

Co-Terpolymerization of m-phenylenediamine, O-Anisidine, 2,3-Xyilidine: Synthesis and Characterization

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Abstract: Copolymers of m-phenylenediamine and O-Anisidine were synthesized by oxidative polymerization at different monomer ratios using ammonium persulfate as oxidant in HCl medium. The yield and the conductivity of the copolymers increase as O-Anisidine ratios increase which leading to increase the polymer chain in the same time increasing of conjugation system. The effect of introducing a third monomer to the copolymer of m-phenylenediamine and O-Anisidine were studied by the addition of 2,3-Xyilidine to obtain different molar ratios of terpolymers. The yield, intrinsic viscosity and the conductivity of the terpolymers were studied and compare with the copolymers. The Co-Terpolymerization of m-phenylenediamine, O-Anisidine and 2,3-Xyilidine were characterized by FTIR and UV-Visible spectroscopy. The terpolymers seem dependency on polymerization yield, conductivity and intrinsic viscosity are 89% for MPD/OA/XY (70/10/20) terpolymer, 1.511 S/m for MPD/OA/XY (70/10/20) and 1.1 dl/g for MPD/OA/XY (70/25/5) compared to the yield obtained of MPD/OA copolymer which is 83% for [(MPD(75)/OA(25))] and conductivity of 1.228 S/m for [(MPD(25)/OA(75))], which may be attributed that the terpolymers chaotic super molecular structure than the copolymer leading to increase the polymer chain and then increasing the conjugation system. The FTIR and UV-Vis investigation suggest that the polymers obtain are actual copolymer of MPD/OA and terpolymer of MPD/OA/XY.

Keywords: Copolymer, terpolymer, conducting polymers, UV-Visible spectroscopy, IR spectroscopy, m-phenylenediamine.

1. Introduction

Conducting polymers have a great interest in the scientific researches due to their various physical, chemical properties and large applications [1,2], conducting polymers have many applications where an organic conducting material is needed, such as photovoltaics, microelectronics, anti-static packaging, corrosion protection, sensors, fuel cells and batteries [3-5]. Polypyrrole, polythiophene, polyphenylene and polyaniline are considered to be conducting polymers [6-8]. Polyaniline (PANI) and its derivatives are one of the most promising classes of organic conducting polymers because of its moderately high conductivity upon doping by protonation, good environmental stability and ease of synthesis [9-12]. However, its insolubility in common solvents, which results in difficult process ability has restricted its applications. To improve the polymer solubility, copolymerization of aniline with aniline derivatives was proposed [13,14]. Polyaniline is partially soluble only in a few organic solvents with high boiling point as N,N-dimethyl

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acetamide (DMA), N,N-dimethyl formamide (DMF) and dimethylsulfoxide (DMSO). Various functional polymers are produced by chemical oxidative polymerization such as polyaniline, polytoluidine, polypyrrole, polyaminopyridine, and polyphenylenediamine. Among them, Polyphenylenediamine homopolymer has attracted attention, however, conductivity and solubility of phenylenediamine homopolymer are low [15-17]. The chemical oxidative polymerization of phenylenediamine, displaying novel macromolecular structure and properties [18-32], has been a very interesting area of research currently. All three isomers of phenylenediamine can be considered as derivatives of the parent aniline contains on additional amino groups in its orto-, para- and meta- positions [33-36]. In the case of poly(m-phenylenediamine) homopolymer, there are two typical structures including rigid rod-like ladder or network type, depending on the coupling orientation in the m-phenylenediamine monomer [37]. Poly(m-phenylenediamine) is considered to be completely insoluble in most organic solvents such as DMSO and H₂SO₄ which are considered to be good solvents of polyaniline polymers [38]. To improve the solubility of poly(m-phenylenediamine), various aromatic amines such as, aniline, anisidine and xylidine have been utilized as co monomer [39,40]. Terpolymerization of m-phenylenediamine, O-Anisidine and 2,3 Xylidine has been reported before [41]. It is interested to find out how the copolymerization of two monomers is influenced by the introducing of the third monomer. In our laboratory, different molar ratios of copolymer and terpolymer of m-phenylenediamine/O-Anisidine/2,3 Xylidine has been prepared. The influence of introducing 2,3-Xylidine as a third monomer to the copolymer of m-phenylenediamine/O-Anisidine has been detected and characterized by FTIR and UV- Visible spectroscopy.

