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Synthesis and Characterization of Copolymers of 2- methyl aniline with aniline and 2-aminobenzoic acid Capacity.

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Research Article

ABSTRACT

The chemical copolymerization of 2-methyl aniline with aniline and 2-aminobenzoic acid has been performed by chemical and inverse emulsion polymerization. 2-methyl aniline–aniline copolymer and 2- methyl aniline–co–2-aminobenzoic acid were synthesized at different molar ratios and at different temperatures. The copolymers of 2-methyl aniline with aniline show a greater resemblance to the poly(2- methyl aniline) due to the higher amounts of 2-methyl aniline in the copolymer, this lead to an increase in the solubility, but a lowering in the conductivity. The synthesis of 2-methyl aniline–2-aminobenzoic acid copolymer show high yield and conductivity values at room temperature compared to those synthesized at 0 and 60^0C due to higher rate of polymerization of poly (2- methyl aniline) at room temperature. The characterization of the copolymers was investigated using a number of techniques including FTIR, UV–Vis, conductivity and elemental analysis.

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 materials 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 processability has restricted its applications. To improve the polymer solubility, copolymerization of aniline with aniline derivatives was proposed [13,14]. In general, an increase in the solubility is achieved at the expense of conductivity in the case of alkyl substituted polyaniline like poly(2-methyl aniline). There are some reports on the copolymers of aniline with 2 and 3 -methyl aniline [15-18]. However, polyaniline derivatives with sulfonic acid groups either on the ring [19], or in the nitrogen atoms [20-24] are more soluble and usually show higher conductivity depending on the substitution. Sulfonic, carboxylic and phosphoric groups are acidic groups which consider as ring substituents influences the acidity constants of the amino groups and the polymerization of aniline may occur even in less acidic medium.

The present work aimed to synthesize the copolymer of aniline with 2-methyl aniline by oxidative copolymerization also to synthesize the copolymer of 2-aminobenzoic acid with 2-methyl aniline to attain the advantages of methyl and carboxylic groups. The resulting copolymers were characterized by different techniques, such as FTIR, UV – Visible, conductivity measurements and elemental analysis.

EXPERIMENTAL

Chemicals and reagent

Aniline (Merck), 2-methyl aniline (Leo chem.), ammonium persulfate (Ranbaxy), hydrochloric acid (Merck), 2-aminobenzoic acid (Fluka).All the other chemicals were analytical grade reagents and were used as received.

Synthesis

1 – poly(aniline–co – 2– methyl aniline) copolymer

The synthesis was performed by using a modified literature procedure [18]. The copolymer of aniline with 2 – methyl aniline was prepared by oxidative copolymerization method .The preparation of poly (aniline (50)- co- 2 – methyl aniline (50) is as follow: A mixture of 1.1 ml of aniline (0.05 *M*) and 1.3 ml of 2–methyl aniline (0.05 *M*) was dissolved in 100 ml of 1 M HCl. This solution was kept at 0-5 °C in an ice bath. An aqueous solution of 0.1 M ammonium per sulfate (5.7 g) was then added drop wise over a period of 20 min with continuous stirring. The total volume of the reaction mixture was 250 ml. This was stirred for 1 h and then kept at 10 °C for 24 h. The green precipitate obtained was filtered, washed with distilled water until the filtrate became colorless, and then further washed with methanol and acetone. The product was dried at room temperature for 72 h under vacuum. Various molar fractions of aniline and 2–methyl aniline in range from 0.25 to 0.75 M were used to obtain copolymers.

2–poly (2–methyl aniline–co–2–aminobenzoic acid) copolymers

The synthesis was carried out using inverse emulsion method in the presence of potassium per sulfate as an oxidant. A 2.3 g of the emulsifier (sodium lauryl sulfate) in 30 ml of water and 3.4g of 2-amino benzoic acid in 120 ml of water, were added with stirring to 6.76 g of the oxidant (potassium persulfate) in 150 ml of water. Then 2.7 ml of 2–methyl aniline was added. To this milky white emulsion, 50 ml of (1 *M*) HCl was added dropwise with continuous stirring over a period of 0.5 h. The emulsion gradually turns green. The polymerization reaction was allowed to proceed for 24h. The organic phase was separated and washed with water. The dark green polymer solution in 150 ml chloroform was then treated with anhydrous 5 g sodium sulfate to remove the excess of water, then the viscous organic solution was then added to 1 L of acetone in order to break the emulsion and precipitate the copolymer. The dark green powder of the copolymer was filtered, washed with acetone and dried in vacuum for 36 h. The copolymer was synthesized at three different temperatures, 0, 60°C and room temperature.

