Supplementary information

Synthesis, Characterization of some Conductive Aromatic Polyamides/Fe_3O_4 NPs/ITO, and their utilization for methotrexate sensing

Mona A. Abdel-Rahman[1*], Waleed A. El-Said[1,2*], Eman M. Sayed[1], and Aboel-Magd A. Abdel-Wahab[1]

[1]Chemistry Department, Faculty of Science, Assiut University, Assiut 71516, Egypt

[2]Department of Chemistry, Faculty of Science, University of Jeddah, Jeddah, Saudi Arabia

Contents

Preparation of Acid Chlorides

A series of acid chlorides **1a-d** was prepared according to previous literature [34-36]

General procedure B for the synthesis of azobenzene dicarboxylic acids

A mixture of nitrobenzoic acid (5.30 mmol) and NaOH (96.00 mmol) were dissolved in water (30 mL) at 50 ºC. A solution of D-glucose (42.00 mmol) in water (11.50 mL) was added dropwise to the mixture and warmed on a water bath until the formation of the precipitate. Then diluted it by water and a stream of air was drawn through the mixture for 5 hours. The mixture was then acidified by acetic acid and the precipitate was filtrated.

General procedure C for the preparation of acid chlorides

A mixture of acid (1 mmol) was suspended in thionyl chloride (12 mmol) in the presence of a few drops of pyridine as a catalyst and was refluxed on a water bath for 12-24 h at 75 ºC. During this period, the acid was dissolved, and HCl and SO_2 gases were evolved. After this period the reaction mixture was distilled to remove the excess thionyl chloride. The residue was diluted with about 10 mL of petroleum ether 60-80 ºC until needles were precipitated then separated by filtration and purified by recrystallization and dried.

Synthesis of terephthaloyl chloride 1a

According to the general procedure **C**: terephthalic acid (1.00 g, 6 mmol), $SOCl_2$ (5.176 mL, 72 mmol) were reacted for 12 h. Purified by recrystallization from petroleum ether 60-80 ºC as a colorless needles, yield: 80 %; m.p.: 80 ºC. Anal. Calcd. for $C_8H_4O_2Cl_2$: C, 47.29; H, 1.97; Cl, 34.98. Found: C, 47.22; H, 1.92; Cl, 34.71.

Synthesis of isophthaloyl chloride 1b

According to the general procedure **C**: isophthalic acid (1.00 g, 6 mmol) and $SOCl_2$ (5.176 ml, 72 mmol) were refluxed for 12 h. Purified by recrystallization from petroleum ether 60-80 ºC as a colorless needles yield: 80 %; m.p.: 41- 44 ºC. Anal. Calcd. for $C_8H_4O_2Cl_2$: C, 47.29; H, 1.97; Cl, 34.98. Found: C, 47.18; H, 1.95; Cl, 34.89.

Synthesis of 4,4'-azodibenzoyl chloride 1c

This was prepared in two subsequent steps as follows:

a) Synthesis of 4,4'-azobenzene dicarboxylic acid

According to the general procedure **B**, *p*-nitrobenzoic acid (1.00 g, 5.98 mmol), NaOH (3.80 g, 95.00 mmol) and D-glucose (7.60 g, 42.22 mmol) gave a pale orange powder yield: 70 %; m.p.: >300 ºC. The solid product was used in the next step without any further purification. Anal. Calcd. for $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.70; N, 10.37. Found: C, 62.62; H, 3.59; N, 10.13.

b) Synthesis of 4,4'-azodibenzoyl chloride ***1c***

According to the general procedure **C,** 4,4'-azobenzene dicarboxylic acid (1.08 g, 4.00 mmol) and $SOCl_2$ (3.45 ml, 48.00 mmol) after reflux for 24 hrs. Purified by recrystallization from petroleum ether 60-80 ºC, gave red needles, yield: 72 %; m.p.: 164 ºC Anal. Calcd. for $C_{14}H_8N_2O_2Cl_2$: C, 54.90; H, 2.61; N, 9.15; Cl, 22.87 Found: C, 54.36; H, 2.51; N, 8.22; Cl, 23.03.

Synthesis of 3,3'-azodibenzoyl chloride 1d

This was prepared in two subsequent steps as follows:

a) Synthesis of 3,3'-azobenzene dicarboxylic acid

According to the general procedure **B,** *m*-nitrobenzoic acid (1.00 g, 5.98 mmol), NaOH (3.80 g, 95.00 mmol) and D-glucose (7.60 g, 42.22 mmol) gave a brown powder yield: 70 %; m.p.: >300 ºC The solid product was used in the next step without any further purification Anal. Calcd. for $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.70; N, 10.37. Found: C, 62.50; H, 3.65; N, 10.22.

b) Synthesis of 3,3'-azodibenzoyl chloride ***1d***

According to the general procedure **C,** 3,3'-azobenzene dicarboxylic acid (1.08 g, 4.00 mmol) and $SOCl_2$ (3.45 ml, 48.00 mmol) were refluxed for 24 hrs and the product recrystallization from petroleum ether 60-80 ºC gave an orange needles yield: 65 %; m.p.: 97 ºC Anal. Calcd. For $C_{14}H_8N_2O_2Cl_2$: C, 54.90; H, 2.61; N, 9.15; Cl, 22.87. Found: C, 54.50; H, 2.45; N, 8.42; Cl, 23.60.

Synthesis of the polyamide P1a-d

Following general procedure A: 4 mmol of 1a-d, diamino monomer 3 (1.09 g, 4 mmol), and LiCl (1.00 g) in NMP gave the title compound after 6 h as a red-orange precipitate (Scheme 3).

P1a yield 70 %; m.p.: 295-298 °C. Anal. Calcd. for $C_{20}H_{16}N_6O_4$: C, 59.40; H, 3.99; N, 20.78. Found: C, 58.90; H, 3.92; N, 19.65. FT-IR (KBr, cm^{-1}): 3420 (N-H, amide), 1712 (C=O, ester) and 1624 (C=O of amide). 1H NMR (400 MHz, DMSO-d6): δ = 8.64 (s, 2H, 2NH amides), 8.16–7.83 (m, 8H, Ar-H), 6.40 (br, 1H, NH), 4.33 (q, 2H, CH_2) and 1.34 (t, 3H, CH_3).

P1b yield 60 %; m.p.: 295 °C. Anal. Calcd. for $C_{20}H_{16}N_6O_4$: C, 59.40; H, 3.99; N, 20.78. Found: C, 59.80; H, 4.03; N, 20.19. FT-IR (KBr, cm^{-1}): 3423 (N-H, amide), 1710 (C=O, ester group), and 1666 (C=O of amide). 1H NMR (400 MHz, DMSO-d6): δ = 8.69–7.67 (m, 10H, 8Ar-H, 2NH amides), 6.39 (br, 1H, NH), 4.51–4.03 (q, 2H, CH_2) and 1.47–1.12 (t, 3H, CH_3).

P1c yield 80 %; m.p.: 300 °C. Anal. Calcd. for $C_{26}H_{20}N_8O_4$: C, 61.41; H, 3.96; N, 22.04. Found: C, 61.02; H, 3.90; N, 21.88. FT-IR (KBr, cm-1): 3408 (N-H, amide), 1712 (C=O, ester), 1676 (C=O of amide) and 1510 (N=N, azo). 1H NMR (400 MHz, DMSO-d6): δ= 8.61 (br, 2H, 2NH amides), 8.44–7.72 (m, 12H, Ar-H), 6.43 (br, 1H, NH), 4.34 (q, 2H, CH_2) and 1.35 (t, 3H, CH_3).

P1d yield 55%; m.p.: 260 °C. Anal. Calcd. for $C_{26}H_{20}N_8O_4$: C, 61.41; H, 3.96; N, 22.04. Found: C, 61.19; H, 3.99; N, 22.30. FT-IR (KBr, cm^{-1}): 3425 (N-H, amide), 1712 (C=O, ester), 1681 (C=O of amide) and 1560 (N=N, azo). ^{1}H NMR (400 MHz, DMSO- d6): δ = 8.82–7.72 (m, 14H, 12Ar-H, 2NH amides), 6.44 (br, 1H, NH), 4.34 (q, 2H, CH_2) and 1.35 (t, 3H, CH_3).

Synthesis of the polyamide P2a-d

Following general procedure A: 4,4'-diaminodiphenyl sulfone (0.99 g, 4.00 mmol), 4.00 mmol of 1a-d, and LiCl (1.00 g) in NMP. The title compound after 6 hours as a white precipitate (Scheme 3).

P2a yield 60%; m.p.: >300 °C Anal. Calcd. for $C_{20}H_{14}N_2O_4S$: C, 63.48; H, 3.73; N, 7.40; S, 8.47. Found: C, 62.02; H, 4.17; N, 6.99; S, 8.19. FT-IR (KBr, cm^{-1}): 3322 for (NH amide), at 1663 for (C=O amide), and 1330 for (O=S=O). 1H NMR (400 MHz, DMSO- d6): δ= 10.73 (s, 2H, NH amides), 8.16–7.90 (m, 12H, Ar-H).

P2b yield 70%; m.p.: >300 °C. Anal. Calcd. for $C_{20}H_{14}N_2O_4S$: C, 63.48; H, 3.73; N, 7.40; S, 8.47. Found: C, 62.68; H, 4.06; N, 7.20; S, 8.21. FT-IR (KBr, cm^{-1}): 3306 (N-H, amide), 1666 (C=O of amide) and 1310 (O=S=O). ^{1}H NMR (400 MHz, DMSO-d6): δ = 10.79 (s, 2H, NH amides), 8.56–7.68 (m, 12H, Ar-H).

P2c yield 85%; m.p.: >300 °C. Anal. Calcd. for $C_{26}H_{18}N_4O_4S$: C, 64.72; H, 3.76; N, 11.61; S, 6.65. Found: C, 64.05; H, 4.07; N, 11.19; S, 6.60. FT-IR (KBr, cm^{-1}): 3362 (N-H, amide), 1663 (C=O of amide), 1520 (N=N, azo) and 1310 (O=S=O). ^{1}H NMR (400 MHz, DMSO-d6): δ= 10.70 (s, 2H, NH amides), 7.50:8.31 (m, 16H, Ar-H).

P2d yield 35%; m.p.: >300 °C. Anal. Calcd. for $C_{26}H_{18}N_4O_4S$: C, 64.72; H, 3.76; N, 11.61; S, 6.65. Found: C, 64.90; H, 4.13; N, 11.61; S, 6.63. FT-IR (KBr, cm^{-1}): 3335 (N-H, amide), 1668 (C=O of amide), 1515 (N=N, azo) and 1320 (O=S=O). ^{1}H NMR (400 MHz, DMSO- d6): δ= 10.81 (s, 2H, NH amides), 8.02 (m, 16H, Ar-H).

Synthesis of the polyamide P3a,b,d

Following general procedure A, 4,4'-diaminodiphenyl ether (0.80 g, 4.00 mmol), 4.00 mmol of 1a,b,d, and LiCl (1.00g) in NMP gave the title compound after 6 hours as a white precipitate (Scheme 3).

P3a yield 85%; m.p.: >300 °C. Anal. Calcd. for $C_{20}H_{14}N_2O_3$: C, 72.72; H, 4.27; N, 8.48. Found: C, 69.62; H, 4.42; N, 8.55. FT-IR (KBr, cm^{-1}) 3308 (N-H, amide) and at 1647 (C=O of amide). ^{1}H NMR (400 MHz, DMSO-d6): δ= 10.36 (s, 2H, NH amides), 7.02-8.13 (m, 12H, Ar-H).

P3b yield 90 %; m.p.: >300 °C Anal. Calcd. for $C_{20}H_{14}N_2O_3$: C, 72.72; H, 4.27; N, 8.48. Found: C, 70.98; H, 4.28; N, 8.05. FT-IR (KBr, cm^{-1}): 3269 (N-H, amide) and 1647 (C=O of amide). ^{1}H NMR (400 MHz, DMSO-d6): δ=10.23 (s, 2H, NH amides), 7.04-8.59 (m, 12H, Ar-H).

P3d yield 90%; m.p.: >300 °C. Anal. Calcd. for $C_{26}H_{18}N_4O_3$: C, 71.88; H, 4.18; N, 12.90. Found: C, 71.42; H, 4.27; N, 12.79. FT-IR (KBr, cm^{-1}): 3248 (N-H, amide), 1648 (C=O of amide) and 1500 (N=N, azo). ^{1}H NMR (400 MHz, DMSO-d6): δ=10.49 (s, 2H, 2NH amides), 7.00-8.6 (m, 16H, Ar-H).

Synthesis of the polyamide P4c, d

Following general procedure A, p-phenylenediamine (0.43 g, 4.00 mmol), 4.00 mmol of 1c, 1d, and LiCl (1.00 g) in NMP gave the title compound after 6 h as a brown precipitate.

P4c yield 80 %; m.p.: >300 °C. Anal. Calcd. for $C_{20}H_{14}N_4O_2$: C, 70.17; H, 4.12; N, 16.37. Found: C, 70.29; H, 4.18; N, 16.31. FT- IR (KBr, cm^{-1}): 3331 (N-H, amide), 1647 (C=O of amide) and 1520 (N=N, azo). ^{1}H NMR (400 MHz, DMSO-d6): δ= 10.42 (s, 2H, NH amide), 7.69-8.65 (m, 12H, Ar-H).

P4d yield: 70%; m.p.: >300 °C. Anal. Calcd. for $C_{20}H_{14}N_4O_2$: C, 70.17; H, 4.12; N, 16.37. Found: C, 71.83; H, 4.59; N, 16.54. FT-IR (KBr, cm^{-1}): 3335 (N-H, amide), 1655 (C=O of amide) 1510 (N=N, azo). ^{1}H NMR (400 MHz, DMSO-d6): δ= 10.50 (s, 2H, NH amide), 7.50-8.50 (m, 12H, Ar-H).

Preparation of Fe_3O_4 NPs/ITO Electrode by the Solvothermal Method

Fe_3O_4NPs/ITO-modified electrodes were prepared by the solvothermal method according to Maosheng's method with some modifications. Typically, a Teflon-lined stainless-steel autoclave was charged with a mixture of $FeCl_3.6H_2O$ (0.5 gm), urea (0.83 gm), and citric acid (0.125 gm) in 60 mL EG. ITO substrates were immersed in the reaction mixture in a horizontal position in which the conducting faces were kept upward and then the autoclave was sealed and maintained at 200°C for 20 hrs, then cooled to room temperature. The modified Fe_3O_4/ITO substrates were rinsed with

DIW and dried under N_2 gas. In addition, the Fe_3O_4 NPs were filtered off from the reaction mixture and the electrode was washed with DIW and ethanol sequentially and dried in an oven at 80°C [37].

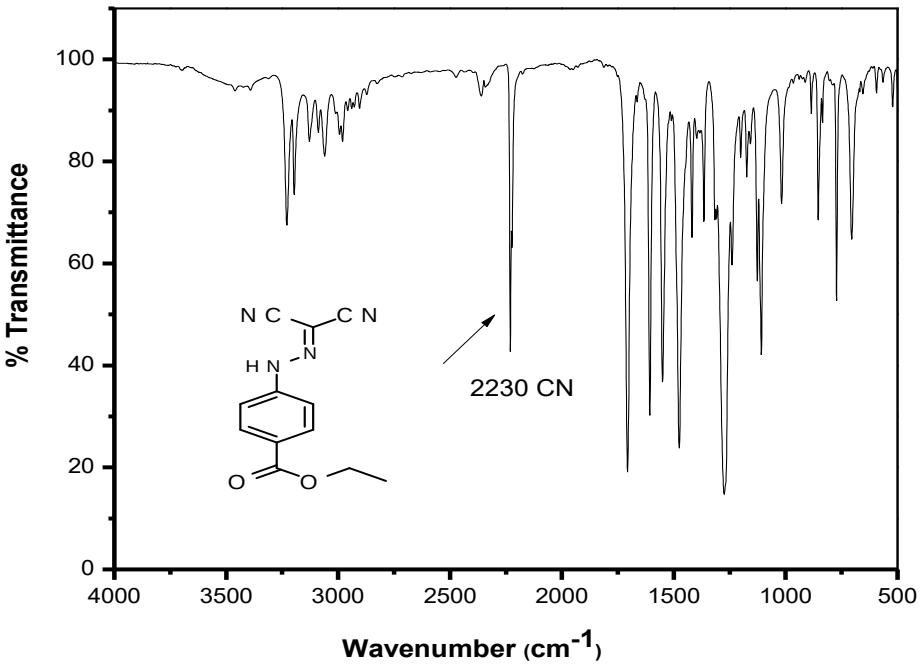

Figure S1. FT-IR spectrum of the dicyano compound **2**.