2. Experimental

2.1. Materials

Different chemicals have been used in this work such as: Aniline (AN) (ADWIC, Egypt), O-Anisidine (OA), m-phenylenediamine (MPD), 2,3-Xylidine ammonium persulfate as oxidant (MERC, Stuttgart, Germany), ammonium hydroxide, Hydrochloric acid (HCL 32 %), Acetone, Lithium Chloride (LiCl) and dimethyl sulfoxide (DMSO) are used as received without further purification.

2.2. Measurements

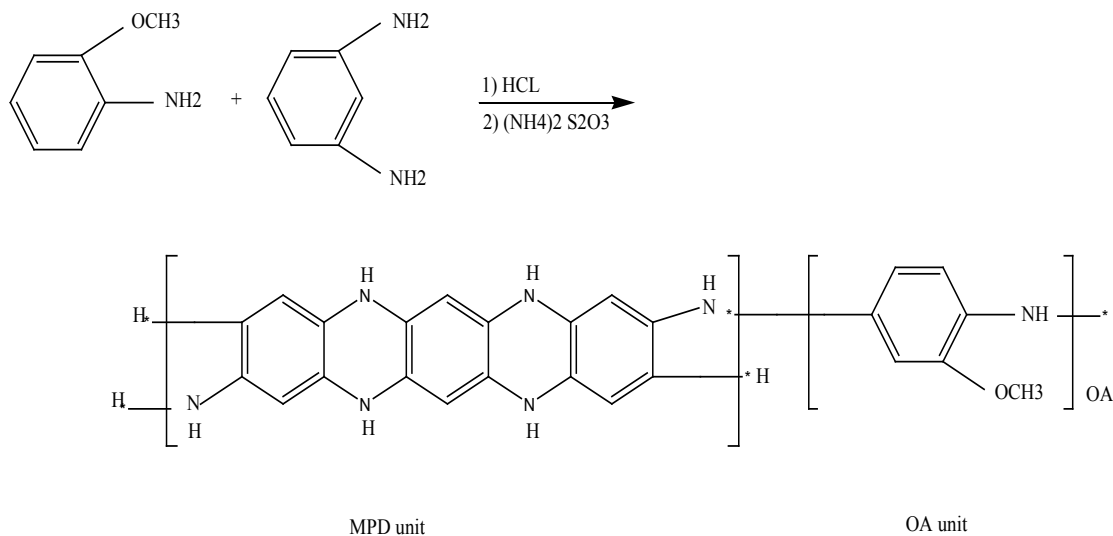
FTIR spectra were recorded using FTIR-8201 PC (SHIMADZU) instrument by KBr pellets technique, and UV-Vis absorption spectra were recorded in spectrophotometer (UV-1601 SHIMADZU). The electrical conductivity was measured at room temperature by using conductivity meter (CM-30V) and the intrinsic viscosity measurements were performed at (25 ± 0.1) with Cannon-Fenske routine type capillary viscometric equipped with a model OSK 2876 thermo stated bath.

2.3. Synthesis Of Poly (O – ANISIDINE – CO – m –Phenylenediamine) Copolymer

A mixture of 1.6 ml of o – anisidine and 1.53 g of m – phenylenediamine were dissolved in 35 ml of distilled water to which was added drop wise a solution of ammonium persulfate of 15.3 g in 175 ml of 1.25 M HCl at 24°C in about 83 min. Immediately, after the addition of the first three drops the reaction solution turned dark. The polymerization was carried out in an ambient water bath at 24 – 27°C for 24 h. The copolymerization seemed to be exothermic, so the reaction temperature increased slightly from 24 to 27°C during dropping the oxidant solution may be due to a very slow rate of adding the oxidant. The desired copolymer was recovered by filtration, washed, and then left to dry in air for

several days. Homopolymers of o – anisidine and m – phenylenediamine and their copolymers, with Co – monomer feed ratio of 25, 50, 75 and 100 were similarly prepared.

