nucleophilc substitution method to produce two di cyano intermediates compounds 4, 4’-Dicyano-2”-chloro-4”- nitro triphenylamine (Di-CN1) and 4, 4’-dicyano-2”,4”,6”-trichloro-triphenylamine (Di-CN2) 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 2”-chloro-4”- nitro -triphenylamine-4, 4'-polyphenylbenzamide (Pa), 2”,4”,6”-trichloro-triphenylamine -4,4'-polyphenylbenzamide (Pb), 2”-chloro-4”- nitro triphenylamine-4,4'- polyphenylbiphenylamide (Pc), 2”,4”, 6”-trichloro-triphenylamine-4,4’-polyphenylbiphenylamide (Pd). The chemical structure of these polymers characterized by FTIR and NMR techniques. The polyamides showed a good thermal stability with height glass transition temperatures (Tg). Thin casting films of these polyamides in cyclic voltammetry (C.V) on glass substrate 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: glass substrate, polyamides, benzidine, thermal stability, working electrode.

1. Introduction

Polyamide compounds containing tri-arylamine groups are positively charged carrier in the application of light emitting polyamide (PLEDs). This type of polymers has received considerable attention because of its important applications in many areas including screens and lighting points [1, 2]. Polyamides with tri-arylamine groups appear as electrochromic materials as whole transporting layer in LED devices [3-8]. These polyamides are known as low ionization of energy and activity and oxidized easily to be converted to stable radical cations [9-13]. These aromatic polyamides are known as a high rigid material resulting from hydrogen bonding between their backbones.

This phenomenon of these polyamides for which there might be a wide range of applications, including optical switching devices, smart windows, memory elements, largearea information panels, electronic papers (e-papers), and chameleon materials. [14–21]. The main application of semiconductor in daily life is used in solar technology, used in 3D printing. machines, temperature sensors which used in air conditioners. In industry, the properties of semiconductor materials make possible numerous technological wonders, including transistors, microchips, solar cells, and LED displays. With the microprocessor, we can control the operation of car, trains and space vehicles. The microprocessor is made up by numerous transistor and other controlling devices, which made up by the semiconductor material

When the big group are incorporated between these backbones lead to break this rigidity and make the chains with high flexibility [22-24]. All aromatic polyamides are high performance polymers due to their high thermal and mechanical stabilities [25-26].

Polyamides are called conducting polymer because of these behaviors as electrochromic materials [27–30].

Withdrawing groups in the polyamids chains increase their oxidation behavior and solubility in organic solvents [31-34].

2. Materials and Methods

2.1. Materials

Sodium hydride (Aldrich, 98%), 4-fluorobenzonitrile (Aldrich, 97.5%), 2-chloro-4- nitro aniline, (Acros, 97%), 2”,4”,6”tri-chloro aniline, (Aldrich, 95%), Dimethylsulfoxide (DMSO) (Merck, 98%), Ethanol (Merck, 99.5%), Triphenyl phosphite (Merck, 98%), CaCl2 (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 spectra of FT-IR for all new materials were measured by Shimadzu, 8400s, spectrometer. ^{1}H and^{13}C- NMR data are recorded by a Bruker spectrometer at 400 MHz, UXNM. UV–vis absorption spectrum were performed in (10^{-5} M) DMSO on Shimadzu, UV-1800,1 nm. DSC and TGA were performed on a Perkin Elmer DSC6 instrument under N2 atmosphere with a scan rate of 20 °C/min and an SDT Q600 thermogravimetric analyzer.

2.3. Synthesis of di-cyanide Intermediates (Di-CN1) and (Di-CN2)

2.3.1. Synthesis of 4, 4’-Dicyano-2”-chloro-4”- nitro triphenylamine (Di-CN1)

In a round flask with stirrer containing 80 mL (DMSO), was added 2 g (0.02 mol) of NaH at a room temperature for half an hour. 2.50 g (0.02 mole) of 4-fluorobenzonitrile, 2.00 g (0.02 mole) of 2-chloro-4- nitro aniline were added alternately. The stirring mixture was heated at 100 °C for 12 h. After cooling, poured into about 300 mL of cold water. After filtering of the yellowish precipitate product recrystallized from ethanol 2.7 g (yield: 73%), m.p = 160 C°. FTIR: 2229 Cm^{-1} (CN), (1579, 1489) Cm^{-1} ($NO2$) stretch. Other di-cyanides prepared by using same above method.

2.3.2. Synthesis of 2”,4”,6”tri-chloro Triphenylamine (Di-CN2)

Red brown precipitate, 1.2 gm (yield: 60 %), m.p = 158 C°. FTIR: 2220.61 cm^{-1} (CN), (1510, 1446) Cm^{-1} ($NO2$) stretch.

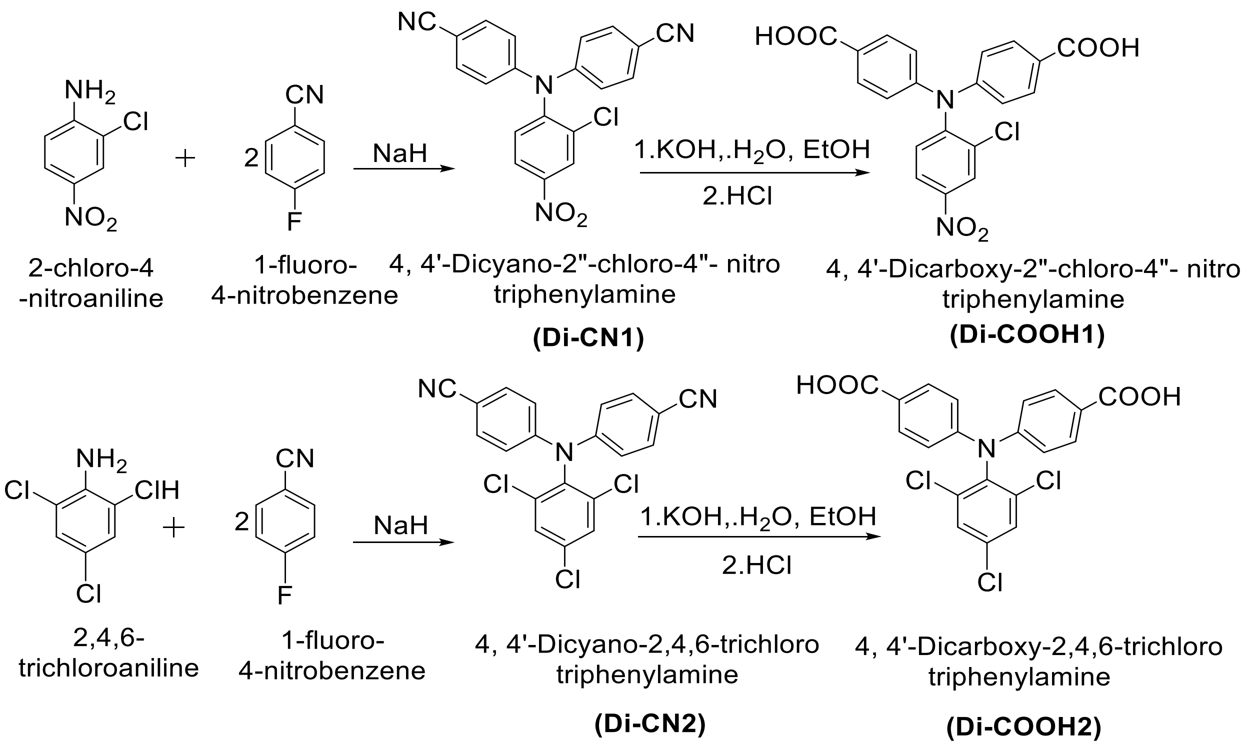
2.4. Synthesis of Di-Carboxylic Monomers