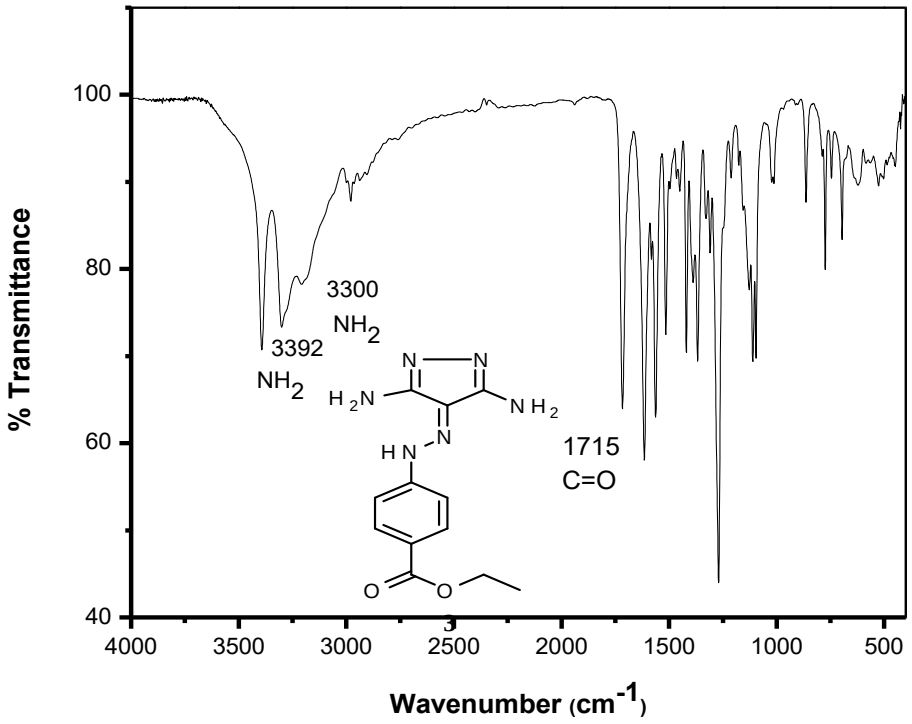

Figure S2. FT-IR spectrum of the diamino monomer **3**.

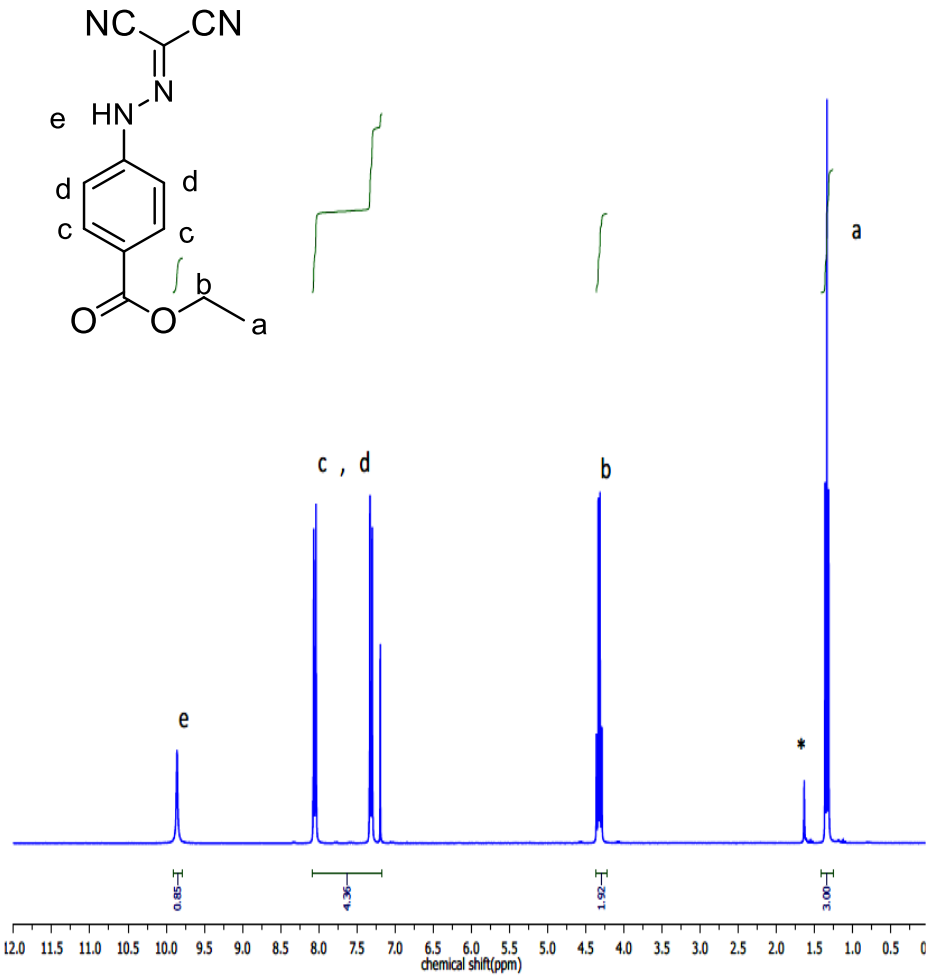

Figure S3. ^{1}H NMR spectrum of the dicyano compound **2** in $CHCl_3$.

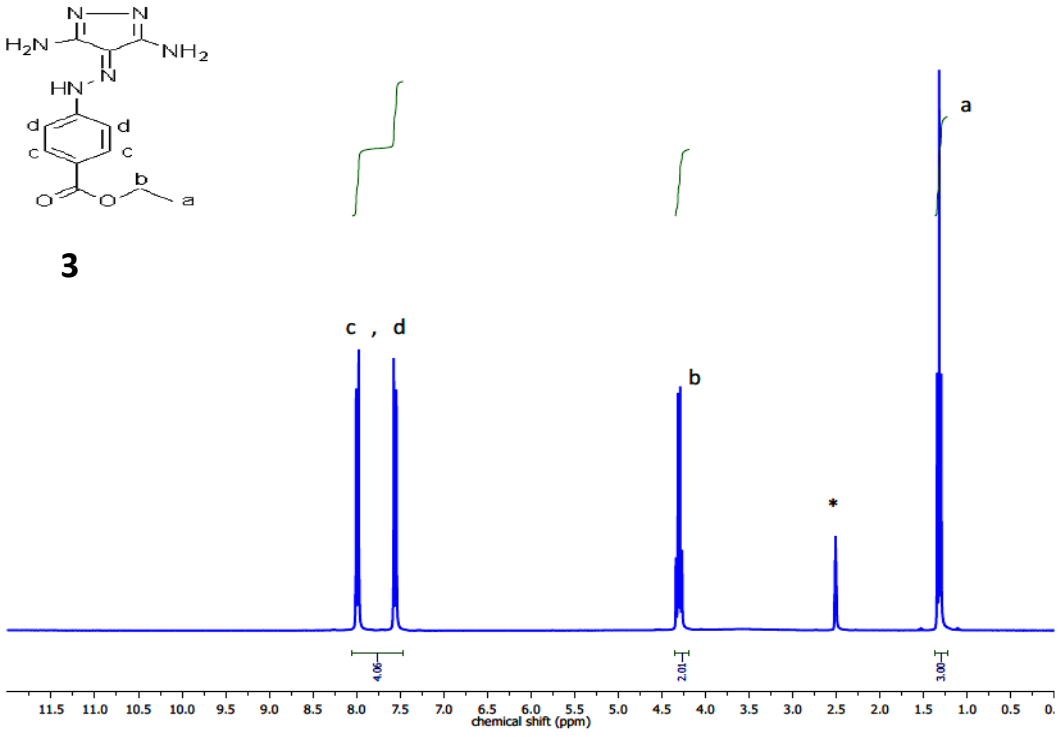

Figure S4. ^{1}H NMR spectrum of diamino monomer **3** in DMSO-*d*$_6$**.**

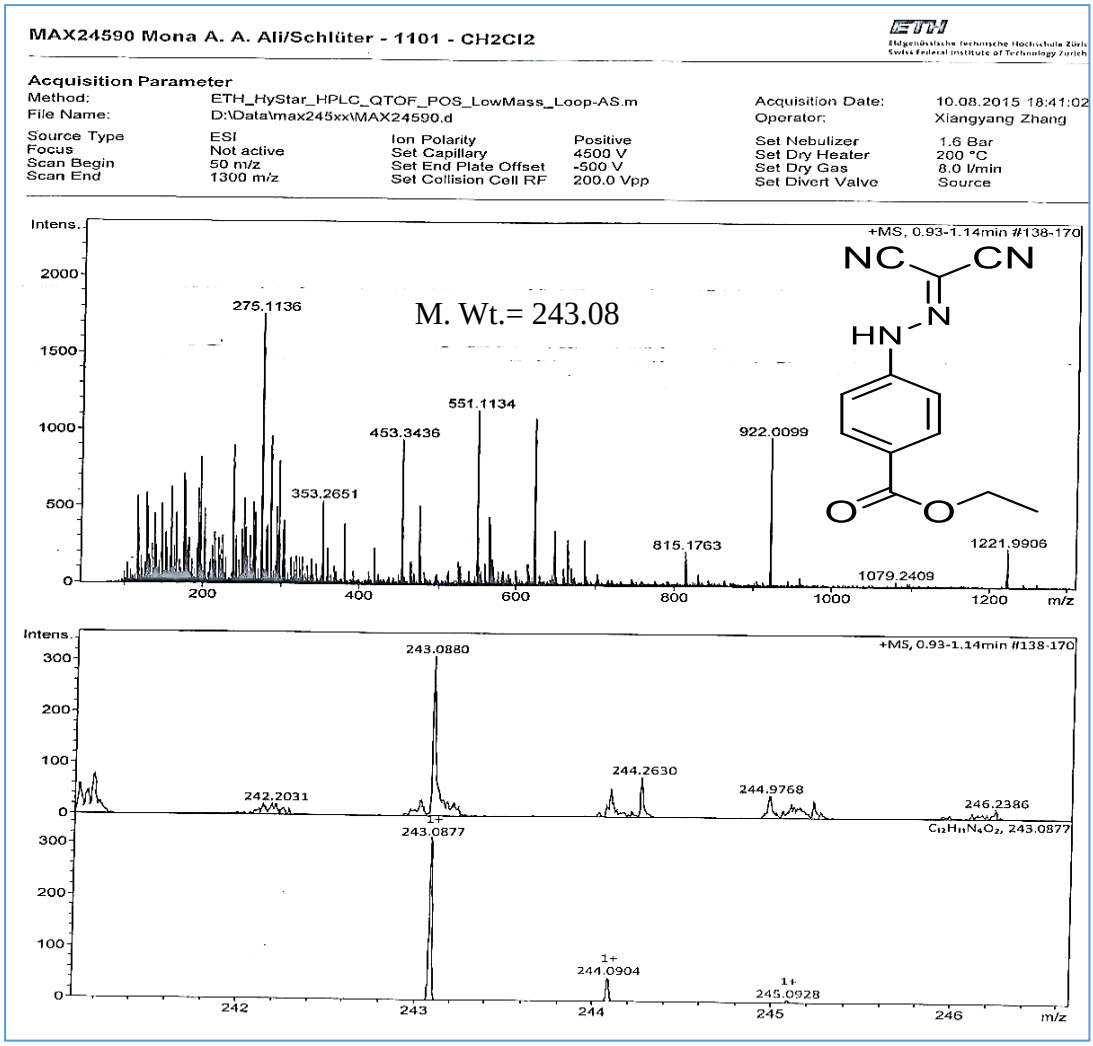

Figure S5. ESI/Mass spectrum of the dicyano compound **2**.

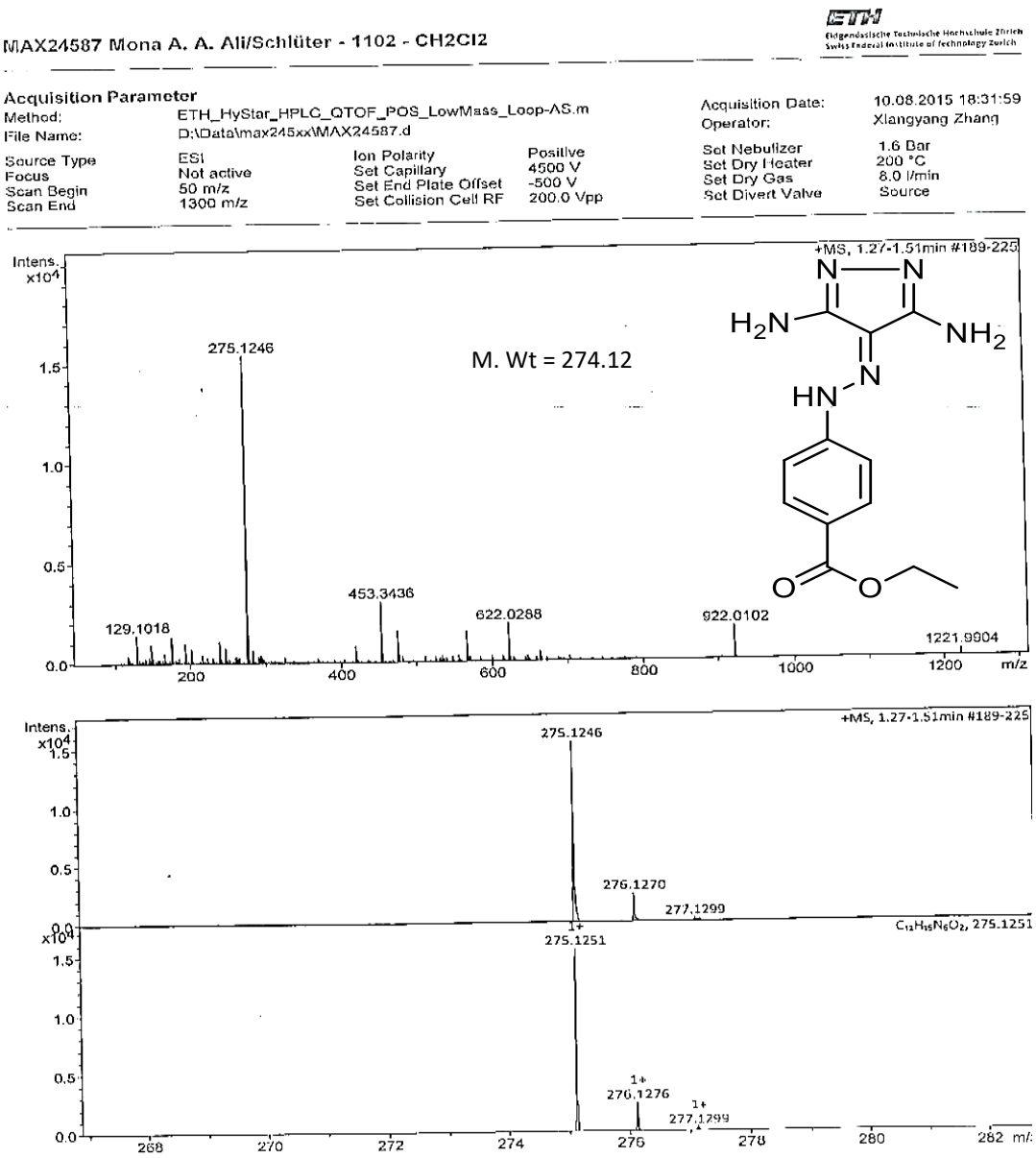

Figure S6. ESI/Mass spectrum of the diamino monomer **3**.