The MPD/OAcopolymer exhibit the following structure:



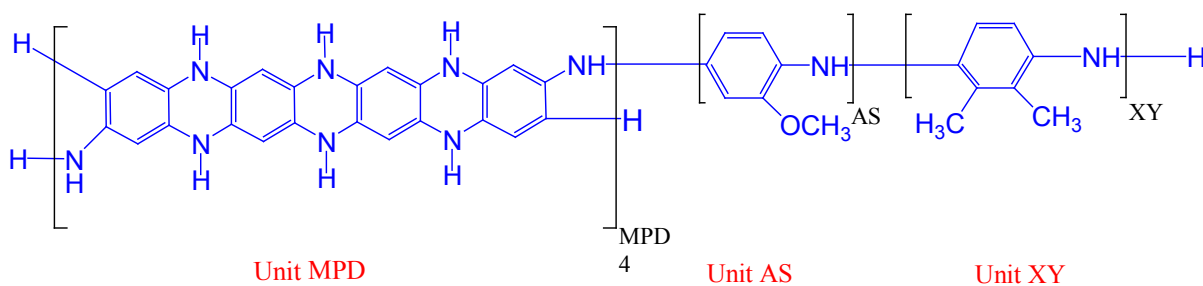
2.4. Synthesis of Terpolymers of m-Phenylenediamine(MPD), o-Anisidine(OA), and 2,3-Xylylidine(XY)

Terpolymers of m-phenylenediamine (MPD), o-Anisidine (OA, and 2,3 Xylylidine (XY), were prepared by the oxidative polymerization with ammonium persulfate as oxidant in 1 M HCl medium. The procedure for the preparation of the MPD/AS/XY (70/25/5), terpolymer is as follows:

2.13 g of MPD, 0.801 ml of OA, and 0.171 ml of XY, were dissolved in 35 ml of distilled water to which was added drop wise a solution of ammonium persulfate of 15.3 g in 175 ml of 1.25 M HCl at 24 °C for about 83 min.

The polymerization was carried out in an ambient water bath at 24-27 °C for 24 h. At the end of the polymerization, the terpolymer was isolated from the reaction mixture by filtration and washed with an excess of distilled water to remove the oxidant and oligomers. In order to obtain a base terpolymer, 100ml of 0.2 M ammonium hydroxide was added. The desired terpolymer was removed by filtration, washed, and then left to dry in air for several days. The product of 2.7 g was obtained with a 85.7 % yield which consider higher than the amounts obtained before [41].

The MPD/OA copolymer exhibit the following structure:



The above procedure was repeated by changing the monomers ratio.

3. Results and Discussion

3.1. Synthesis of Poly (m – Phenylenediamine – co – o – Anisidine) Copolymer

To improve the solubility of m – phenylenediamine (MPD), aniline derivatives such as o – Anisidine will improve the solubility of m – phenylenediamine. Different molar ratios of m – phenylenediamine and o – Anisidine in the ranging 0.25, 0.50 and 0.75 were used to obtain copolymers. From Table [3.1] can be observed the yield and the conductivity of the copolymers which increase as o – Anisidine ratios increase where o – Anisidine consider an aniline derivatives which leading to increase the polymer chain in the same time increasing of the conjugation system.

Table 3.1 Yield and conductivity of poly (m – Phenylenediamine – co – o – Anisidine) copolymer in DMF.

Sample	Yield (%)	Conductivity (S.cm ⁻¹)
PMPD	87	1.250
POA	79	1.290
Poly[MPD(25)-OA (75)]	80	1.228
Poly[MPD(50)]-OA(50)]	70	1.000
Poly[MPD(75)]-OA (25)]	83	0.980

3.1.1. FTIR Spectra of Poly (m – Phenylenediamine – co – o – Anisidine) Copolymers

The FTIR spectra of poly (o – Anisidine – co – m – phenylenediamine) copolymers are show in Fig. 3.1. It can be observed the strongest –NH– vibration band at 3430 cm⁻¹ are due to phenazine ring in the MPD homopolymer. At 1624 – 1630 cm⁻¹ is consider the second strongest band is due to the C=C stretching vibration in the aromatic phenazinering. Two weak band at 2925 and 2850 cm⁻¹ are due aliphatic C-H stretching vibration on the methoxy group as well as impurity. A small and broad band at 1100 – 1120 cm⁻¹ could be due to C-N stretching vibration in the benzenoid unit.

3.1.2. UV-Visible Spectra of Poly (m – Phenylenediamine – co – o – Anisidine) Copolymer

The UV-Visible spectra of the homopolymer as well as the copolymer were studied.

Table 3.2 shows the UV-Visible spectra obtained for PMPD , POA, and their copolymers with different ratios in DMF.