2.4.1. Synthesis of 4, 4’- Di-carboxylic -2”-chloro-4”- nitro triphenylamine (Di-COOH1)

A mixture of 2.00 g (0.02 moles) of di-cyanide intermediate **(Di-CN1)** and 8.00 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, 1.8 g (82% yields), mp = 222°C. FTIR: 1681cm^{-1} (C=O), 2787-3358 cm^{-1} (O-H).

2.4.2. Synthesis of 4, 4’- Di-carboxylic -tri-chloro- triphenylamine (Di-COOH2)

Red brown precipitate, 1.7 g (77% yields), m.p = 210 C°. FTIR: 1678 cm^{-1} (C=O), 2776-3342cm^{-1} (O-H).



Scheme 1. The synthesis routes of di-cyanide intermediates and the monomers**.**

2.5. Synthesis of Polyamides (P1-P4)

2.5.1. Synthesis of (P1)

The stirring mixture of 0.10 g (0.03 mole) of p-phenylenediamine, 0.4 g (0.03 mole) of the monomer **(Di-COO1)**, 4.0 mL of triphenyl phosphite (TPP), 0.5 g of calcium chloride, 2.0 mL of (NMP) and 2 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 dark brown precipitate collected after filtration, washed by hot water and dried in thermal oven for 24 h [35]. (76 % yield), mp = 255°C. The FTIR spectrum band of amide group was at 3312.25 (N-H stretching), and 1648.07 cm^{-1} (amide carbonyl).

By using same above method, other polyamides (**P2) - (P4)** were prepared.

2.5.2. Synthesis of (P2)

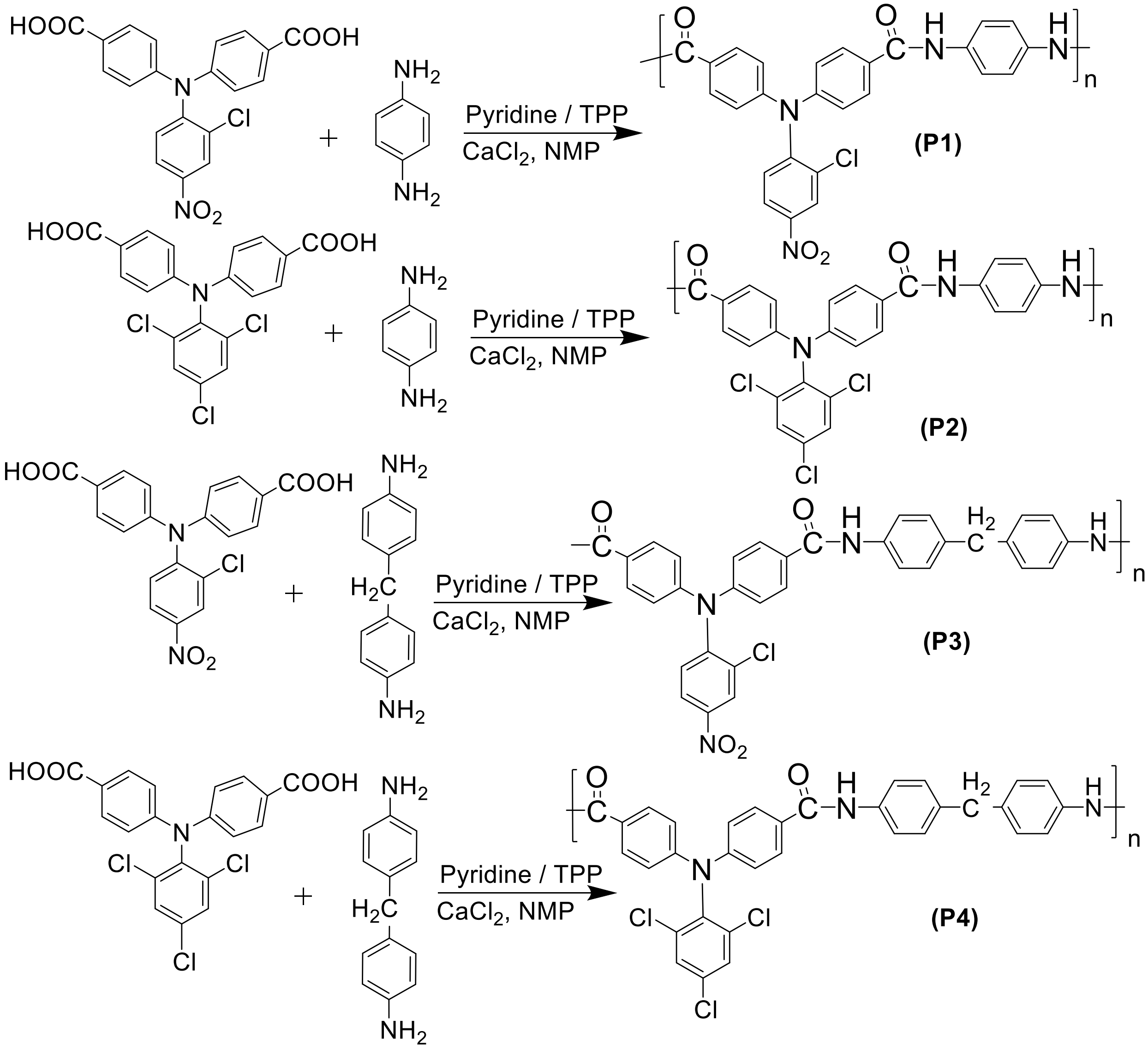
Dark brown precipitate, m.p= 241 °C, (78 % yield), IR spectrum 3344 cm^{-1} (N-H stretching) and 1639 cm^{-1} (amide carbonyl).