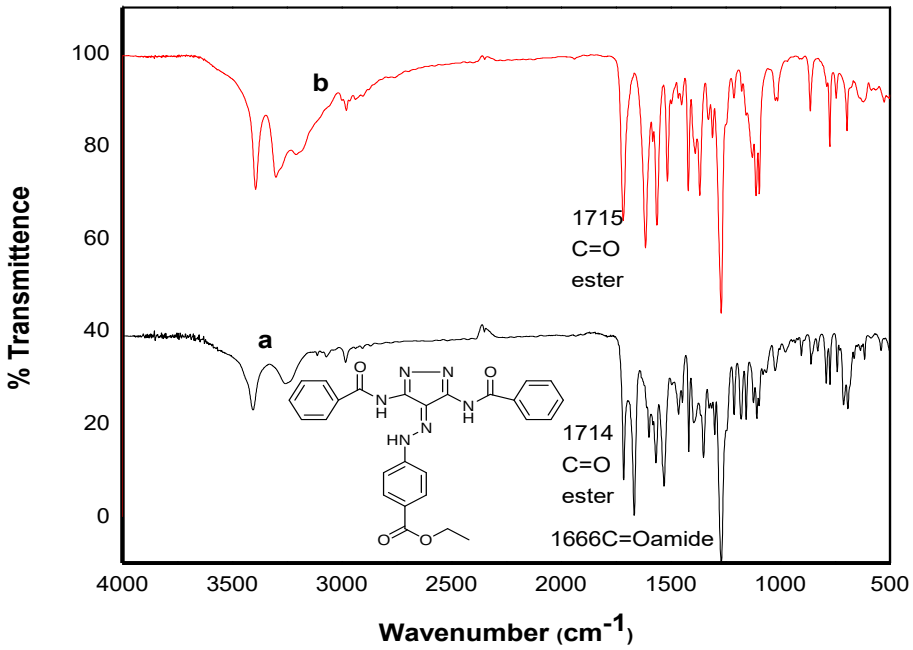

Figure S7. FT-IR spectra of a) model compound **4** and b) diamino monomer **3**.

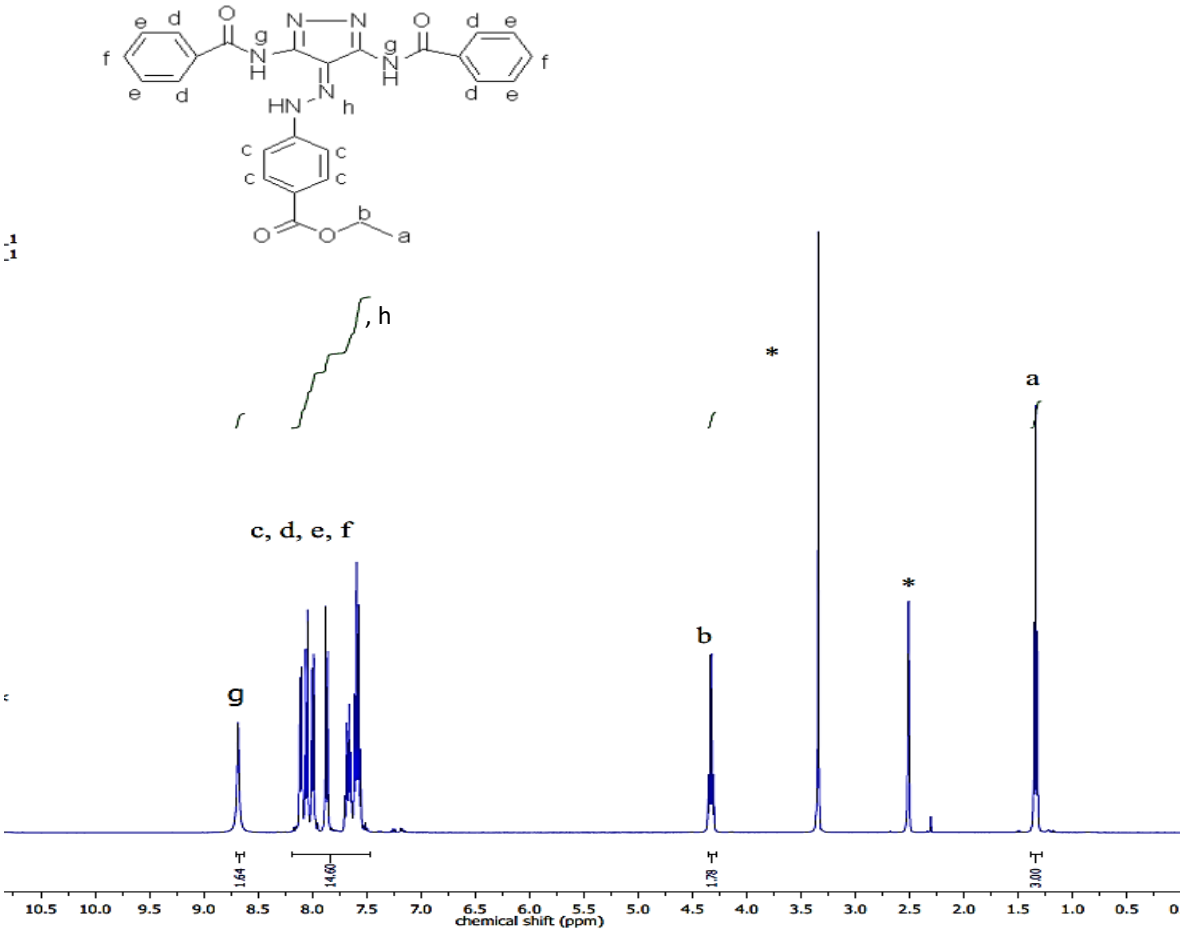

Figure S8. [1]H NMR spectrum of the model compound **4** in DMSO-*d6*.

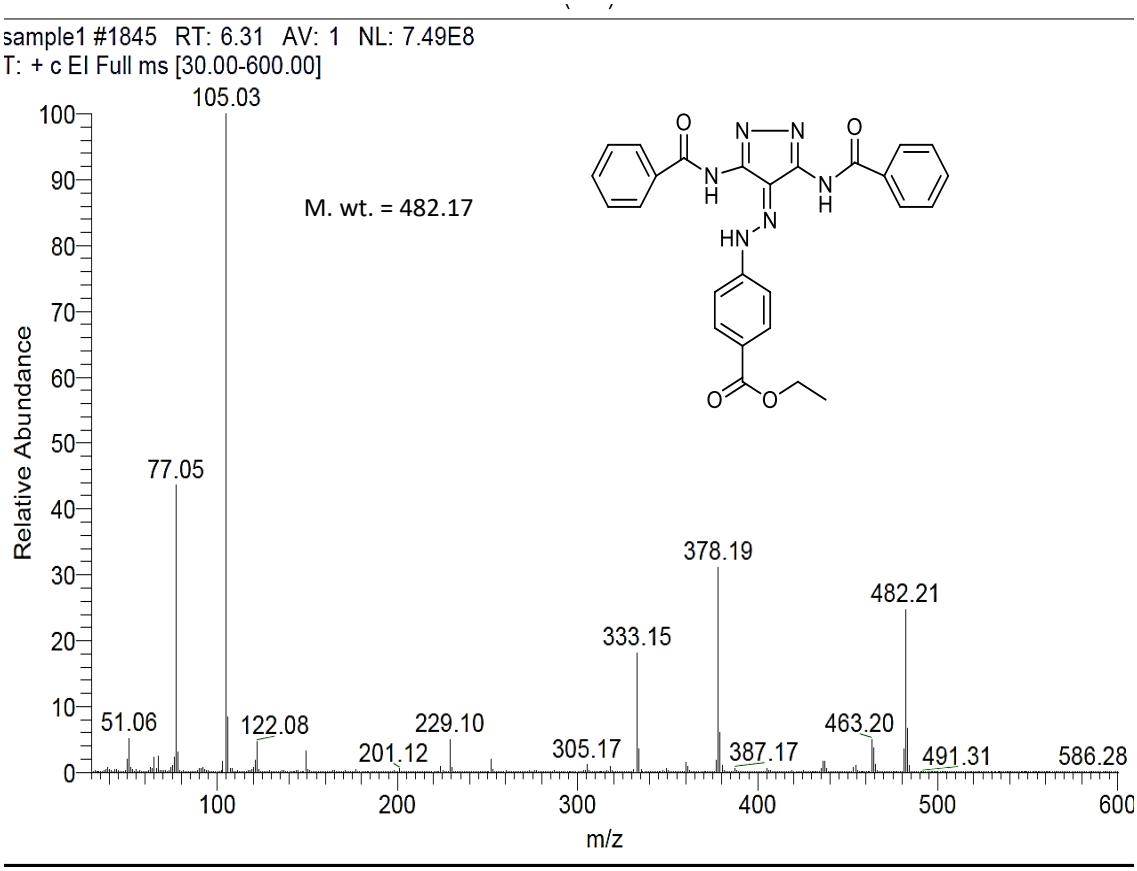

Figure S9. Mass spectrum of the model compound **4**.

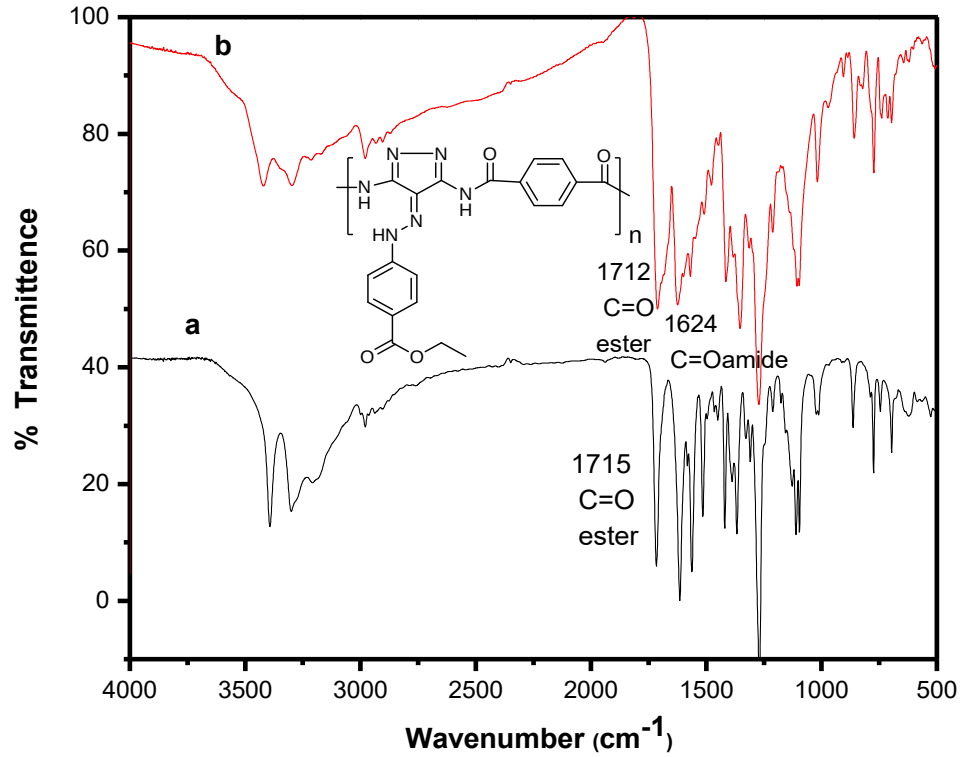

Figure S10. FT-IR spectra of a) diamino monomer **3** and b) polyamide **P1a**.

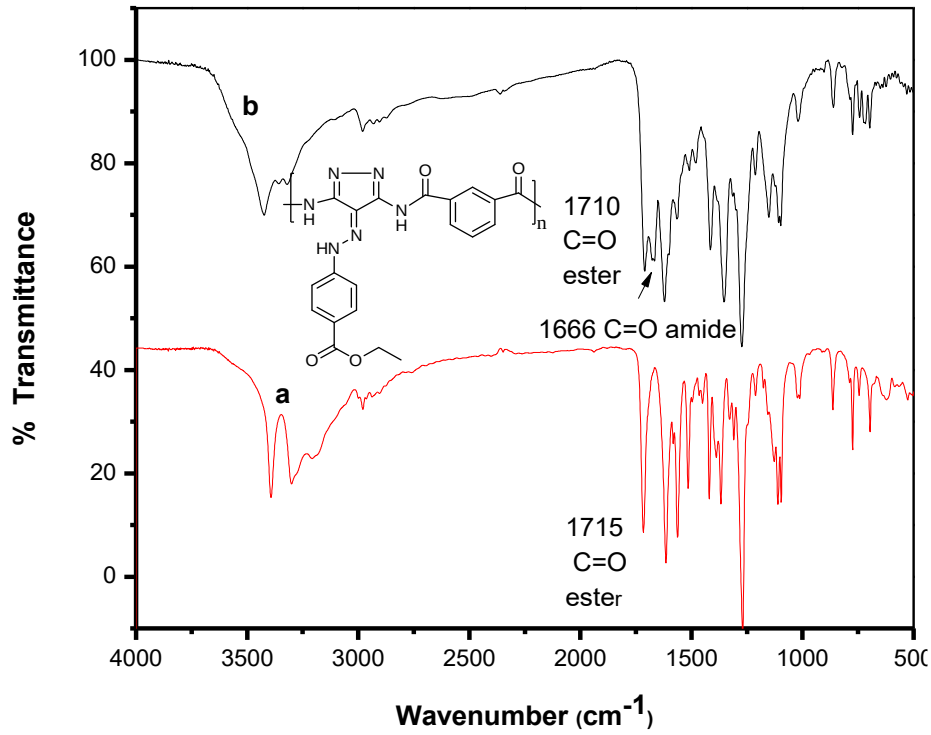

Figure S11. FT-IR spectra of a) diamino monomer **3** and b) polyamide **P1b**.

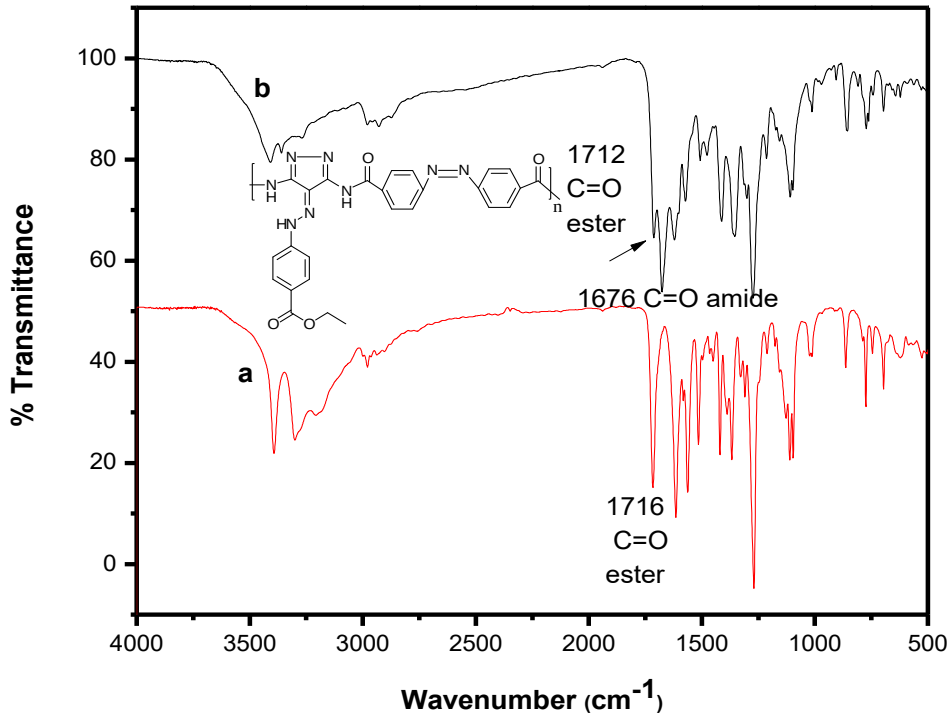

Figure S12. FT-IR spectra of a) diamino monomer **3** and b) polyamide **P1c**.