Sample	λ_{\max} DMF
PMPD	276 453
POA	308 595
Poly[MPD(25)- OA(75)]	283 504
Poly[MPD(50)- OA(50)]	275 507
Poly[MPD(75)-OA(25)]	273 512

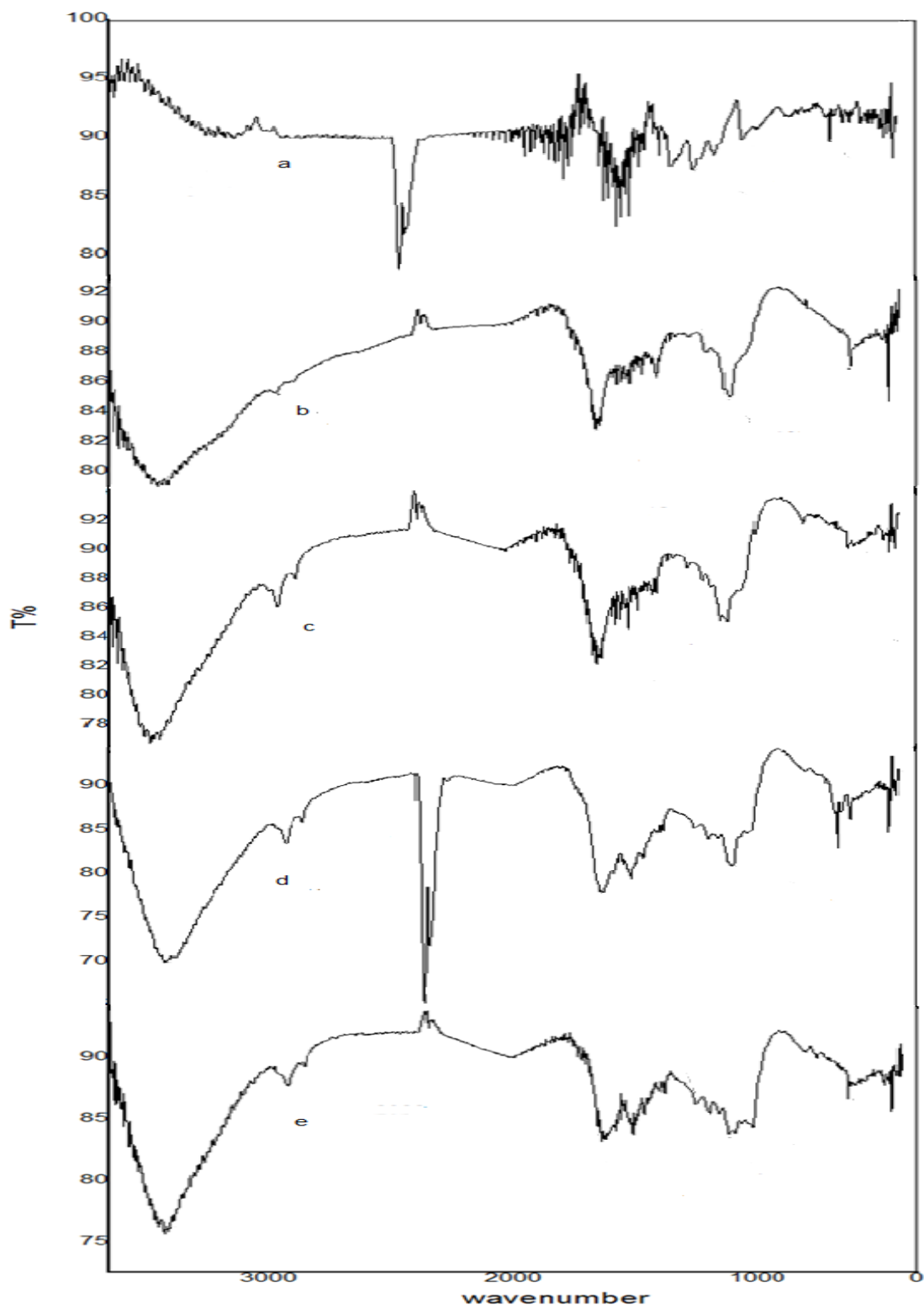


Fig. 3.1 FTIR absorption spectra of the copolymers with MPD/OA monomers ratio of a) Poly[OA(100) – MPD(00)]; b) Poly[OA(00) – MPD(100)]; c) Poly[OA(25) – MPD(75)]; d) Poly[OA(50) – MPD(50)]; e) Poly[OA(75) – MPD(25)].