Measurements

The FTIR spectra were recorded using FTIR-8201 PC (SHIMADZU) instrument by KBr pellet techniques. For measuring the UV-Vis absorption spectra, spectrophotometer (UV- 1601 SHIMADZU) was used. UV-Vis spectra were recorded in solution. Conductivity measurements were made by using conductivity meter (CM-30V). The (C, H, N) analysis was carried out using EA 1110 elemental analyzer.

RESULT AND DISCUSSION

1- Characterization of poly(aniline–co–2–methyl aniline) copolymer.

The synthesis of poly(aniline–co–2–methyl aniline) copolymer was conducted by using oxidative copolymerization method. The copolymer was synthesized at different molar ratios of aniline and 2–methyl aniline, within the range (0.25 to 0.75). Table 1 shows the yields and conductivity measurements of poly aniline, poly–2–methyl aniline and other synthesized copolymers.

Table 1: Yields and conductivity for the poly (aniline – co – 2 – methyl aniline) Copolymers

Sample	Yield(%)	Conductivity S/Cm
Poly aniline	97.5	1.095
Poly (2 – methyl aniline)	80	1.070
POLY(aniline (25)- 2 – methyl aniline (75)	46.4	1.69
POLY(aniline(50)- 2 – methyl aniline (50)	82	1.84
POLY (aniline (75)- 2 – methyl aniline (25)	76.5	2.50

It could be observed that the yield decreases at higher molar ratio of 2–methyl aniline with respect to aniline. This effect could be attributed to the steric hindrance caused by 2–ethyl aniline. The conductivity increases as the amount of poly aniline predominates.

FT-IR Spectroscopy

Figure 1 shows the characteristic bands in the IR spectrum of the PANI occur at: 1562, 1477, 1290, 1239,1110 and 798cm^{-1}. The band at 1562 cm^{-1} corresponds to the C=C ring stretching vibrations of the benzonid ring, while the peak at 1477 cm^{-1} is related to stretching of the quinoid ring. The band at 1290 and 1239 cm^{-1} are related to the N – H bending while the other spectra are related to the in–plane and out–of– plane C – H bending [25]. As shown in Figure 1 the IR spectra of poly 2 – methyl aniline is similar to those of the PANI

with slight shift to higher frequencies for the bands occur at 1585,1489,1377,1263,1106 and 806 cm^{-1}. The band at 1155 cm^{-1} which is not present in the IR spectrum of the PANI may be due the presence of methyl in poly (2– methyl aniline). Figure 2 shows the IR spectra of the copolymers which are similar to poly aniline and poly (2 – methyl aniline) with slightly shift to higher values.The bands related to –CH$_3$ in the copolymer at several molar ratios of poly aniline (25, 50, 75) are 1154, 1147, 1153 cm^{-1}, respectively. A slight increase in the intensity of the band near 1155 cm^{-1} with increasing the amount of 2 – methyl aniline in the copolymer was observed.
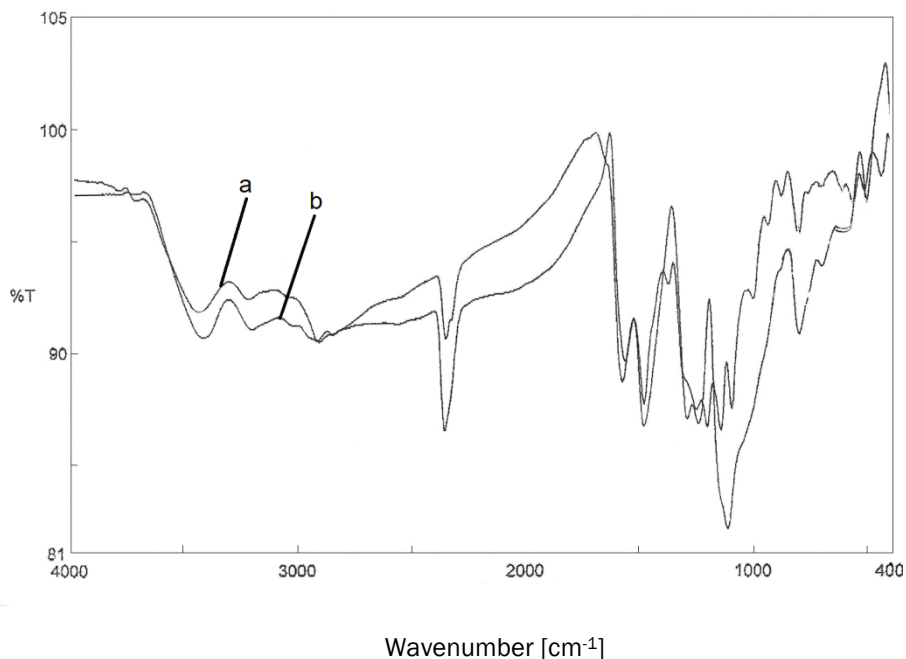