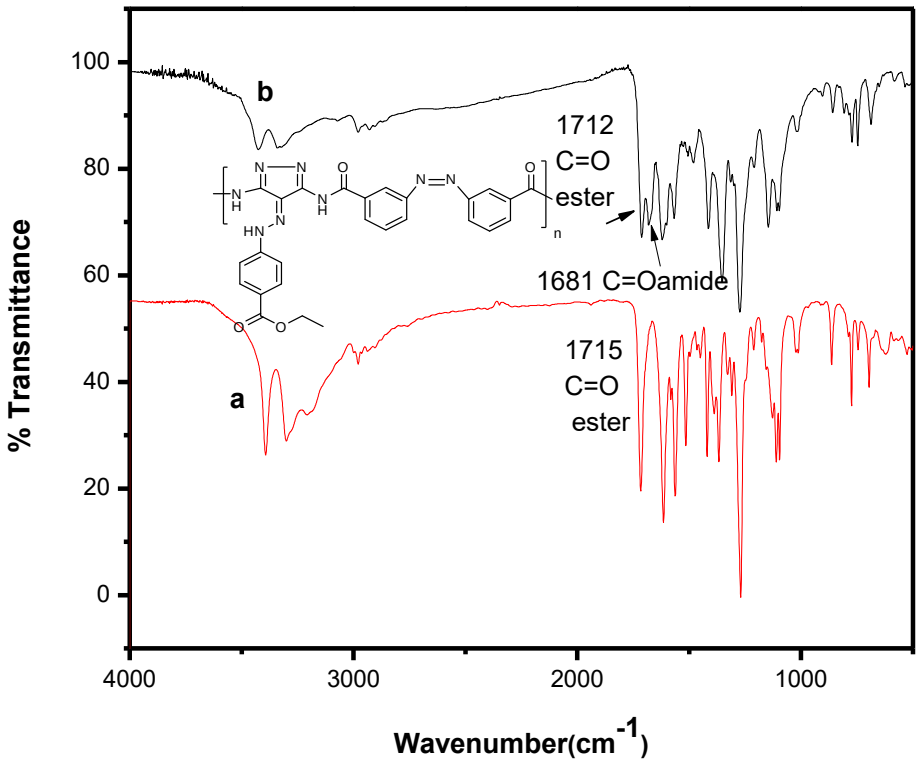

Figure S13. FT-IR spectra of a) diamino monomer **3** and b) polyamide **P1d**.

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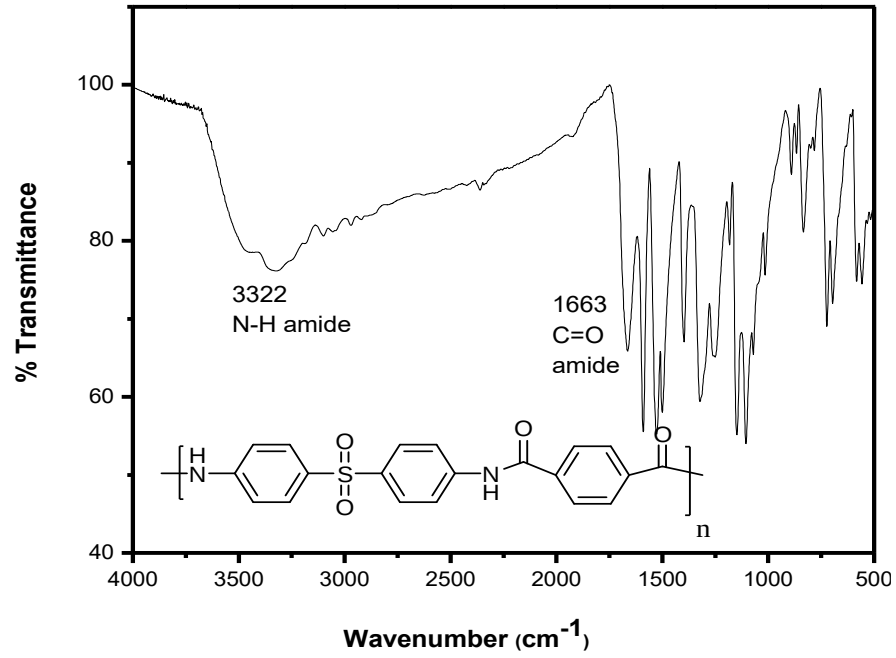


Figure S14. FT-IR spectrum of the polyamide **P2a**.

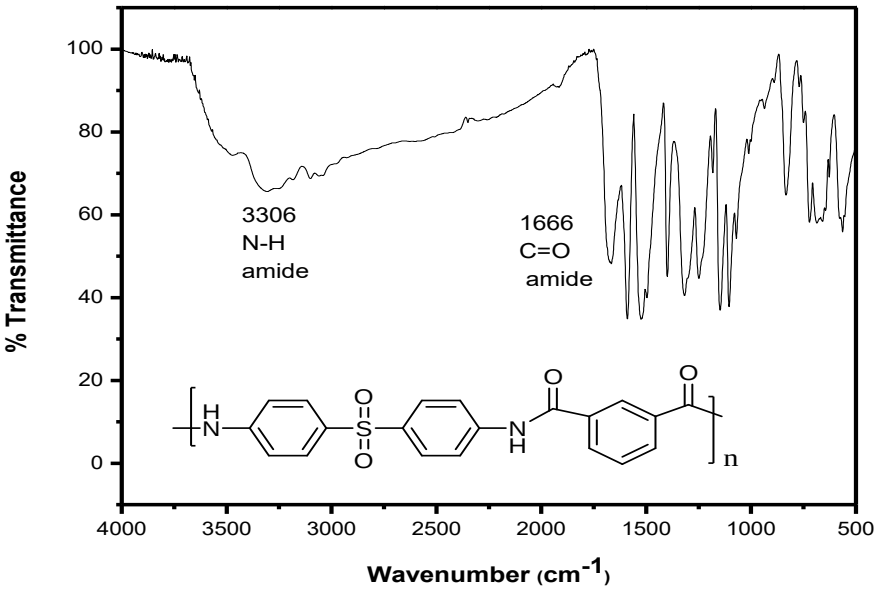


Figure S15. FT-IR spectrum of the polyamide **P2b**.

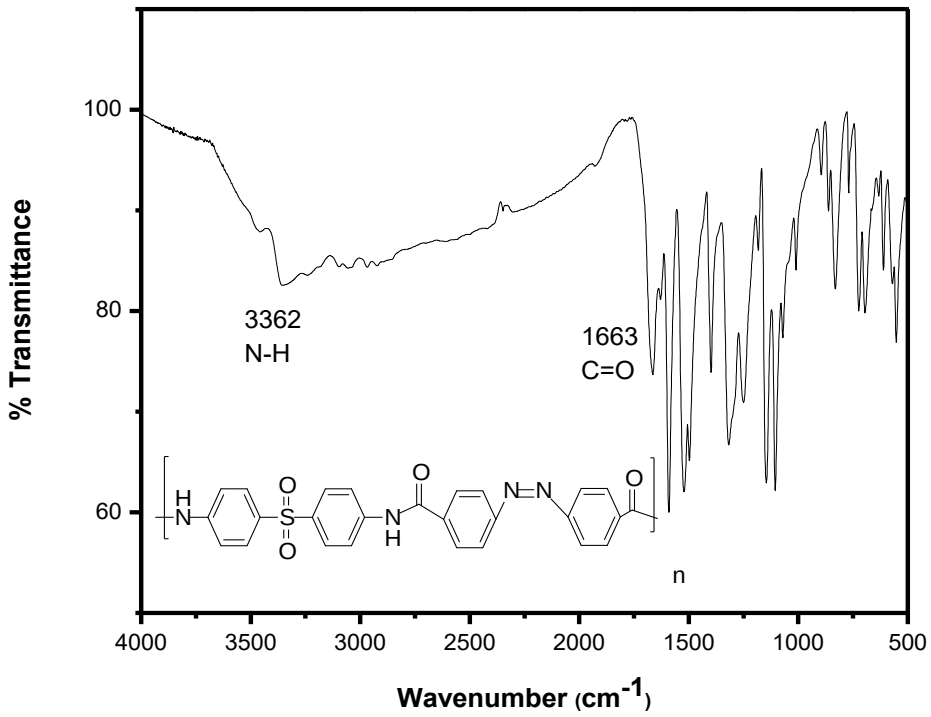


Figure S16. FT-IR spectrum of the polyamide **P2c**.

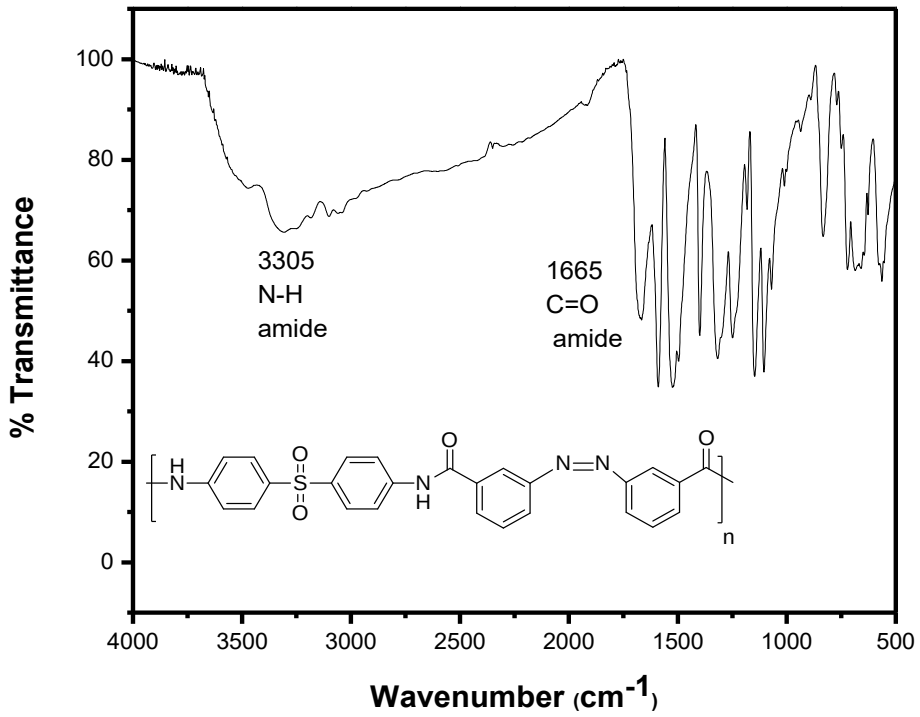


Figure S17. FT-IR spectrum of the polyamide **P2d**.

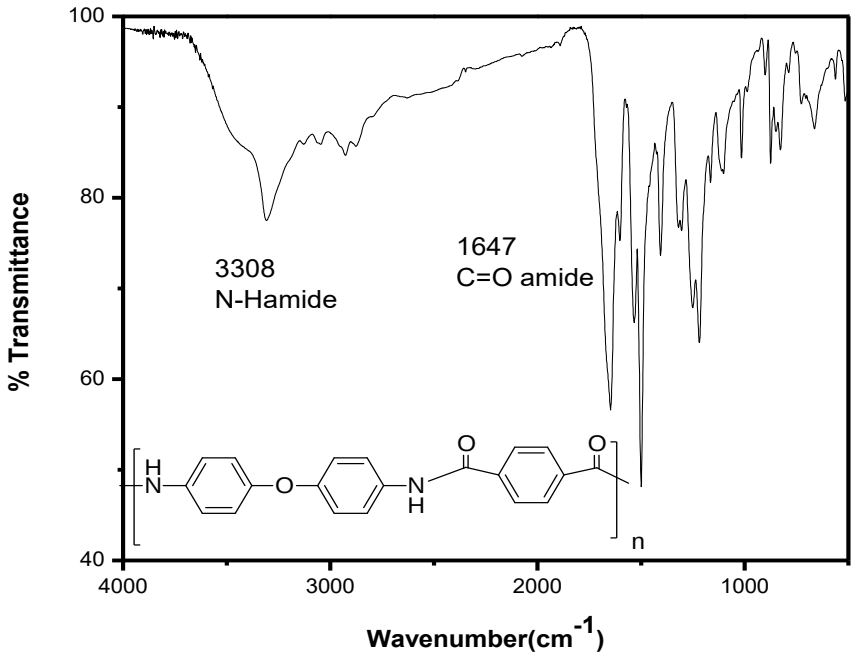


Figure S18. FT-IR spectrum of the polyamide **P3a**.

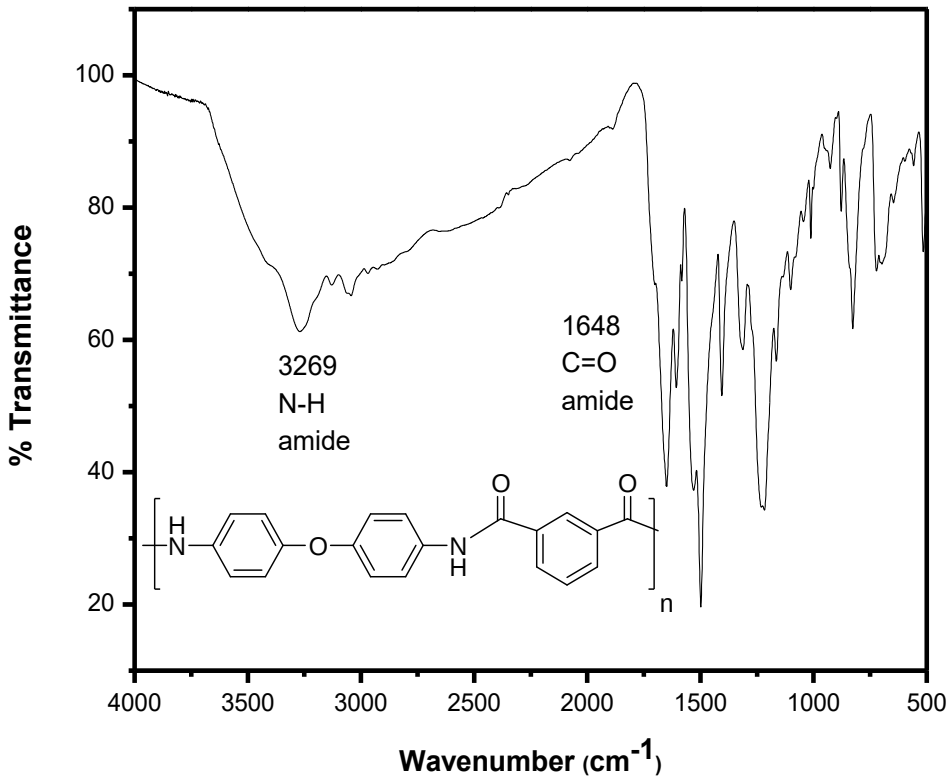


Figure S19. FT-IR spectrum of the polyamide **P3b**.