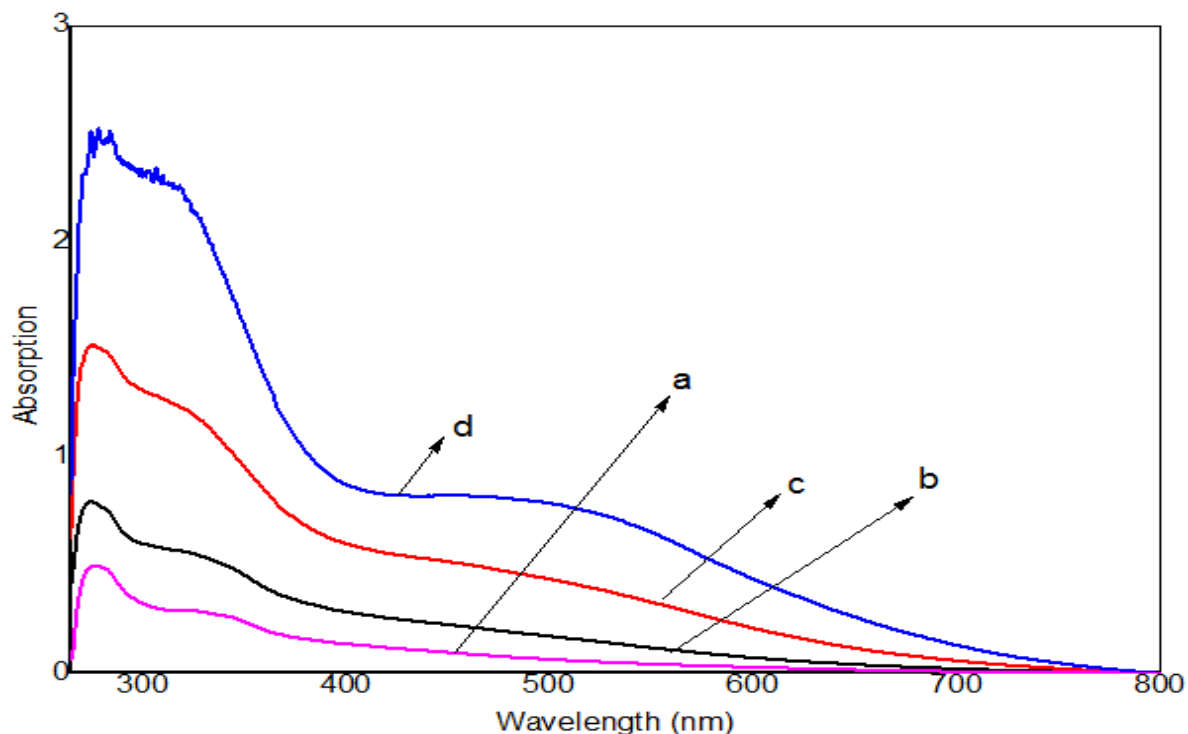


Fig. 3.2. UV-Visible Spectra of a) Poly[OA(0) – MPD(100)]; b) Poly[OA(25) –MPD(75)]; c) Poly[OA(50) – MPD (50)]; d) Poly[OA(75) – MPD(25)] in DMF.

Two strong bands at 273 – 308 nm and 453 – 595 nm with the certain resolution are observed for OA/MPD copolymer. The molecular structure of the OA/MPD copolymer in DMF depends on MPD feed content, that means shifts of peaks will increase with an increasing MPD unit.

3.2. Synthesis of The Terpolymers of *m*-Phenylenediamine (MPD), *o*-Anisidine (OA), and 2,3-Xylylidine (XY)

The effect of introducing a third monomer to the copolymer of *m*-phenylenediamine and *O*-anisidine were studied by the addition of 2,3-xylylidine to obtain different molar ratios of terpolymers.

3.2.1. The Terpolymerization Yield, Intrinsic Viscosity and Conductivity of MPD/AS/XY

Table 3.3 shows the terpolymerization yield, intrinsic viscosity and conductivity of MPD/AS/XY at different monomers ratio, the MPD/AS/XY (70/10/20), terpolymerization with the highest XY producing a highest yield and conductivity values compared to the copolymers, which may be attributed that the terpolymers show more chaotic super molecular structure than the copolymer and lead to increase the polymer chain at the same time increase of conjugation system. The OA homo polymerization shows the lowest yield possibly owing to its lowest molecular weight because the oligomer with the lower molecular weight can't be obtained by filtration. The yield for other MPD/AS/XY terpolymerization systems is maintained in a narrow range from 80 to 84%.