Wavenumber [cm^{-1}]

Figure 1: IR spectra of a) poly 2-methyl aniline b) poly aniline
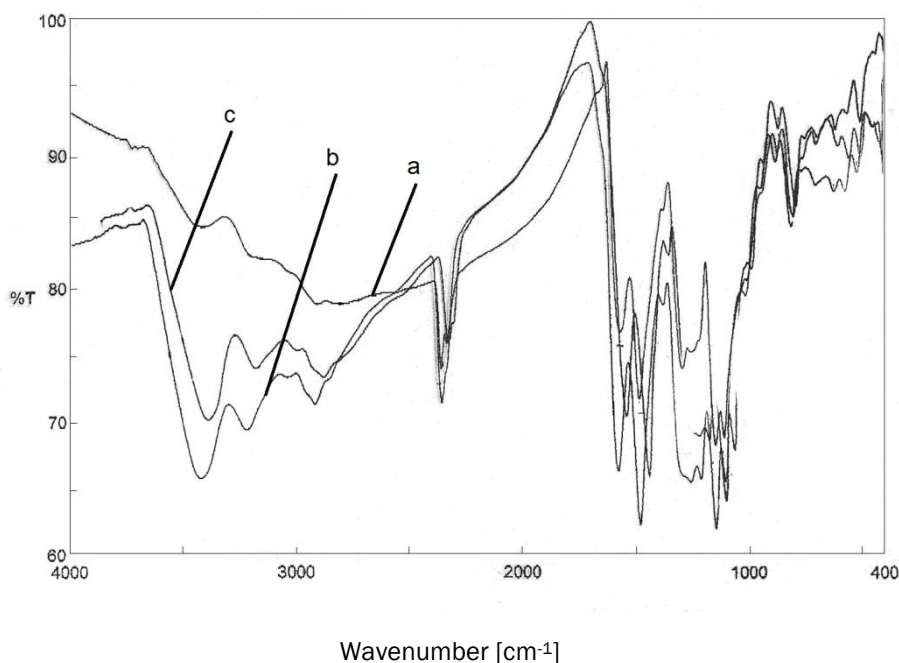

Wavenumber [cm^{-1}]

Figure 2: IR spectra of : a) poly(aniline(50)-2-methyl aniline (50), b) poly(aniline(25)- 2-methyl aniline (75), c) poly(aniline(75)-2-methyl aniline (25).

UV-Visible spectroscopy

Fig. 3-5 show the UV-Visible spectra of poly aniline and poly 2–methyl aniline , as well as the copolymers at various molar fractions of aniline and 2 – methyl aniline in the feed ranging from 0.25 to 0.75 *M* in DMF, THF and DMSO, respectively . For polyaniline in THF and DMSO, one absorption band was observed around 320 nm corresponds to the π – π* transition of phenyl ring, while in DMF, one absorption band around 610 nm corresponds

to the excitation transition (n–π* transition) [26,27]. These peaks of poly(2–methyl aniline) show slightly shifts to around 305 nm and 590 nm in the DMF, THF, DMSO, respectively. The copolymer of (aniline–2–methyl aniline) shows blue shifts and lie near to those of poly (2–methyl aniline). This fact could be attributed to the higher 2–methyl aniline content in the copolymer in comparison with aniline.