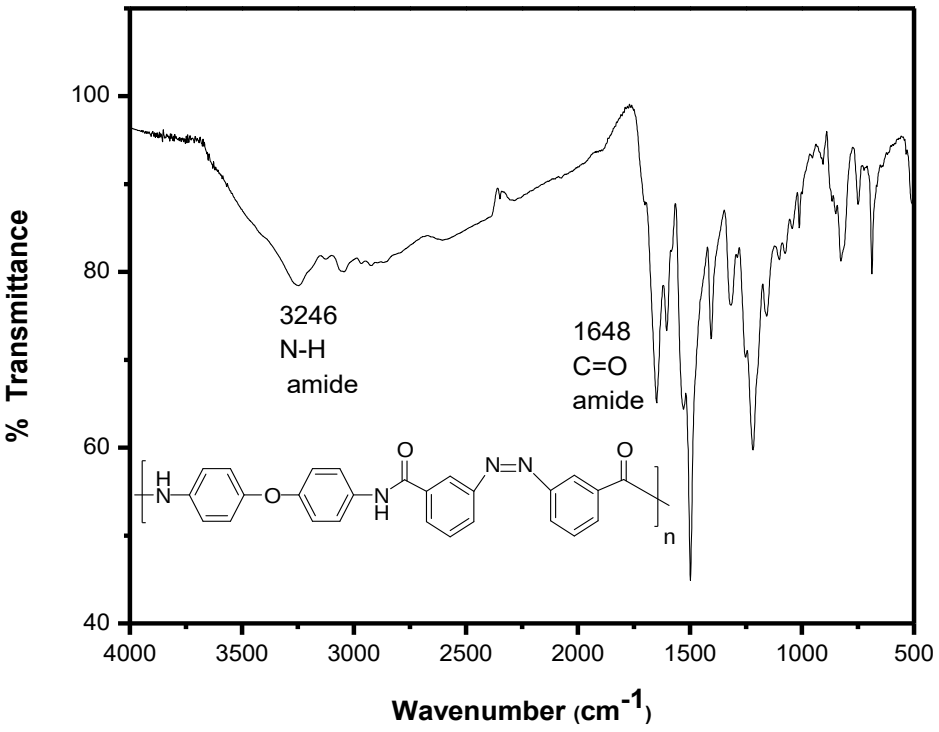


Figure S20. FT-IR spectrum of the polyamide **P3d**.

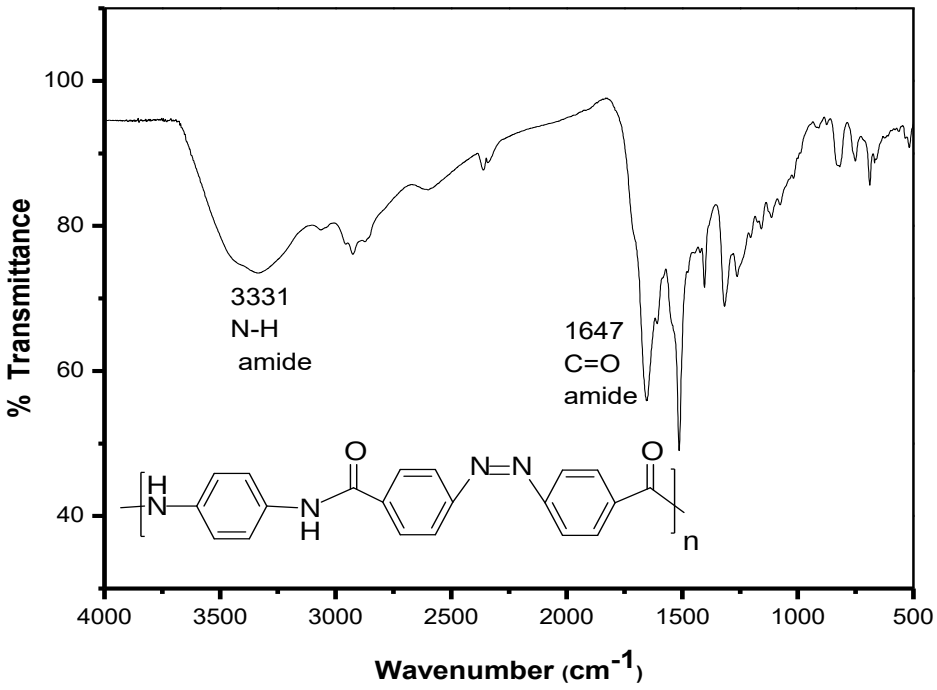


Figure S21. FT-IR spectrum of the polyamide **P4c**.

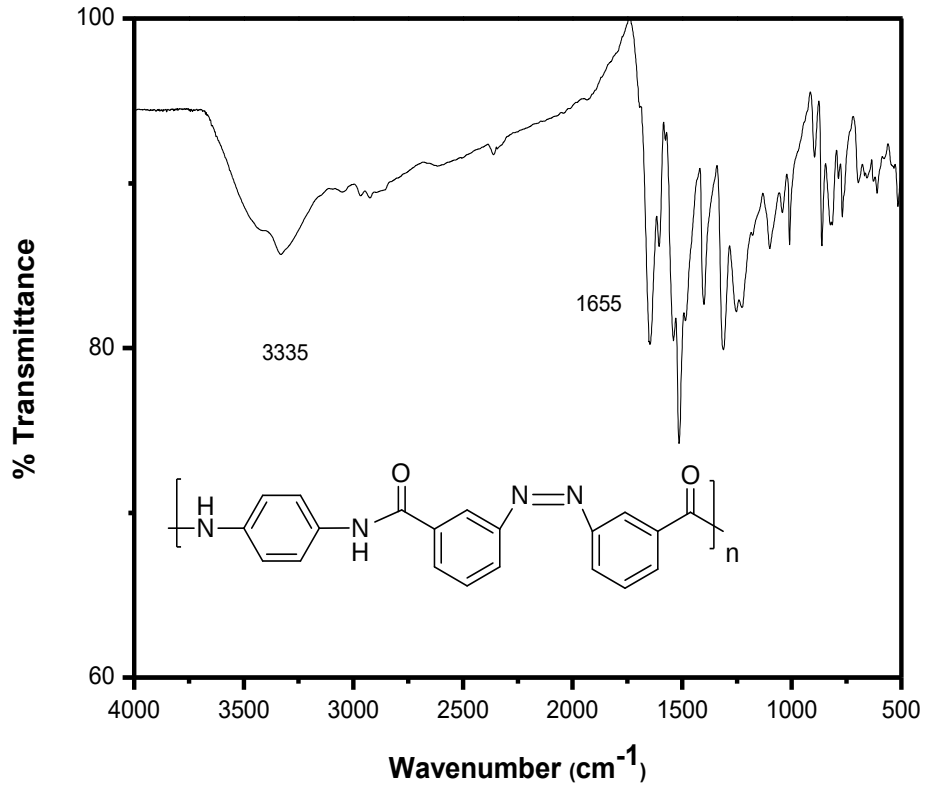


Figure S22. FT-IR spectrum of the polyamide **P4d**.

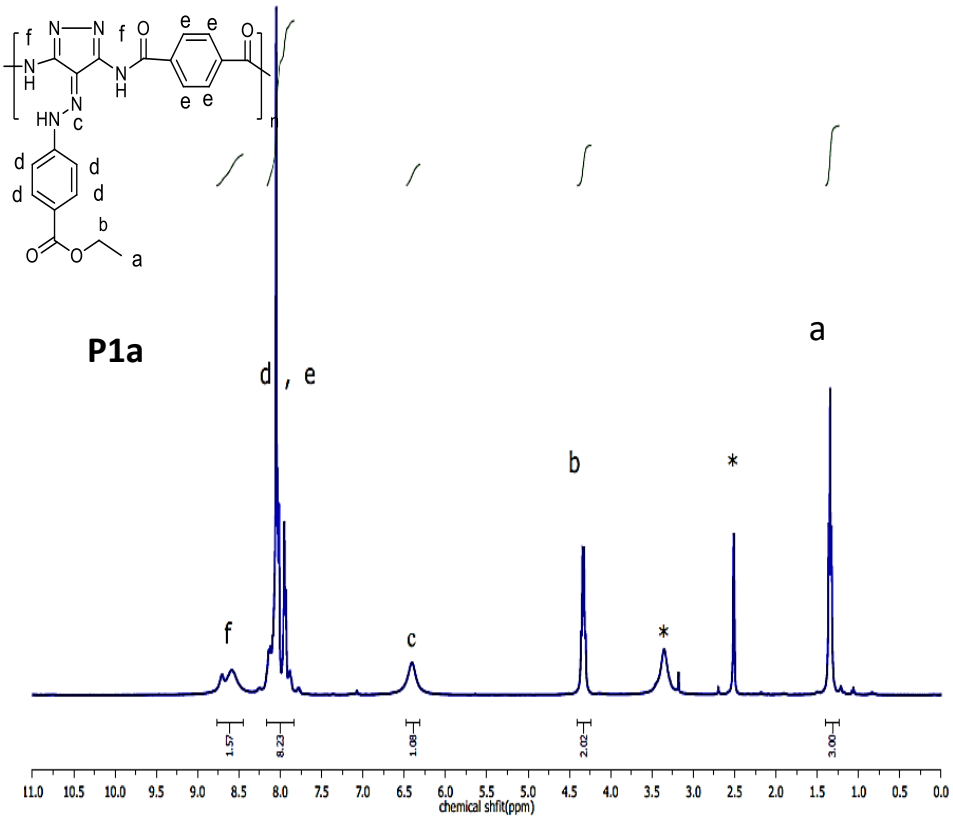


Figure S23. ^{1}H NMR spectrum of the polyamide **P1a** in DMSO-d_6 .

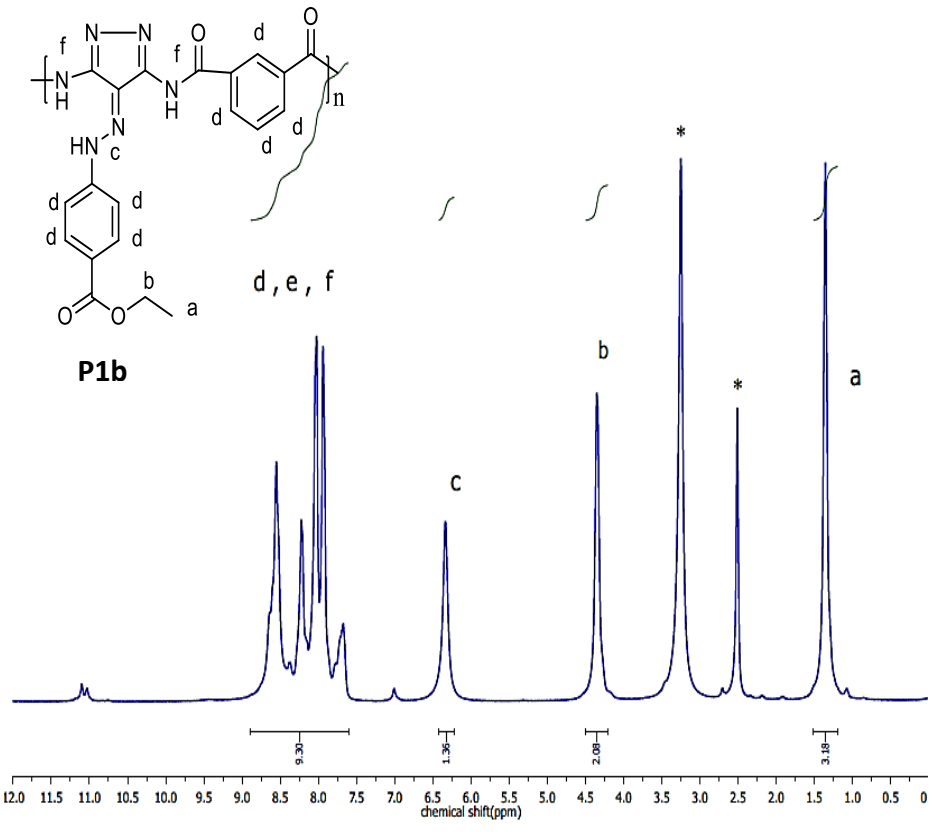


Figure S24. ^{1}H NMR spectrum of the polyamide **P1b** in DMSO-d_6 .

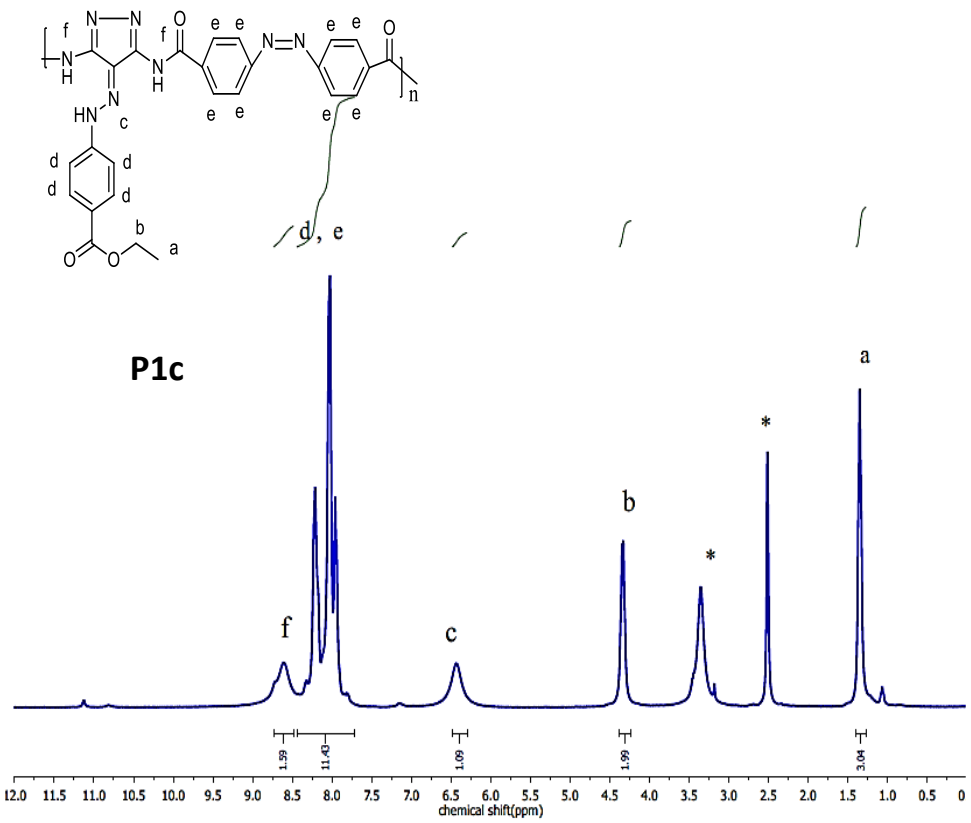


Figure S25. ^{1}H NMR spectrum of the polyamide **P1c** in DMSO-d_6 .