2.5.3. Synthesis of (P3)

Brown precipitate, m.p= 160 °C, (71 % yield), IR spectrum 3360 cm^{-1} (N-H stretching) and 1654 cm^{-1}(amide carbonyl).

2.5.4. Synthesis of (P4)

Dark brown precipitate, m.p= 120 °C (68 % yield), IR spectrum 3394 cm^{-1} (N-H stretching) and 1654 cm^{-1}(amide carbonyl). **Scheme 2.** Shows the synthesis routs of (P1-P4).



Scheme 2. The synthesis routs of **(P1-P4).**

3. Result and Discussion

3.1. Monomer Synthesis

The new monomers (DI-COOH1) and DI-COOH1) were synthesized by the hydrolysis of synthesized intermediates (DI-CN1) and (DI-CN1) to form the final product s shown in **Scheme 1.** All the chemical characterization of the intermediate and monomers were confirmed by FTIR and NMR technique. Intermediate Compounds (Di-cyanides) showed a characteristic band in the range (2220- 2229) cm^{-1} (C≡N stretching). The (di-carboxylic) monomers gave after the intermediates hydrolysis, absorption band in the ranges (1678-1681) cm^{-1} (C=O), broad band (2787-3358) cm^{-1} (O-H) for (Di-COOH1) and 1678 cm^{-1} (C=O), 2776-3342cm^{-1} (O-H) for (Di-COOH2) **Figures 1, 2.**

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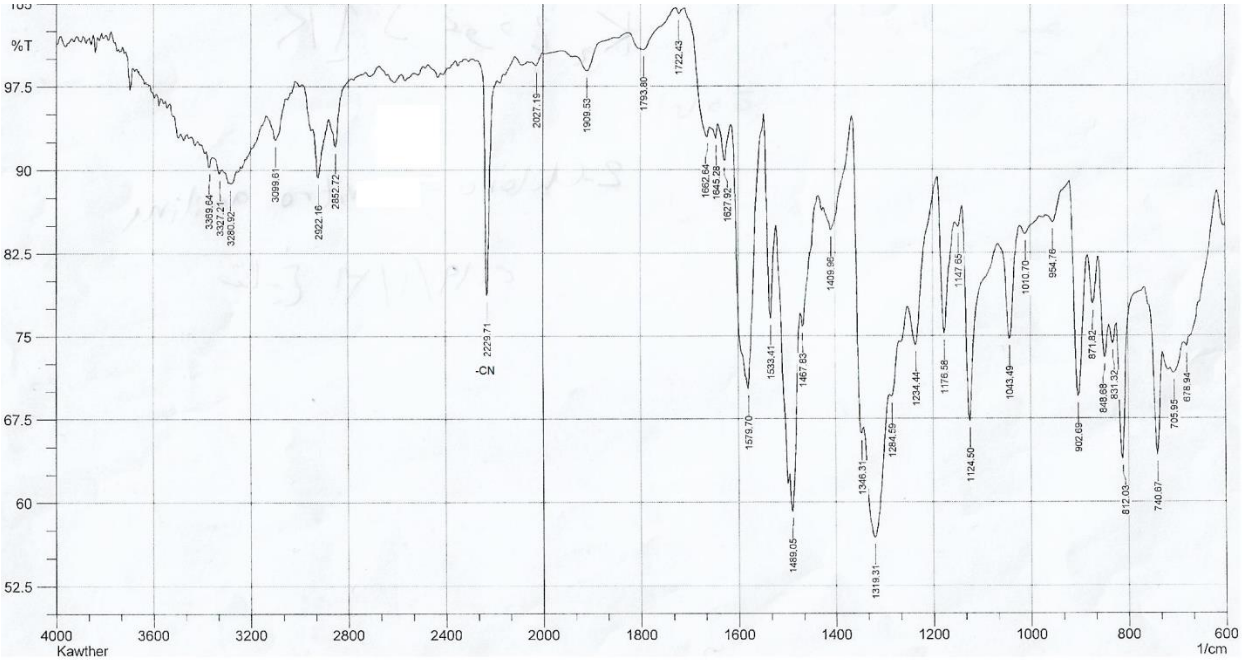

Figure 1. FTIR spectra of the intermediate (Di-CN1) before hydrolysis.