Which can be attributed to the presence of bulky methyl substituent on the benzene ring which includes the additional deformation along the polymer backbone, owing to an increase in the steric hindrance also, the absorption maxima in poly (2–methyl aniline) located at relatively shorter wave length is due to non planer conformation of the polymer backbone. In the copolymer blue shift can be observed in DMSO rather than DMF or THF which is related to a high dielectric constant of DMSO.
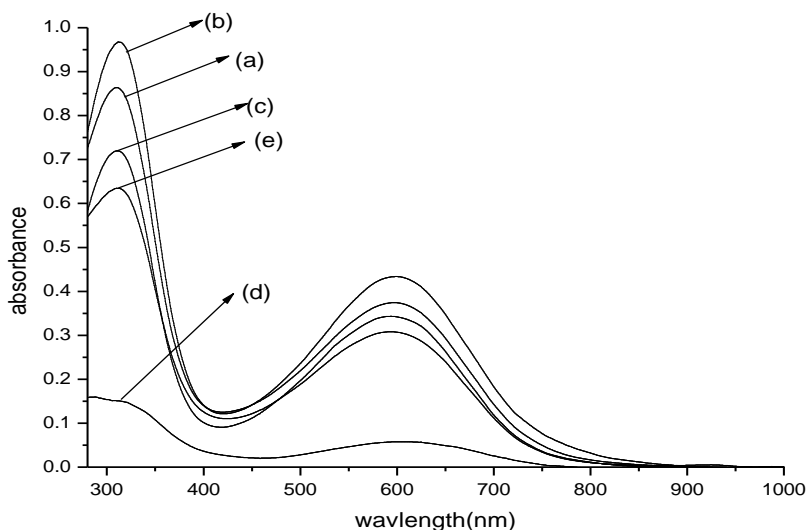

Figure 3. UV-Vis spectra of poly (aniline-co-2-methyl aniline) in DMF. (a) poly(aniline(50)-2–methyl aniline (50) (b) poly(aniline (25)- 2-methyl aniline (75), (c) poly (aniline (75)-2 –methyl aniline (25), (d) poly(aniline(100) 2–methyl aniline (0), (e) poly(aniline(0)-2–methyl aniline (100)
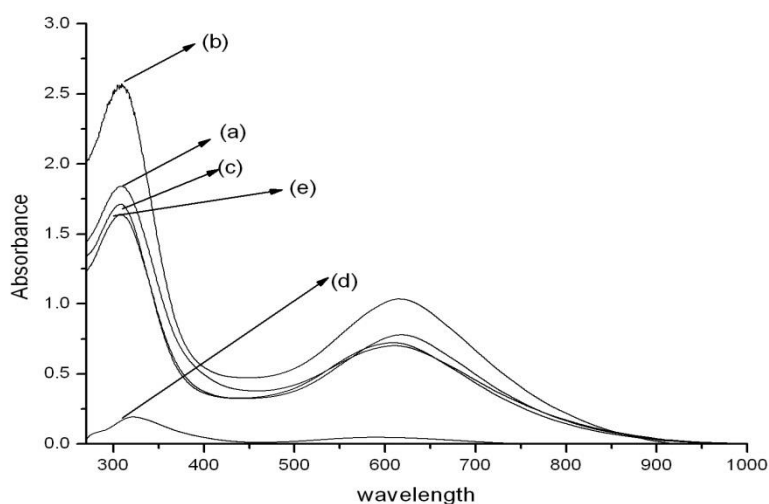