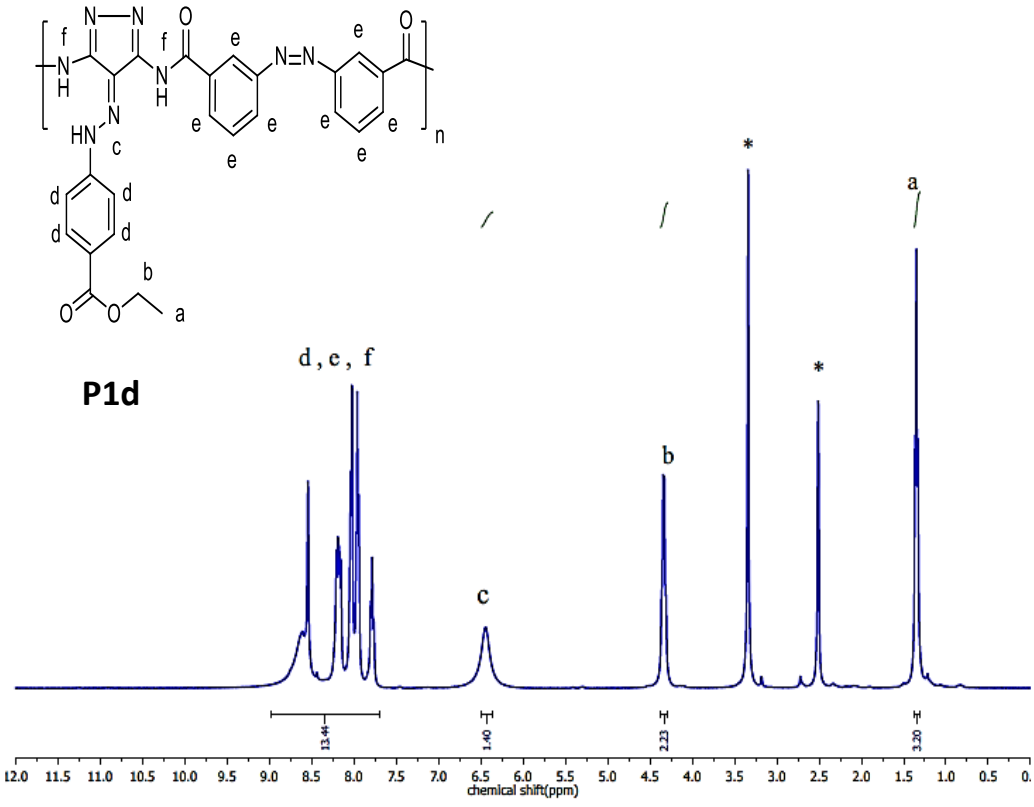


Figure S26. ^{1}H NMR spectrum of the polyamide **P1d** in DMSO-d_6 .

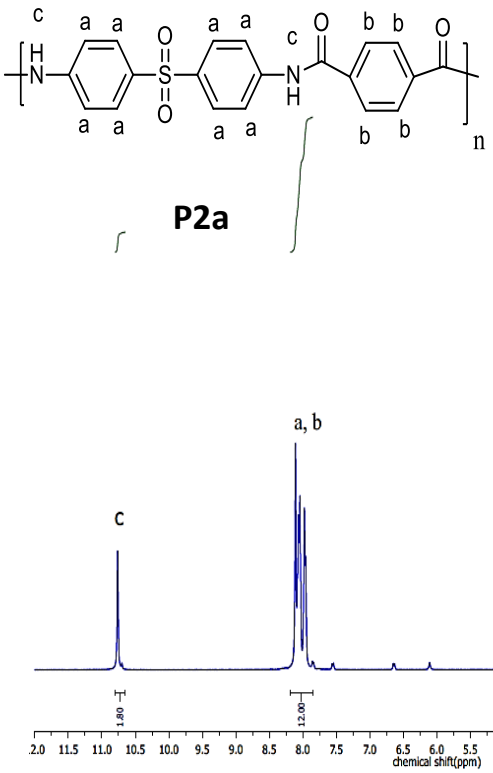


Figure S27. ^{1}H NMR spectrum of the polyamide **P2a** in DMSO-d_6 .

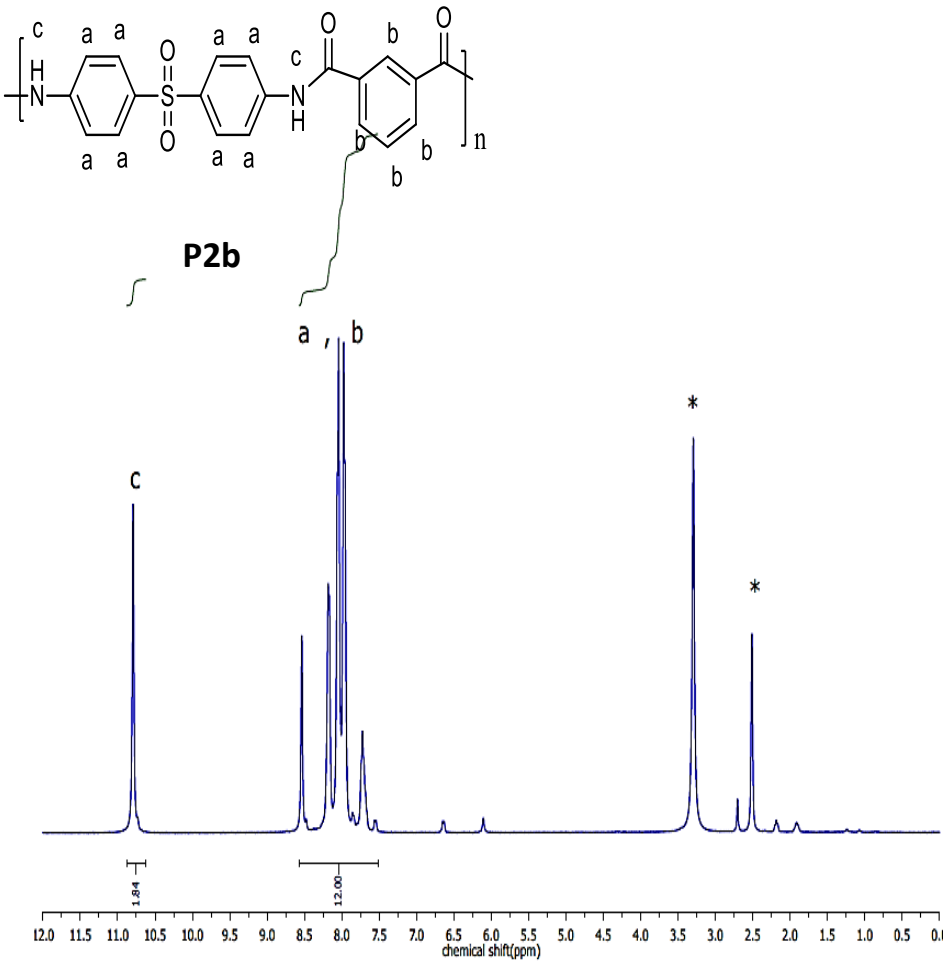


Figure S28. ^{1}H NMR spectrum of the polyamide **P2b** in DMSO-d_6 .

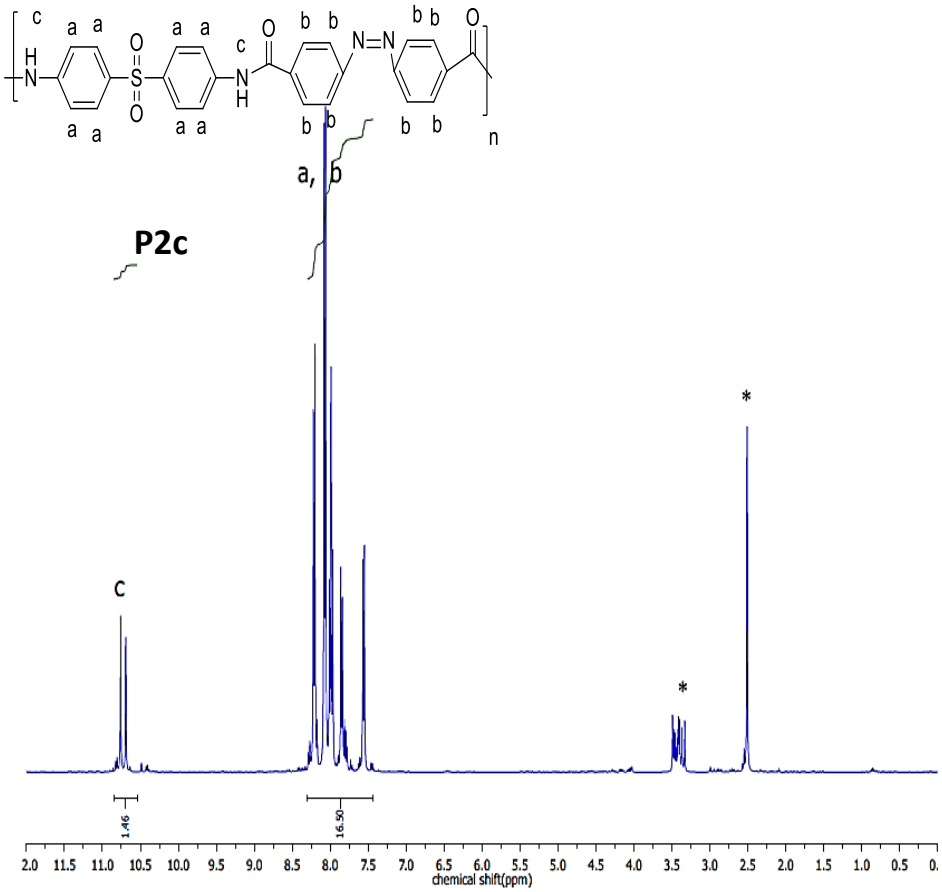


Figure S29. ^{1}H NMR spectrum of the polyamide **P2c** in DMSO-d_6 .

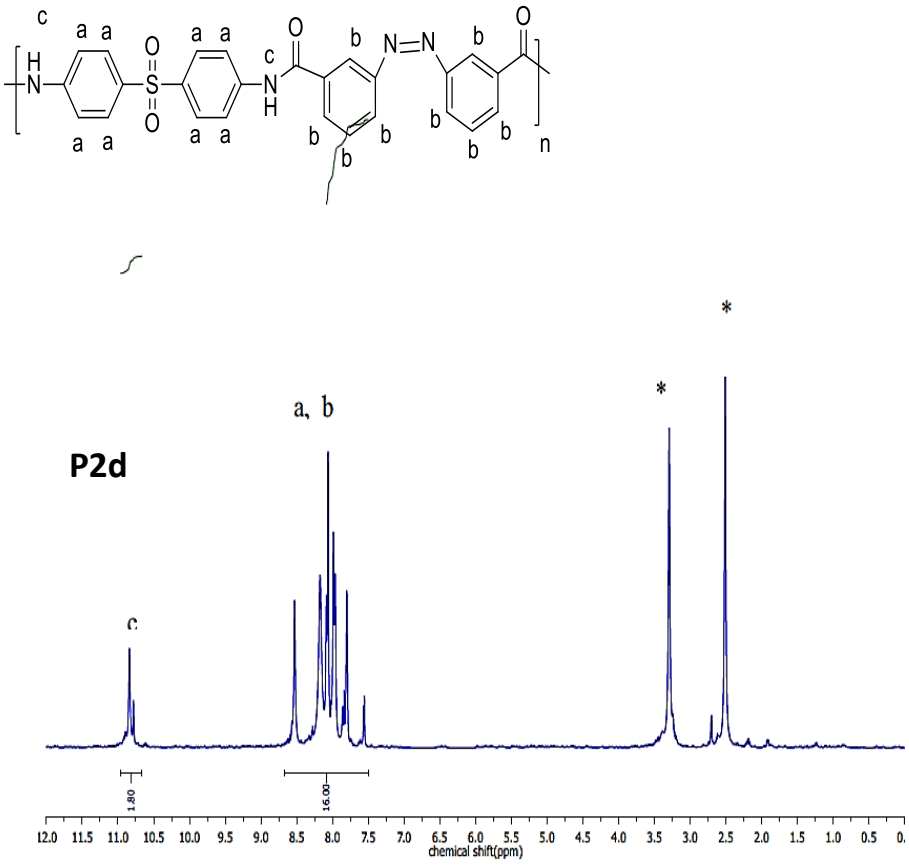


Figure S30. ^{1}H NMR spectrum of the polyamide **P2d** in DMSO-d_6.

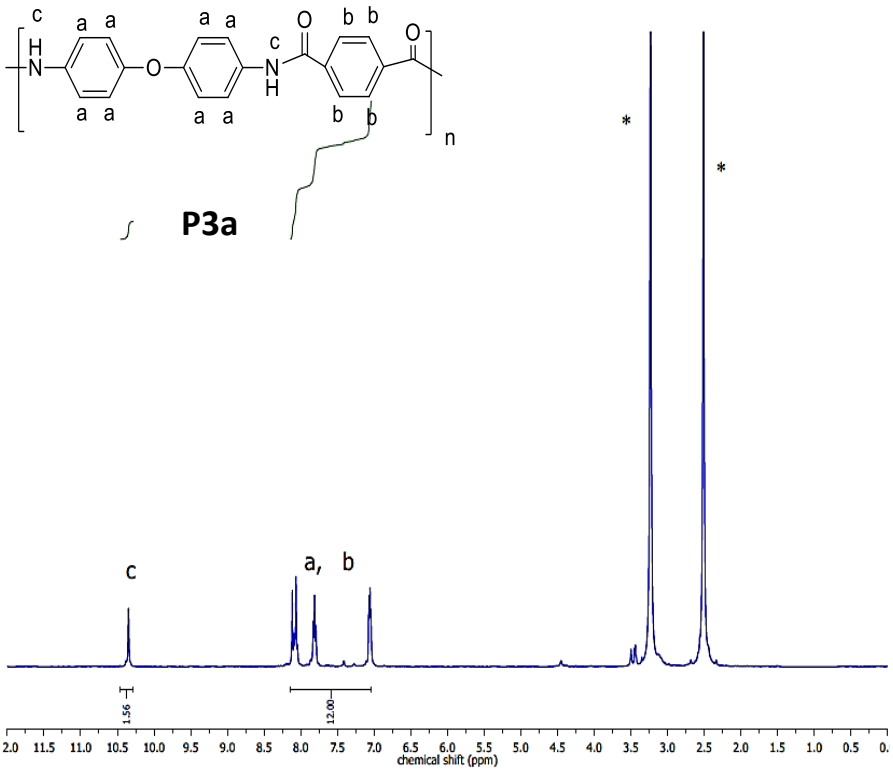


Figure S31. ^{1}H NMR spectrum of the polyamide **P3a** in DMSO-d_6 .

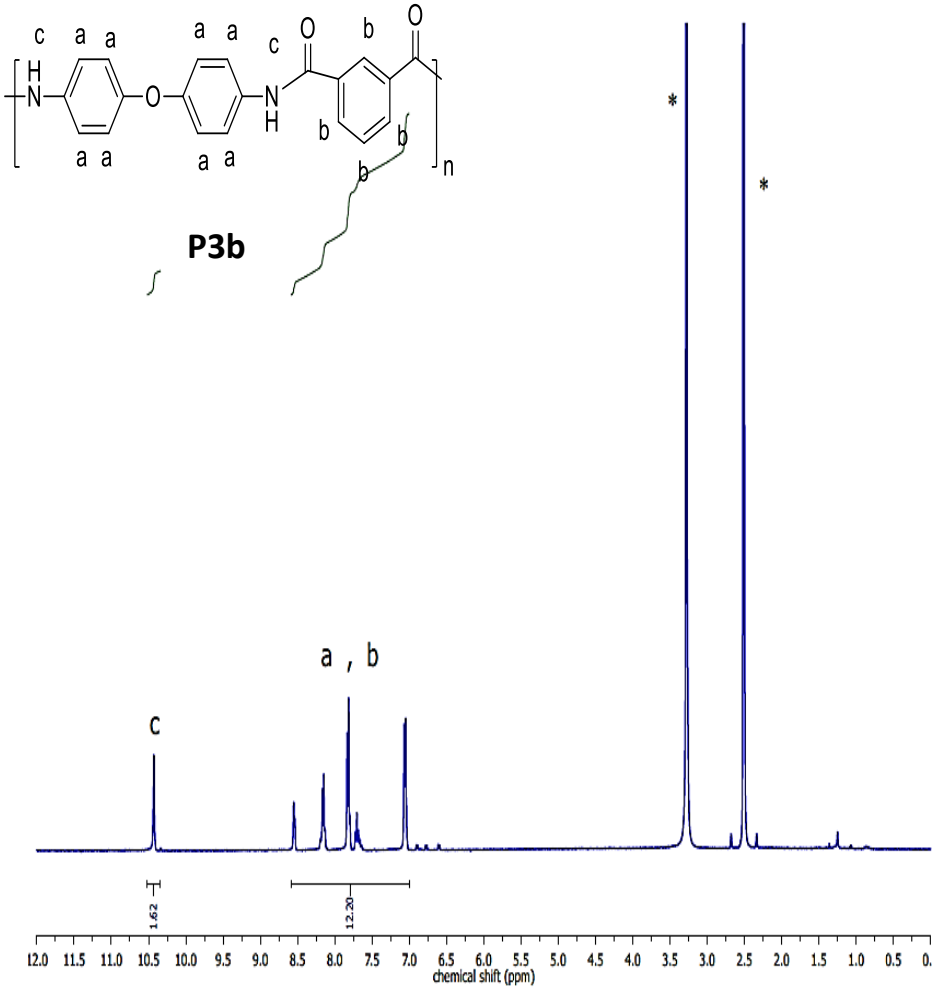


Figure S32. ^{1}H NMR spectrum of the polyamide **P3b** in DMSO-d_6 .