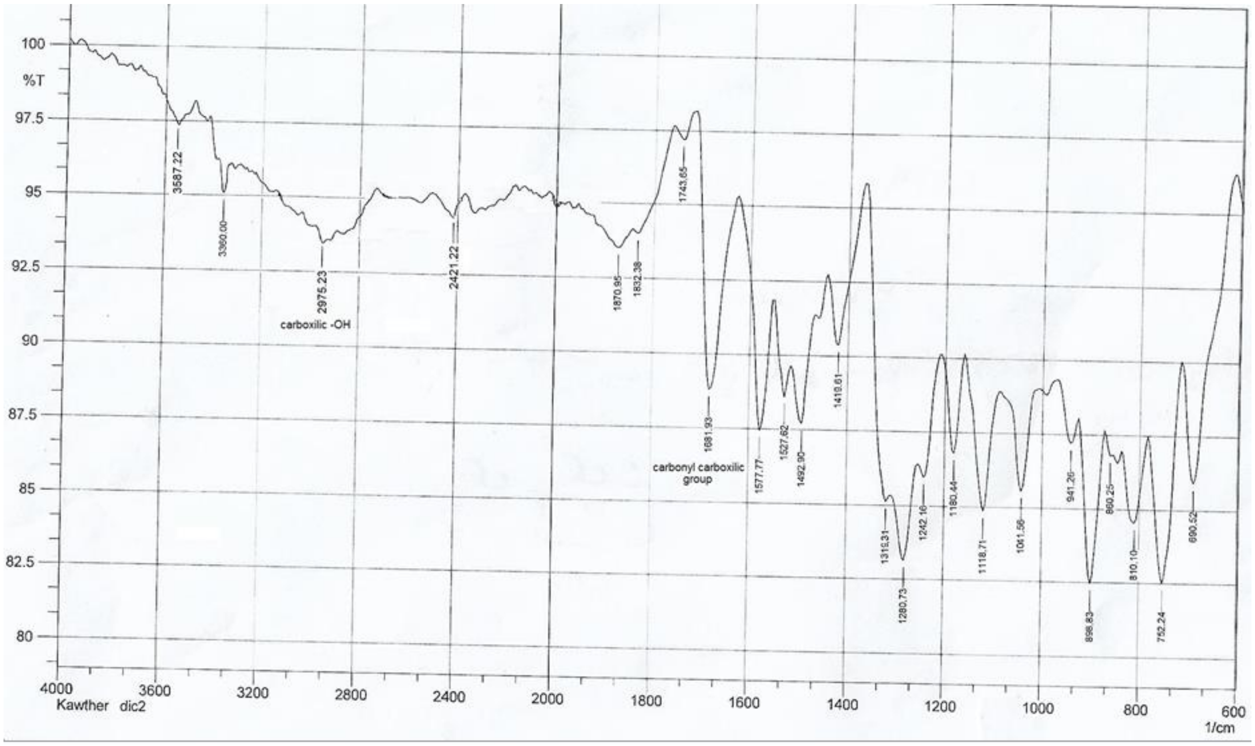

Figure 2. FTIR spectra of the monomer **(Di-COOH1)** after hydrolysis.

^{1}H and ^{12}C-NMR spectrum are used to confirm the structures of (Di-CN1) and (Di-COOH1). **Figure 3.** Shows big sharp doublet peaks (a) and (b) resulting from four phenylene protons **(a)** and **(b)** respectively. Two doublet peaks **(e)** and (**d)** are assignable to protons He and Hd. One singlet proton is assignable to proton **(c)** Hc.

^{13}C NMR spectra as shown in **Figure 3.** Showed the two mains peaks of carbon atoms 2 and 3 assignable to the four carbon atoms No. 2 four atoms No. 3. One peak is resulting from two carbon atoms of (CN) group. Peak No. 4 is assignable to two carbon atoms. Finally, singlet peaks 5,6,7,8,9,10 are resulting from carbon atoms with same numbers.