Table 3.3 Terpolymerization yield, intrinsic viscosity and conductivity of MPD/OA/XY terpolymers at different monomers ratio

MPD/OA/XY Monomers Ratio	Polymerization Temperature Initial / Highest / ΔT	Yield (%)	Intrinsic Viscosity (dl/g)	Conductivity S/m and C = C
100/0/0	24.3 / 27.5 / 3.2	81		1.250
70/10/20	24 / 25.1 / 1.1	89	0.52	1.511
70/20/10	23.8 / 27.3 / 3.5	86	0.74	1.293
70/25/5	23.7 / 27.1 / 3.4	85	1.10	1.488
50/40/10	23.7 / 25.8 / 2.1	84	0.39	0.988
0/100/0	18.4 / - / -	73	0.18	1.290

The MPD/OA/XY (70/10/20), terpolymer with the highest XY content exhibits the third lowest intrinsic viscosity, and the MPD/OA/XY (50/40/10), and (0/100/0), polymers with the highest OA content exhibit the second lowest and lowest intrinsic viscosity respectively. The highest value of 1.10 dl/g seems to exist for the MPD/OA/XY (70/25/5), terpolymer with lowest XY content. The intrinsic viscosity of MPD homopolymer can't be obtained because of its insolubility in DMSO. Therefore it's not possible for us to compare the intrinsic viscosities of MPD/OA/XY terpolymers with MPD homopolymers. The presence of the third monomer in the terpolymer system which considered aniline derivative and has releasing group like methyl, methoxyl group where some transfer of electrical charge is desired modifications to the polymer must be made to increase conductivity. However, the polymerization yield, intrinsic viscosity and even conductivity of MPD/OA/XY terpolymer were significantly influenced by the monomers ratio.

3.2.2. FTIR Spectra of The Terpolymers of m-Phenylenediamine (MPD), o-Anisidine (OA), and 2,3-Xyilidine (XY)

The FTIR spectra for the terpolymers with six MPD/OA/XY monomers ratio are shown in (Figure 3.3). It can be observed that the four terpolymers and MPD homopolymers all exhibit the strongest -NH- vibration band at 3435 cm⁻¹ are due to phenazine rings in the MPD homopolymer. There is a small -NH- vibration band at 3435 cm⁻¹ in the IR spectrum of AS homopolymer, may be due to the small amount of -NH- groups in its molecular chain. At 1624-1628 cm⁻¹ is considered the second strongest band is due to the c=c stretching vibration in the aromatic phenazine ring. At 569-578 cm⁻¹, abroad band which is not observed in the IR spectrum of OA homopolymer, may be due to the aromatic fused ring deformation. Two weak bands at 2925 and 2854 cm⁻¹ are due aliphatic C-H stretching vibrations on the methyl and methoxyl groups as well as impurity because MPD homopolymer has not methyl and methoxyl group. The bands at 1509-1512 cm⁻¹ are as a result of the stretching vibration of the OA content. A small and sharp band at 1384

cm^{-1} could be due to C-N stretching vibration in aromatic phenazine rings derived from MPD monomer because there is almost no similar band in the IR spectrum of AS homopolymer. A small and broad band at $1263\text{-}1280\text{ cm}^{-1}$ could be due to C-N stretching vibration in the benzenoid unit. The intensity and wave number of three weak bands at 1129 and $873\text{-}874\text{ cm}^{-1}$ do not change significantly with terpolymer composition, indicating that these bands may be attributed to the MPD unit. Four terpolymers all exhibit similar band intensity at 1042 cm^{-1} but MPD homopolymer does not. These bands may be due to OA unit because there is no strong band at 1042 cm^{-1} in the spectrum of OA homopolymer. So the IR spectral results confirm the formation of MPD/OA/XY terpolymer.