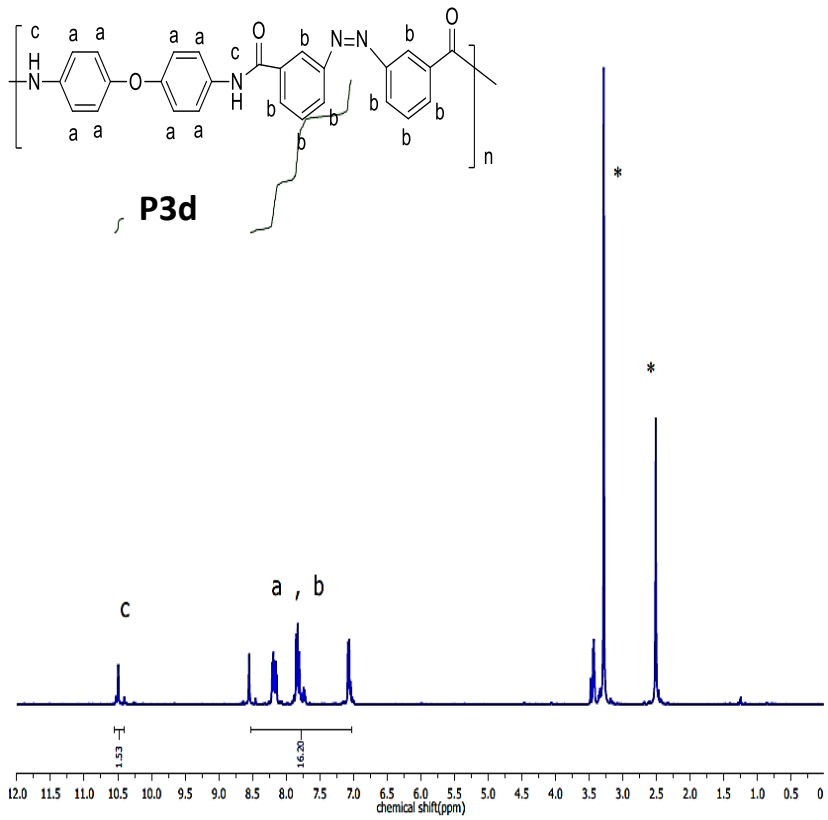


Figure S33. ^{1}H NMR spectrum of the polyamide **P3d** in DMSO-d_6 .

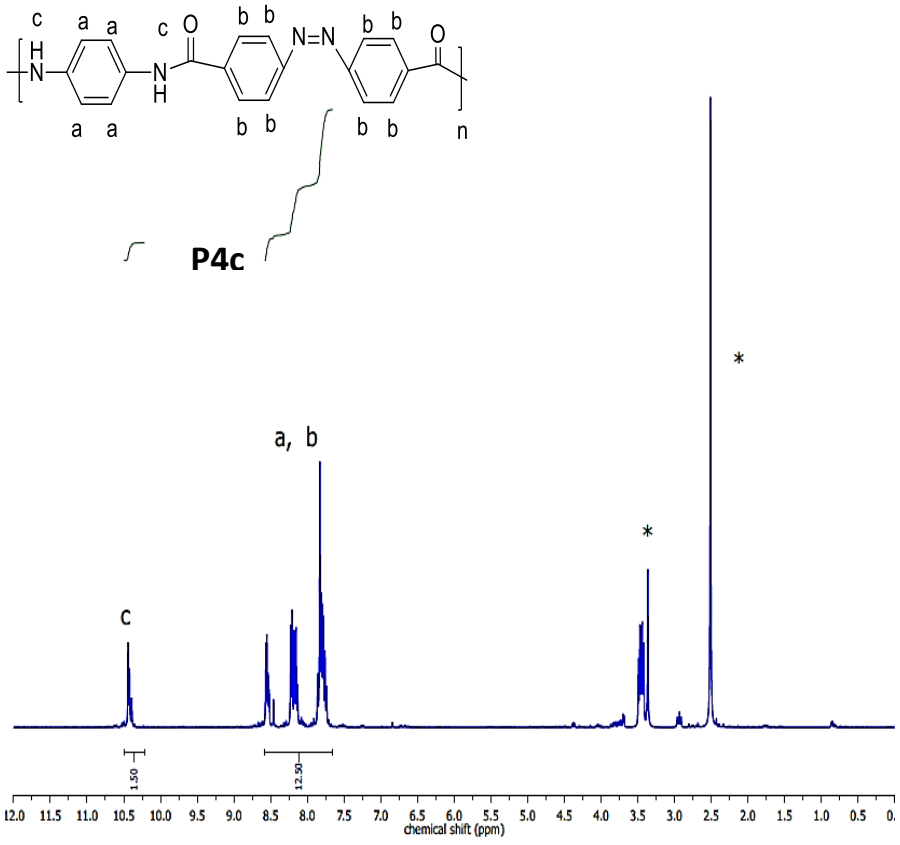


Figure S34. ^{1}H NMR spectrum of the polyamide **P4c** in DMSO-d_6 .

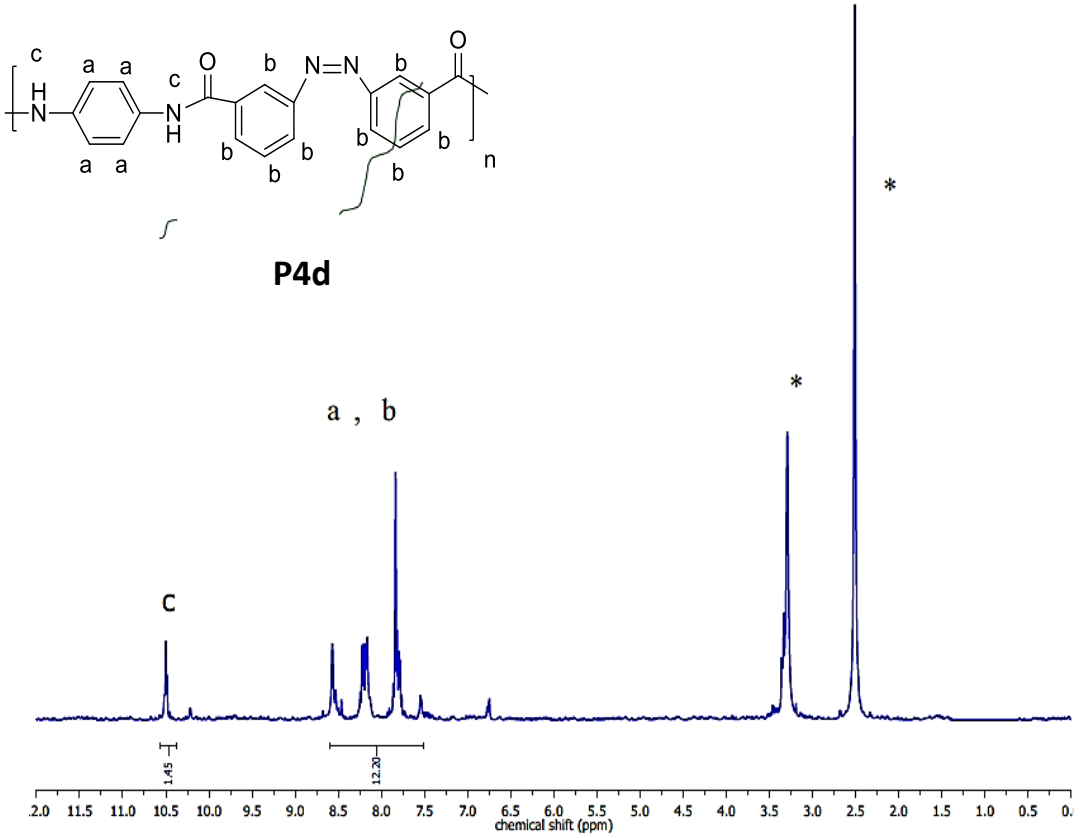


Figure S35. ^{1}H NMR spectrum of the polyamide **P4d** in DMSO-d_6 .

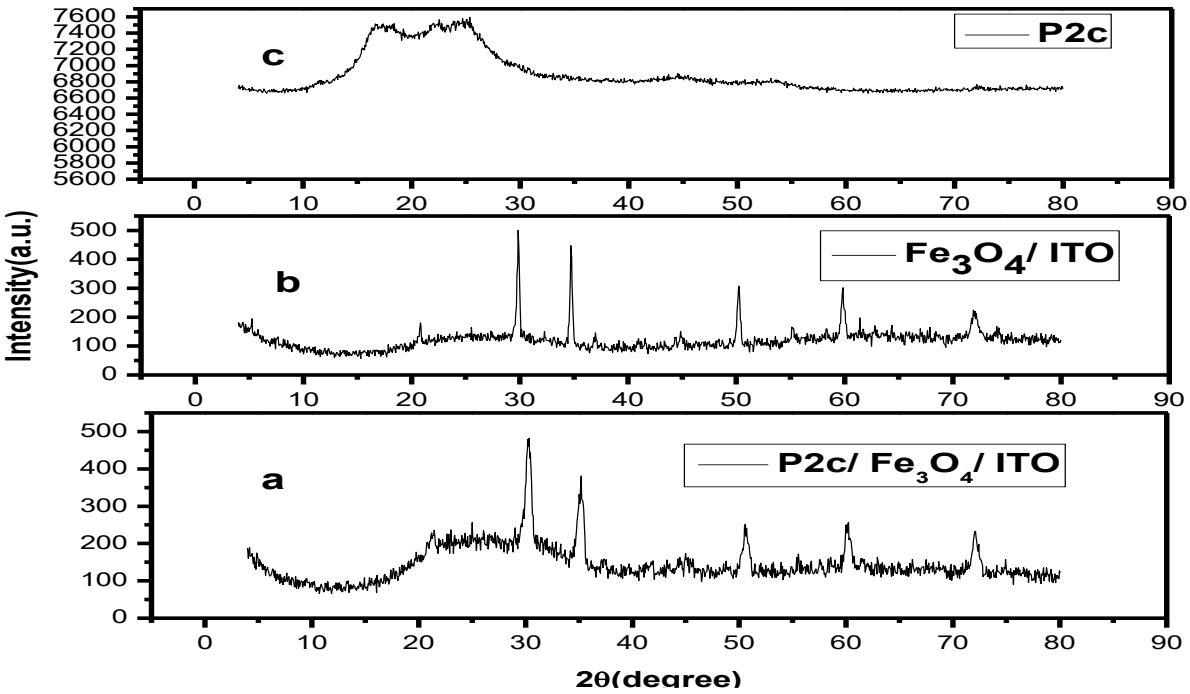
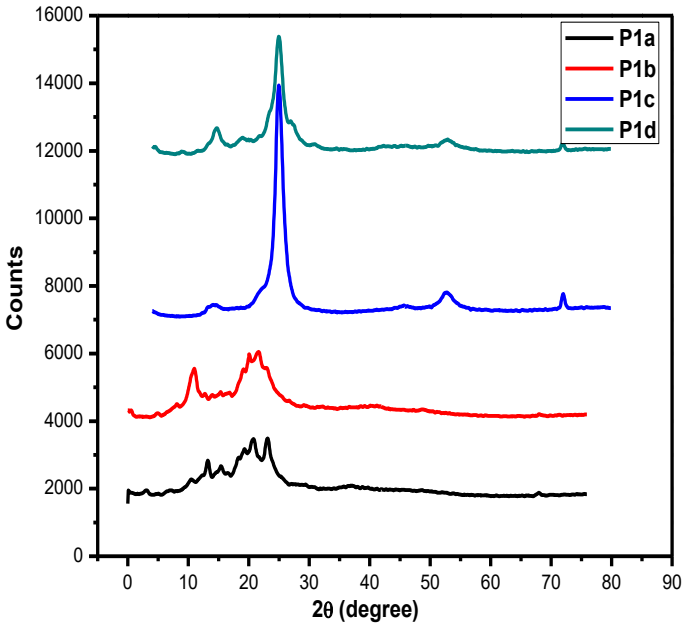
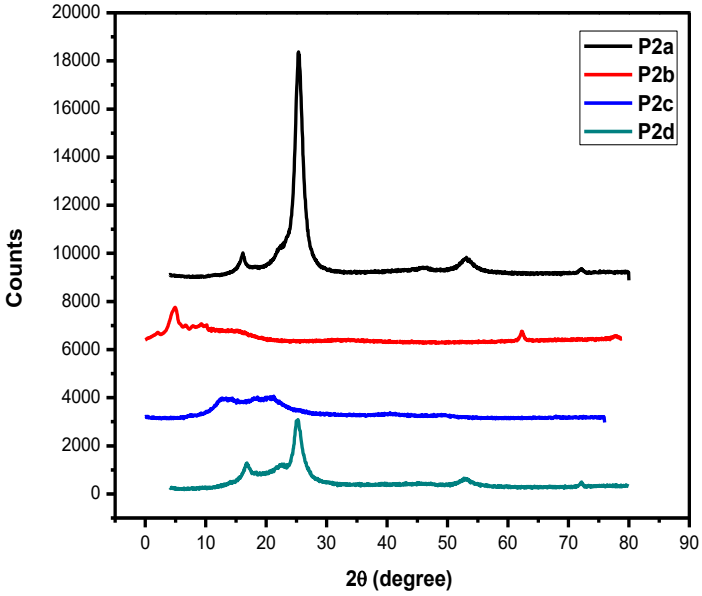
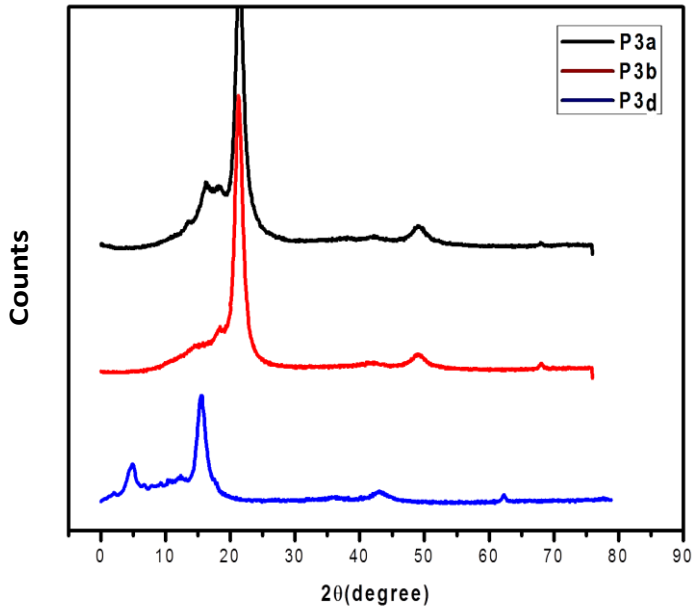


Figure S36. X-ray diffraction patterns of a) hybrid polyamide **P2c**/iron oxide/ ITO, b) iron oxide/ ITO and **c) P2c**.