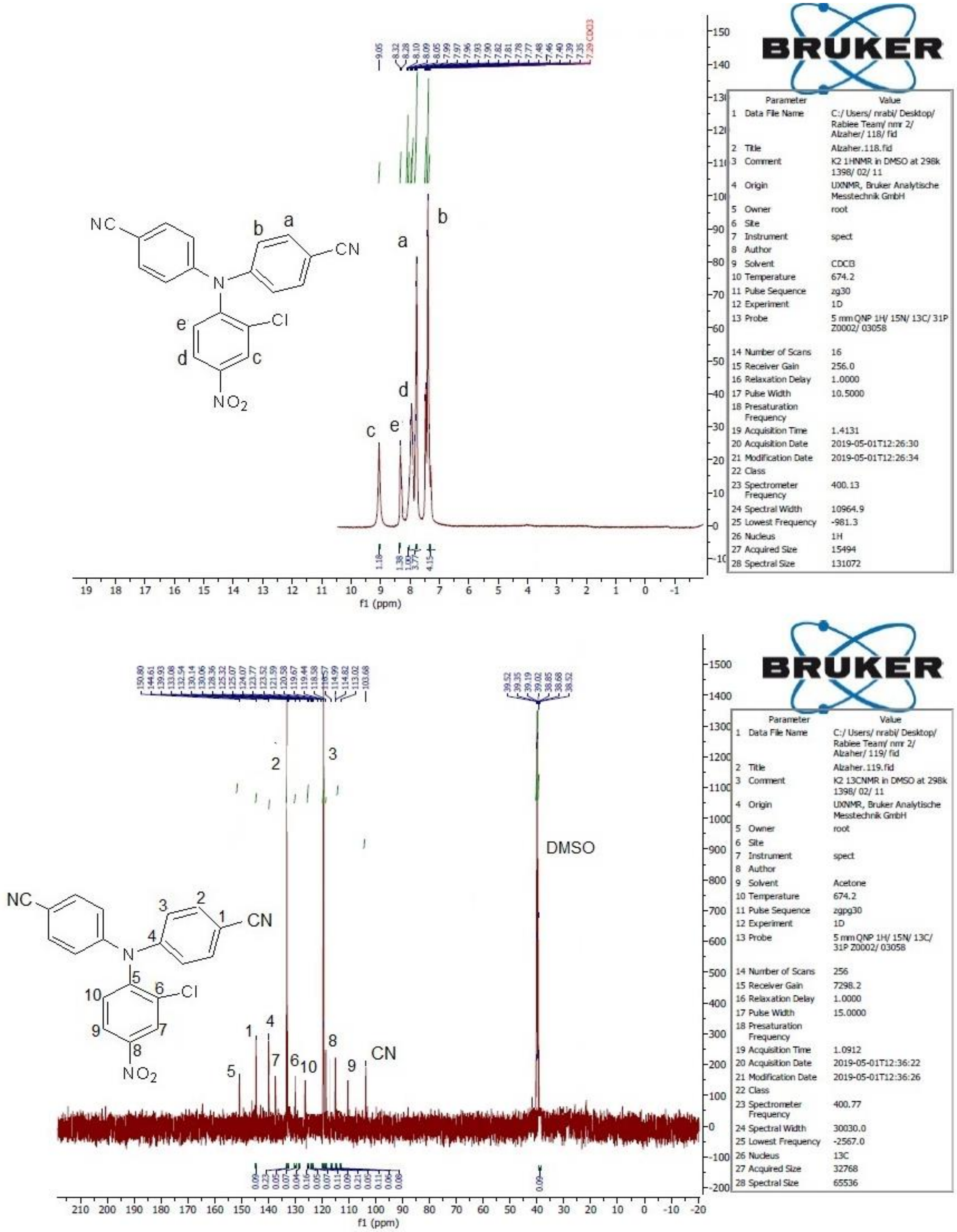

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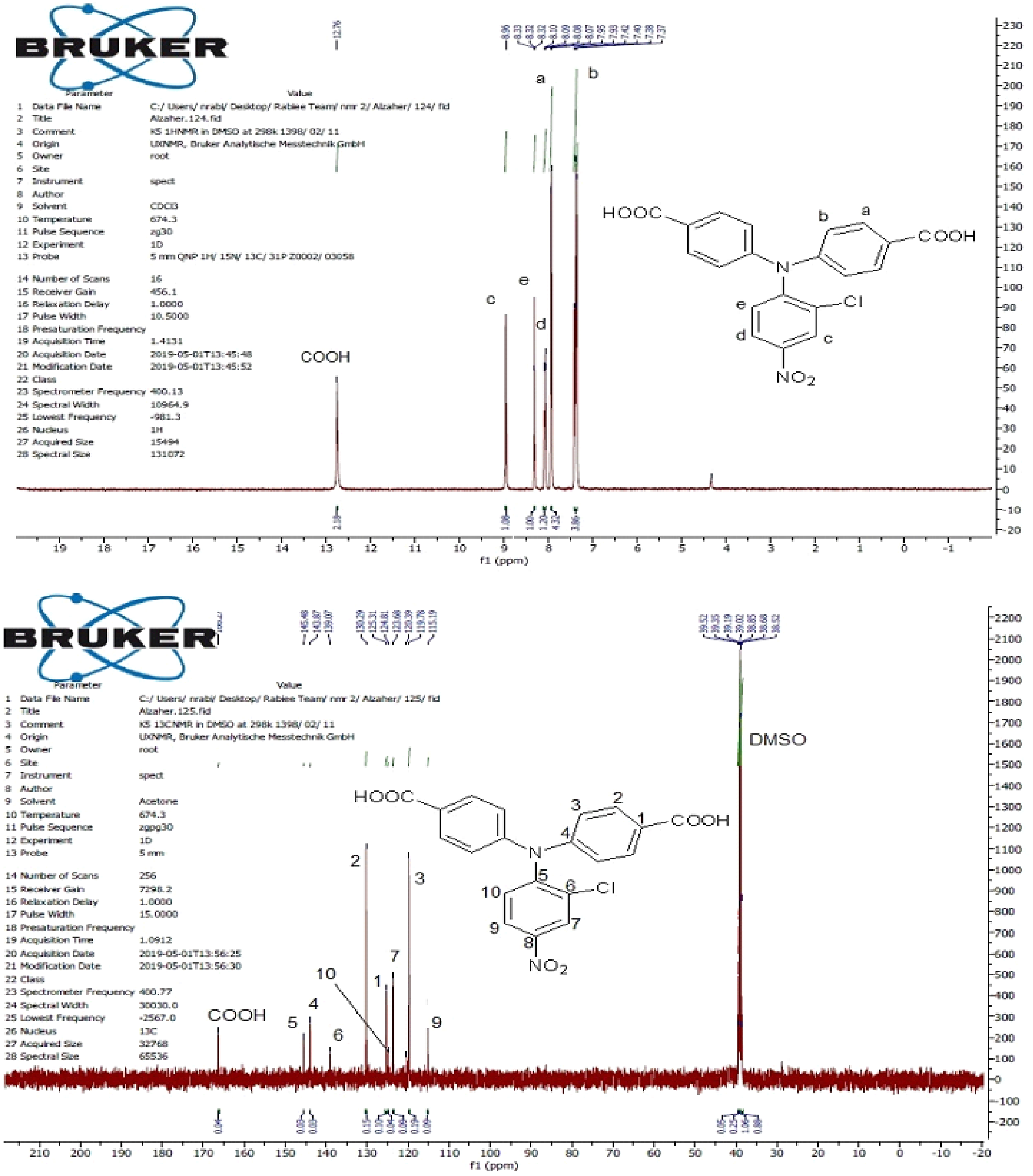
Figure 3. ^{1}H and ^{13}C NMR spectrum of the (Di-CN1).



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26	Nucleus	13C
27	Acquired Size	32768
28	Spectral Size	65536

Figure 4. ^{1}H and ^{13}C NMR spectrum of the monomer (Di-COOH1).

Figure 4. Shows a very broad singlet peak and hardly observable proton of carboxylic group at the chemical shift 12.76 resulting from the proton substitution of the carboxylic group with deuterium of DMSO solvent and H-bonding formation. Other evidence is disappearance of the carbon atom of the CN peak at 103.68 ppm and appearance of the carboxylic peak at 167.67ppm.

3.2. Polyamides Synthesis

The structure form of the synthesized (P1-P4**)** were confirmed by FTIR spectra which showed absorption bands in the range (3313- 3318) cm^{-1} (N-H stretching) and (1639- 1654) cm^{-1} (C=O stretching of amide group) as shown in **Figure 5.**