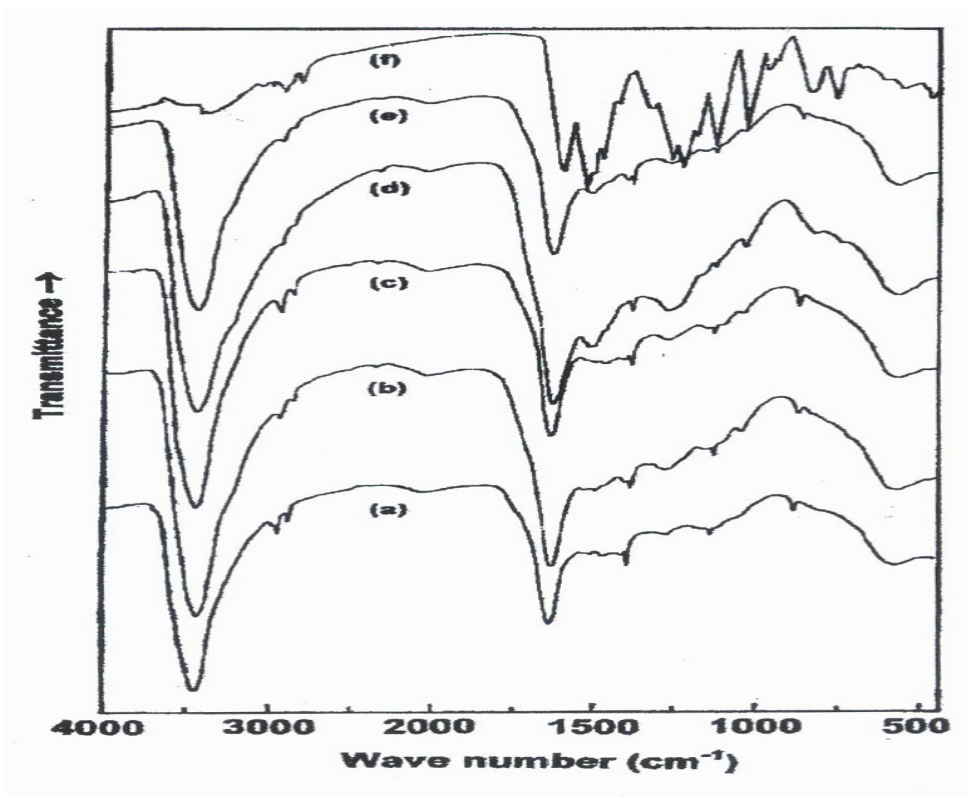


Fig. 3.3 FTIR absorption spectra of the terpolymers with MPD/OA/XY monomers ratio of a) 100/0/0 , b) 70/10/20 , c) 70/20/10 , d) 70/25/5 , e) 50/40/10 , f) 0/100/0.

3.2.3. UV-Vis Spectra of the Terpolymers of *m*-Phenylenediamine (MPD), *o*-Anisidine (OA), and 2,3-Xylylidine (XY)

Fig. 3.4 exhibits the UV-Vis spectra of the terpolymers of MPD/OA/XY with various monomers ratio in DMSO.