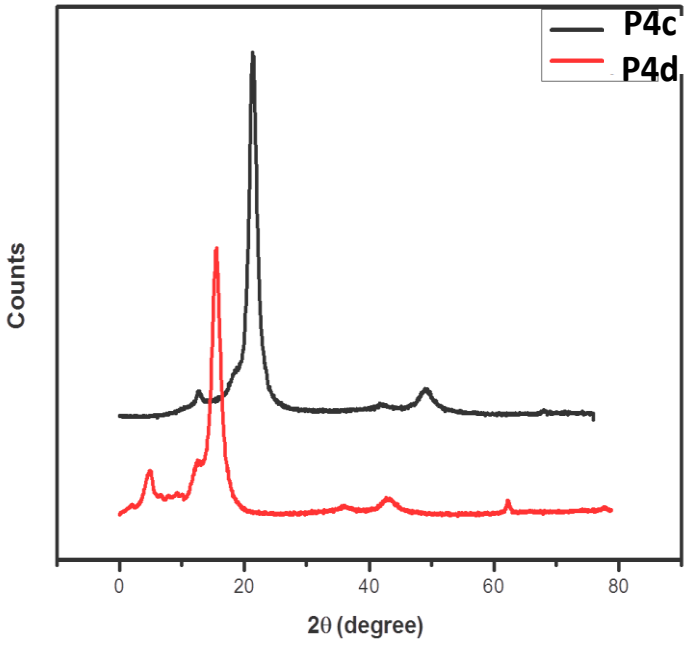


Figure S37. X-ray diffraction patterns of polyamides **P1a-d**, **P2a-d**, **P3a,b,d** and **P4c,d**.

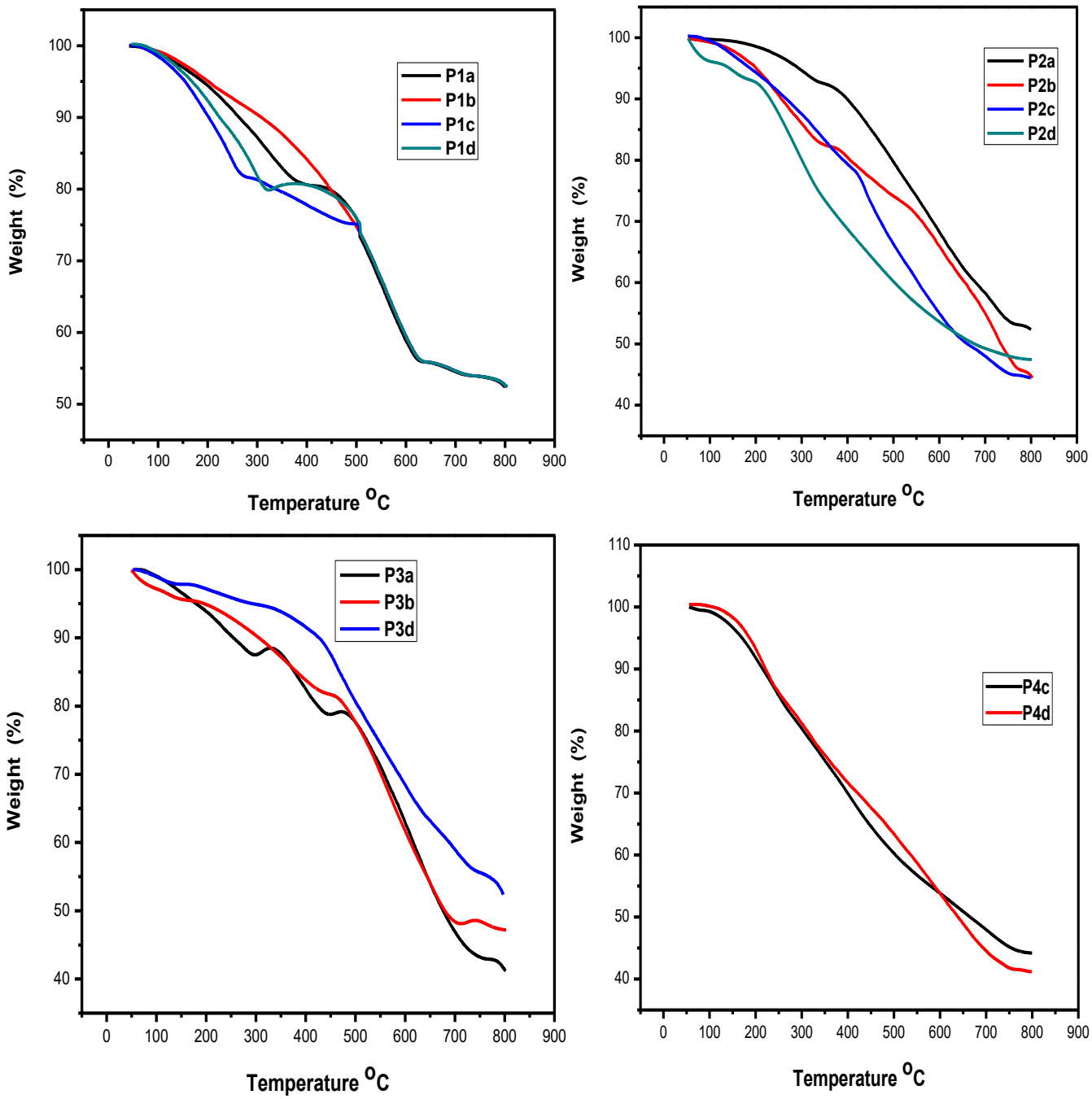


Figure S38. TGA analyses for polyamides **P1a-d**, **P2a-d**, **P3a,b,d** and **P4c,d**.

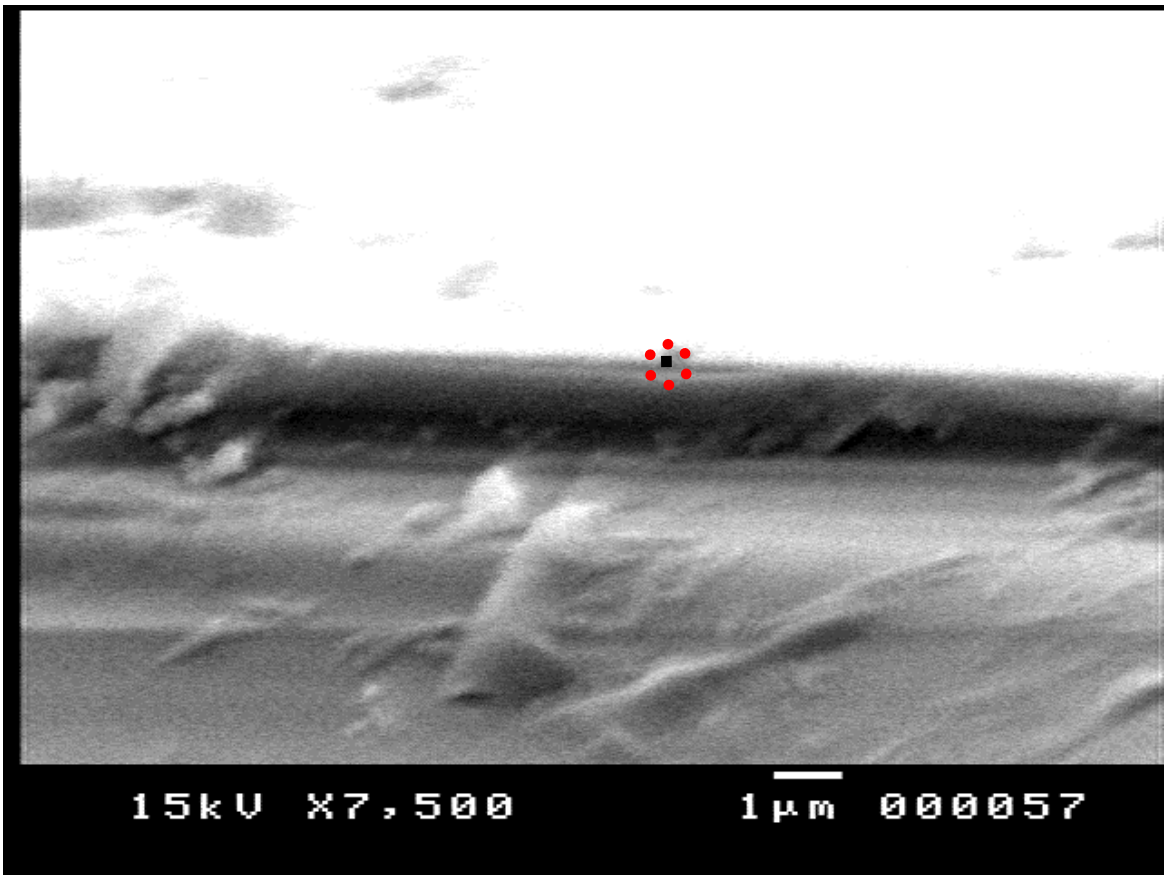


Figure S39. SEM image of a cross-section of polymer/Fe3O4/ITO electrode

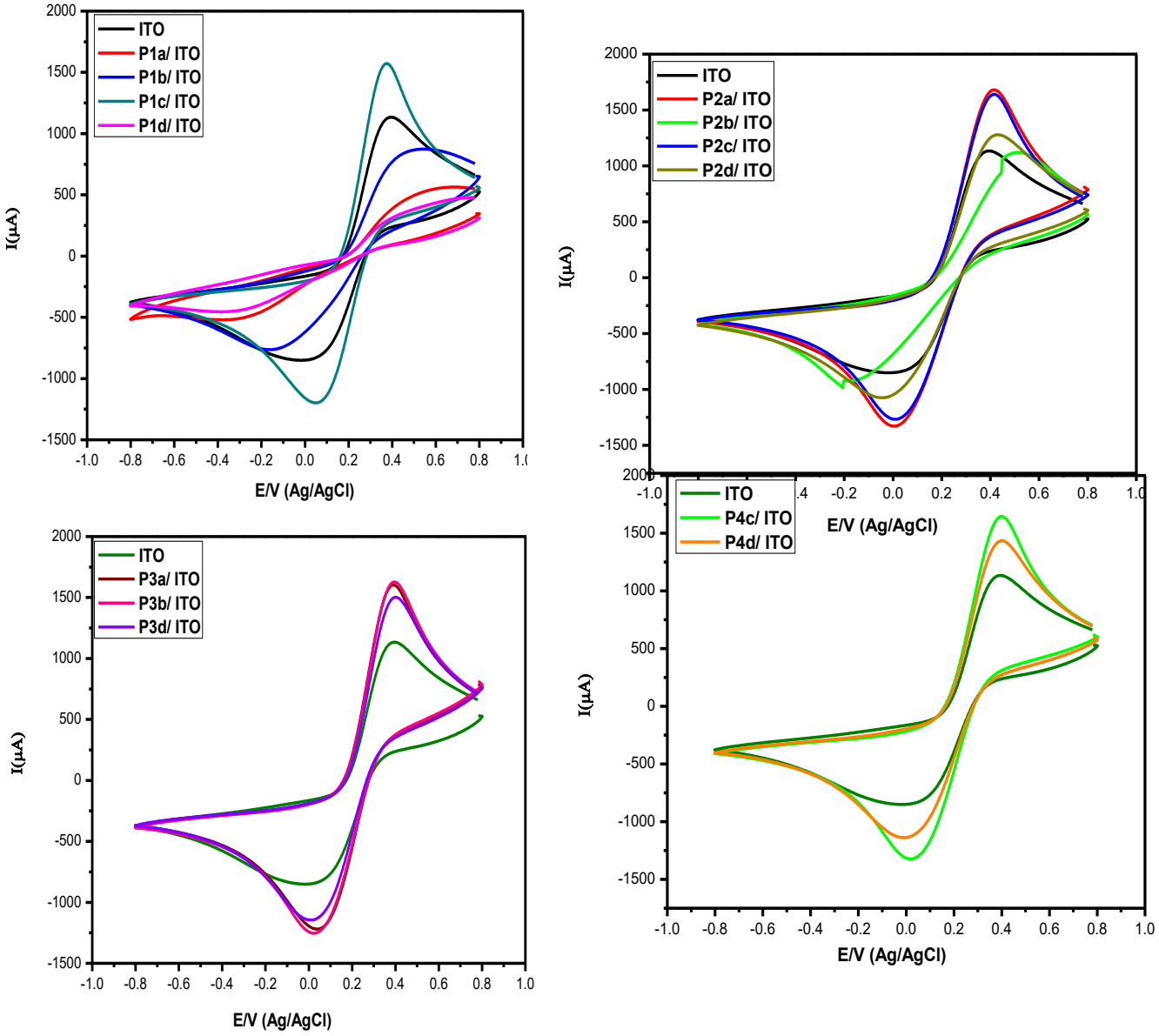


Figure S40. Electrochemical conductivity of the polyamides **P1a-d**, **P2a-d**, **P3a,b,d** and **P4c,d** in 5 mM $[Fe(CN)_6]^{-3/-4}$ (a) **P1a-d** , (b) **P2a-d** , (c) **P3a,b,d** and (d) **P4c,d**.

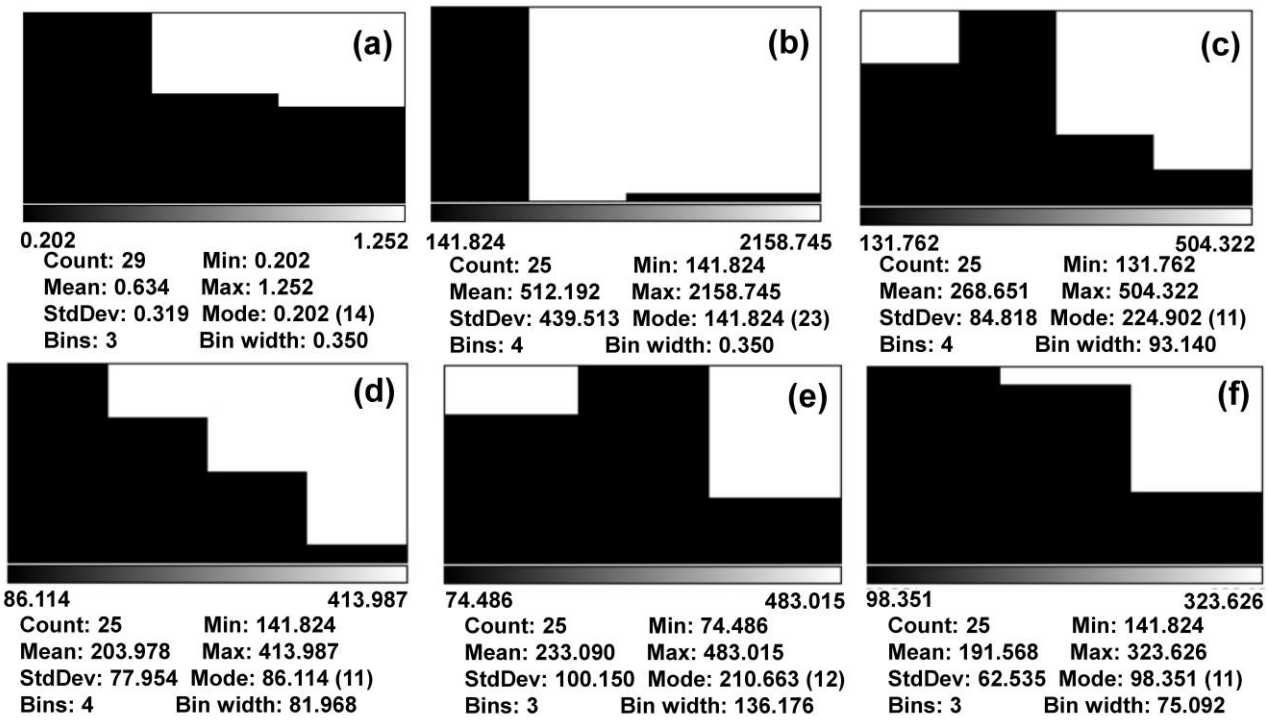


Figure S41. Distribution of the particle sizes of (a) P1a, (b) P1c, (c) P2a, (d) P2c, (e) P3a, and (f) P3d