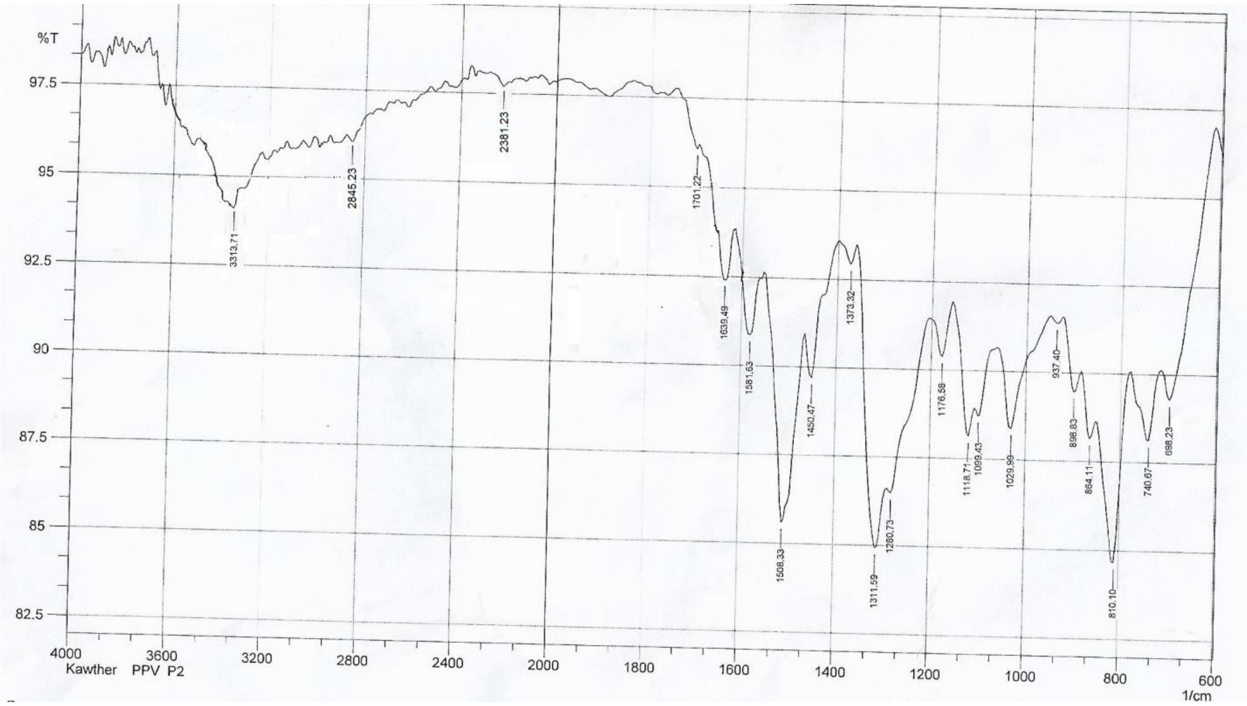
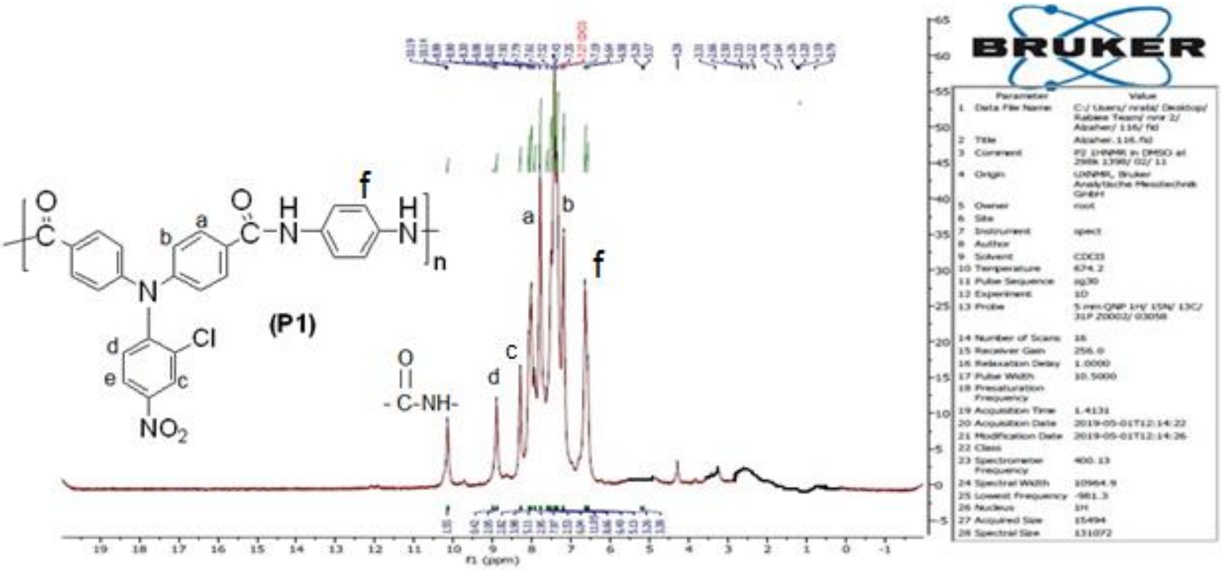


Figure 5. FTIR spectra of the synthesized polyamide **(P1)**.

The ^{1}H NMR spectrum of (P1) showed that the peak of COOH proton at 12.76 ppm is disappeared with appearance of singlet peak of the amide group at 10.19 after polymerization. The main doublet peaks at 7.79-7.61 ppm **(a)** and 7.43-7.35 ppm (b**)** are resulting from the four protons (a) and four protons (b) in the triphenylamine group respectively. Doublet peak in the region 6.5-6.8 ppm is assignable to four equivalent protons f of the phenylene diamine group **Figure 6.**

The ^{13}C NMR spectrum of the polyamide (P1**)** showed the main peak at 165.03 ppm which is assignable to the carbonyl carbon atom of the polyamide. The higher chemical shift of four carbon atoms of peak 6 attached to carbonyl group in the region 133.01 ppm. The lower chemical shift peak 7 of four carbon atoms in the region 124.77 ppm **Figure 7**.



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8 Author	
9 Solvent	CDCl3
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11 Pulse Sequence	zg30
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13 Probe	5 mm QNP 1H/ 15N/ 13C/ 31P Z0002/ 03058
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27 Acquired Size	15494
28 Spectral Size	131072