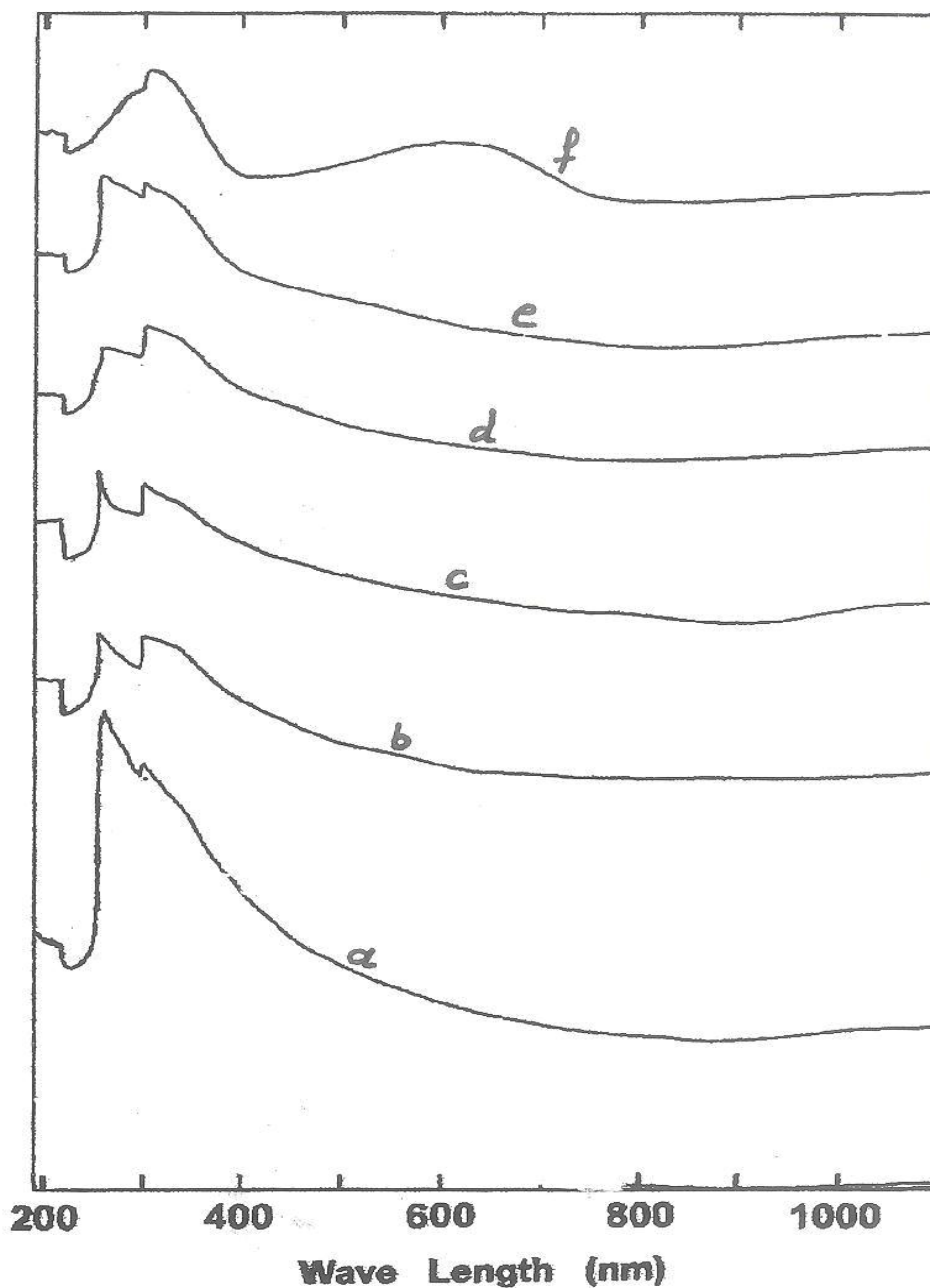


Fig. 3.4 UV-Vis absorption spectra of the terpolymers MPD/OA/XY solution in DMSO at different monomers ratio of a) 100 / 0 / 0, b) 50 / 40 / 10, c) 70 / 10 / 20, d) 70 / 20 / 10, e) 70 / 25 / 5, f) 0 / 100 / 0 .

Two strong bands at 255.4 - 261.2 and 299.2 - 301.6 nm with the certain resolution are observed for the four MPD/OA/XY terpolymers. For OA homopolymer a broad strong band at 290.9 and 614.4 nm are observed. The molecular structure of the soluble part of the MPD/OA/XY terpolymers in DMSO depends on the MPD feed content, that means the strong bands becomes shorter with an increasing MPD unit. In other words, the polymer prepared should be a real terpolymer.

4. Conclusion

Copolymers of MPD/OA were synthesized by oxidative polymerization. The effect of introducing a third monomer to the copolymer of MPD/OA was studied by the addition of XY to obtain by oxidative polymerization a series of MPD/OA/XY terpolymers. The oxidative polymerization is seemed to be exothermic. The terpolymers seem dependency on polymerization yield, conductivity and intrinsic viscosity are 89% for MPD/OA/XY (70/10/20) terpolymer, 1.511 S/m for MPD/OA/XY (70/10/20) and 1.1 dl/g for MPD/OA/XY (70/25/5) compared to the yield obtained of MPD/OA copolymer which is 83% for [(MPD(75)/OA(25))] and conductivity of 1.228 S/m for [(MPD(25)/OA(75))], which may be attributed that the terpolymers chaotic supermolecular structure than the copolymer leading to increase the polymer chain and then increasing the conjugation system. The FTIR and UV-Vis investigation suggest that the polymers obtain are actual copolymer of MPD/OA and terpolymer of MPD/OA/XY.

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