Figure 6. ^{1}H NMR spectrum of the polyamide **(P1)**

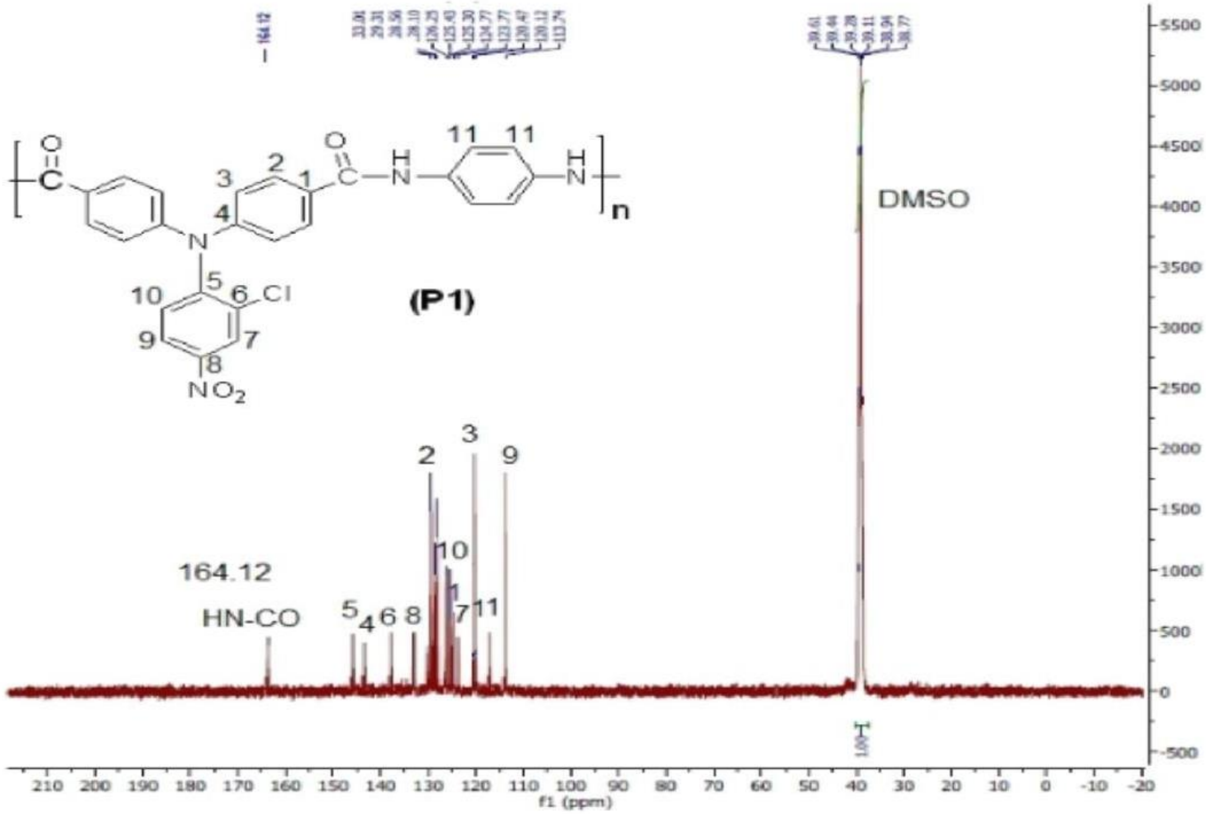

Figure 7. ^{13}C NMR spectrum of the polyamide **(**P1**).**

3.3. XRD Analysis

The synthesized polyamides (P1-P4) were investigated by WAXD**. Figure 8.** Shows that there is no clear sharp peak because the bulky TPA groups along the polymer chain which decrease the chain–chain interactions lead to inhibit the crystallinity and an enhance the solubility **Figure 8.**

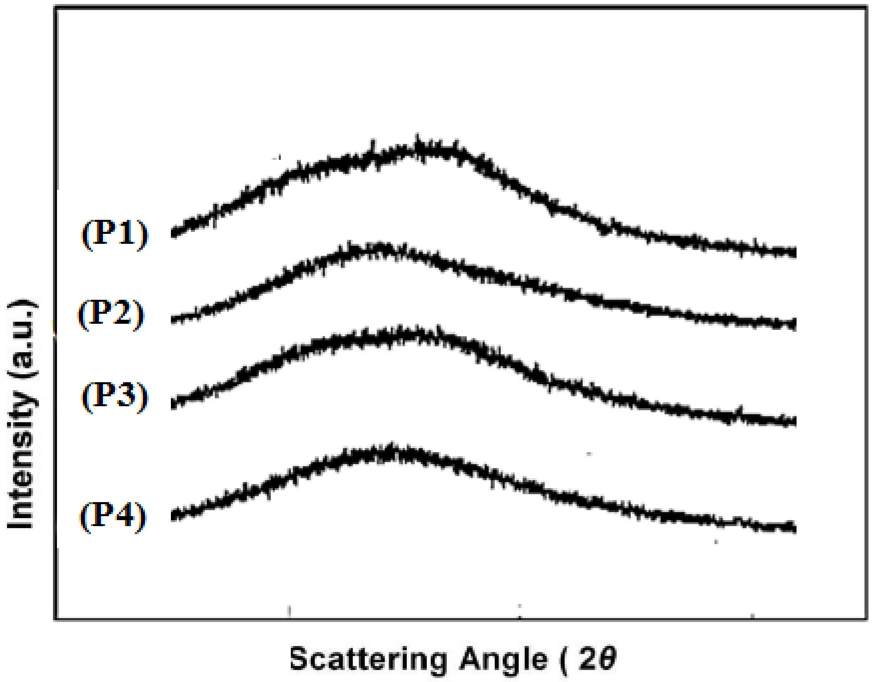

Figure 8. WXRD of the polyamides (P1) - (P4).

3.4. Electrochemical Properties the Synthesized Polyamides

Electrochromic consists in the formation of new optical transitions in an electroactive surface film or an electroactive solute as the result of electrochemical oxidation or reduction [36]. Polyamides are called conducting polymer which are important part of electro chromic materials. Electro chromic materials can convert color reversibility by mean of important result of energy saving and sufficient electrochemical potential or redox steps [37]. The redox behavior of polyamides was investigated by cyclic voltammetry (CV) where the cast films on an ITO-coated glass substrate as a working electrode.

Cyclic voltammetry (CV) was used to verify the redox properties of synthesized polyamides. The method support 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 process is dry CH_3CN contains 0.1 M of tetrabutylammonium perchlorate (Bu4NH4ClO$_4$).

Figure 10. Shows a typical cyclic voltammetry curve for the synthesized polyamides (P1)-(P4). All polyamides showed the half-wave at oxidation potential in the range E1/2 = (1.07-1.16) 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+} [38].

By change the potential scans between 0.0 - 1.8 V lead to conversion the pale yellowish color to the blue. HOMO and LUMO) energy levels of the compatible polyamides are calculated from the oxidation half-wave potential E1/2 and the onset absorption wavelength of the UV-Vis absorption (λabs onset) of the solution [39]. The result data are listed in **Table 1.** 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 9.**

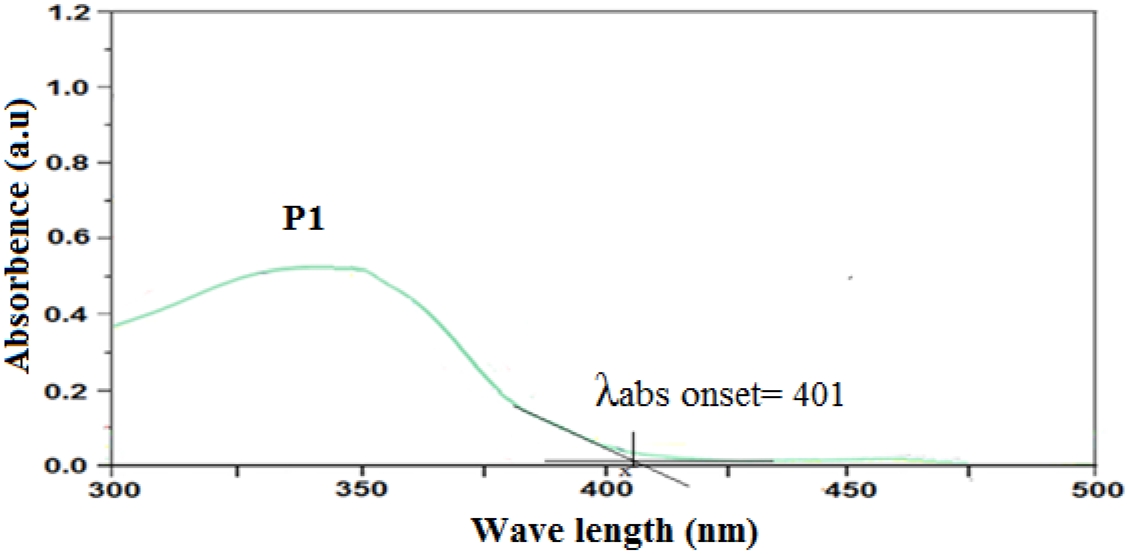

Figure 9. Uv-Vis absorption spectrum of polyamide **(P1)** in (10^{-5} M) DMSO.

Therefore, the HOMO energy for (P1) 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 (P1) as following:

E1/2 = (Ered + Eox) /2

E1/2 = 1.61 V + 0.72 V / 2 =1.164 V

E_{HOMO} = [E1/2 - E1/2(ref.) +4.8] eV = [1.164 V - 0.41 V + 4.8] eV =5.55 eV

E_{gap} = 1240/λabs.onset = 1240/401 = 3.097 eV

E_{LUMO} = E_{HOMO} - Egap

E_{LUMO} = 5.55─3.097 = 2.45 eV

Table 1. contain all calculated data fpr all synthesized polyamides

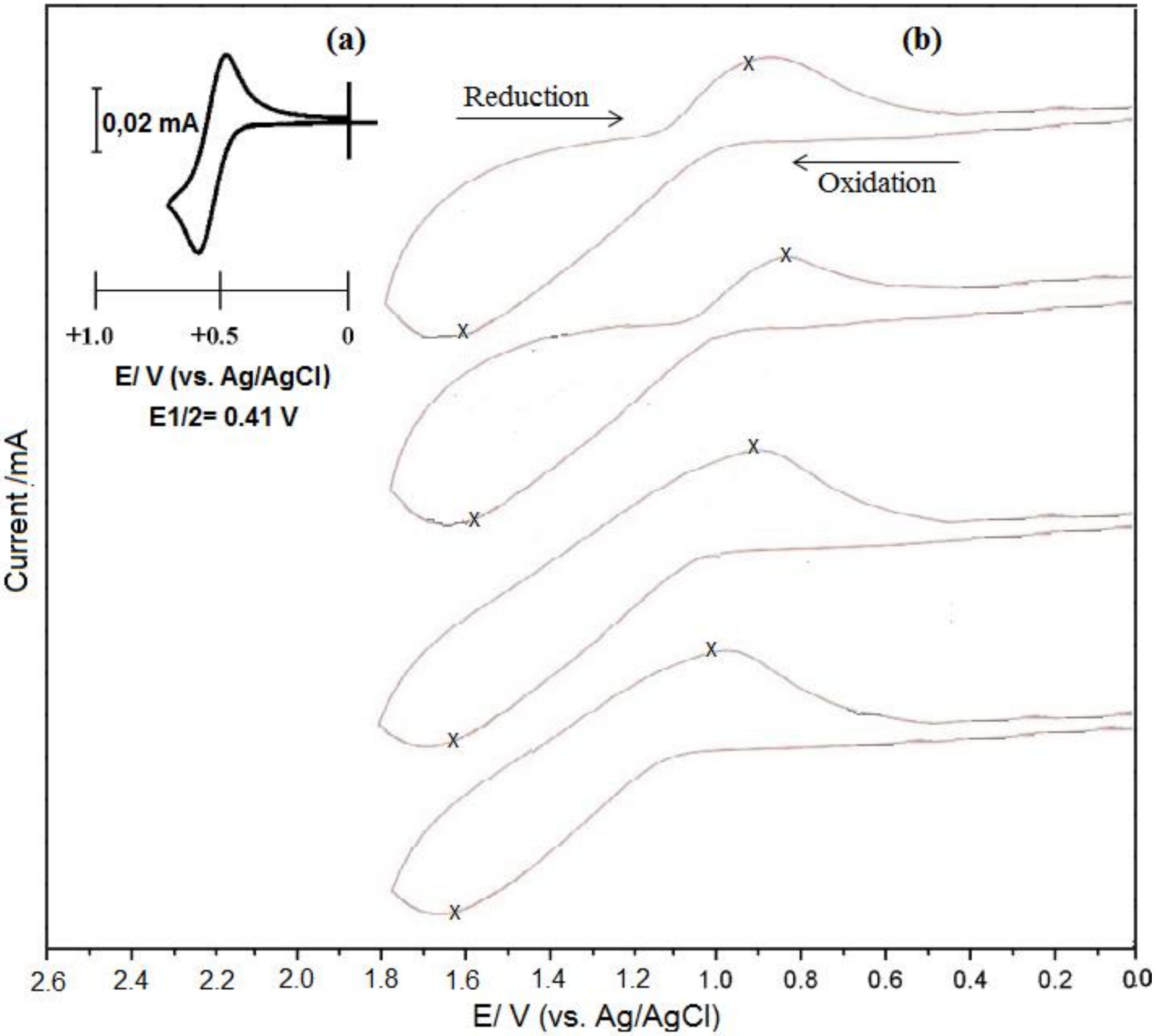

Figure 10. (C.V) of (a) Ferrocene as reference and (b) the cast film of polyamides.

Table 1. electrochemistry data for all the synthesized polyamides.

Polymer codes	**E1/2 V vs.Ag/AgCl**	**λabs, onset (nm**	**EHomo a (eV)**	**ELumo b (eV)**	**EHomo -ELumo c gap (eV)**
(P1)	1.16	401	5.55	2.45	3.097
(P2)	1.07	405	5.46	2.39	3.066
(P3)	1.12	410	5.51	2.48	3.029
(P4)	1.13	408	5.52	2.47	3.044

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

b: ELumo =EHomo – Egap.

c: Energy gap data.

4. Conclusion

In this research, a new non-crystalline aromatic polyamide containing triphenylamine group along its chains, was prepared by poly condensation reaction method. The solutions of all synthesized polyamides showed good electrochemical properties after manufacture of anode electrode by coating a special type of glass plate by solution of this polyamide, which it is used a part of an electrochemical cell. After applied the electric voltage, the anode layer changed from yellow to blue color that mean electronic transmission took place between the cathode and anode.

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