Figure 4: UV-Vis spectra of poly (aniline-co-2-methyl aniline) in DMSO. (a) poly(aniline(50)-2–methyl aniline (50) (b) poly(aniline (25)- 2-methyl aniline (75), (c) poly (aniline (75)-2 –methyl aniline (25), (d) poly(aniline(100) 2–methyl aniline (0), (e) poly(aniline(0)-2–methyl aniline (100)
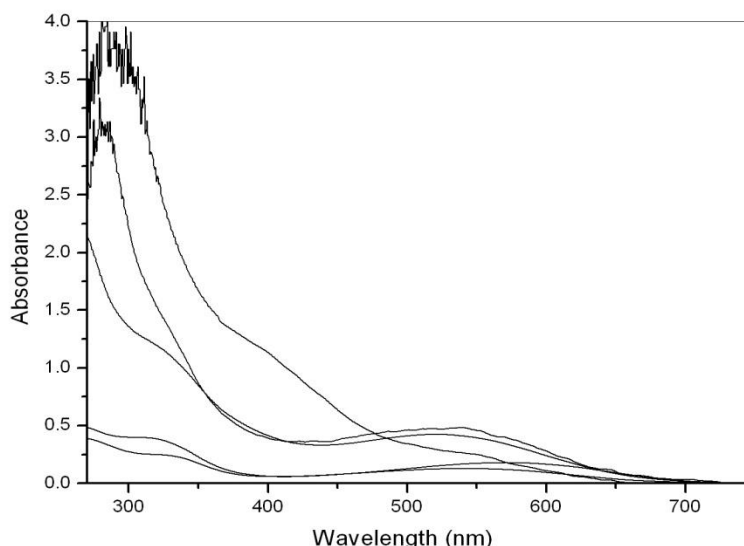
Figure 5: UV-Vis spectra of poly (aniline-co-2-methyl aniline) in THF. (a) poly(aniline(50)-2–methyl aniline (50) (b) poly(aniline (25)- 2-methyl aniline (75), (c) poly (aniline (75)-2 –methyl aniline (25), (d) poly(aniline(100) 2–methyl aniline (0), (e) poly(aniline(0)-2–methyl aniline (100)

Elemental analysis

The elemental analysis was carried out in order to know the composition of the polymer. Table 2 shows the measured and calculated elemental analyses values of poly aniline , 2–methyl aniline at different molar fractions of aniline and 2 – methyl. The higher values of %C and %H observed in poly(2–methyl aniline) and in copolymers with higher also if the molar fractions of 2–methyl aniline it could be attributed to the presence of the methyl substituent on the benzene ring. From Table 2 also we observed a great agree between the calculated and found percentage of the different elements

Table 2: Elemental composition of poly (aniline – co – 2 – methyl aniline) copolymers

Sample	C%		H%		N%		S%
	Found	Cal.	Found	Cal.	Found	Cal.	Found
oly aniline	55.77	66.06	4.75	4.85	11.03	12.84	1.62
oly 2-methyl aniline	57.37	68.29	6.16	5.94	9.45	11.38	1.08
OLY(aniline (25)- 2 – methyl aniline (75)	59.64	59.25	6.89	4.60	9.74	10.24	0.94
OLY(aniline(50)- 2 – methyl aniline (50)	57.92	58.45	5.71	4.53	10.27	10.48	1.28
POLY (aniline (75)- 2 – methyl aniline (25)	59.35	57.60	5.91	4.45	10.34	10.75	0.98

2- Characterization of poly(2–methyl aniline–co–2–amino benzoic acid) copolymer

The synthesis of this copolymer was carried out using inverse emulsion method in the presence of potassium persulfate as an oxidant and at three different temperatures: room temperature, 0 ˚C and 60 ˚C. Table 3 shows the yields and conductivity measurements of the copolymer of 2–methyl aniline with 2 –amino benzoic acid at different temperatures. It was observed that the yields obtained at room temperature are higher than at 0°C and 60°C. This may be attributed to the rate of polymerization, which could be increased at room temperature if poly(2–methyl aniline) predominates but if amino benzoic acid predominates, the rate of polymerization increases at higher temperature. The conductivity of the copolymer is dependent of the temperature at which the

polymerization was carried out. As shown in Table 3, the conductivities of the copolymers synthesized at 0°C and 60°C are lower than those observed at room temperature. This may be attributed to a more homogenous protonation of the imine nitrogen and a more order chain conformation of the copolymer.

Table 3 : Yields and conductivity for the poly (2 – methyl aniline – co – 2 – amino-benzoic acid) copolymer at different temperatures.

Sample	Yield (%)	Conductivity S/Cm
poly 2 – methyl aniline – co – 2 – amino benzoic acid at (R.T)	78	1.92×10^{-2} S/Cm
poly 2 – methyl aniline – co – 2 – amino benzoic acid at (0°C)	30.5	0.012×10^{-2} S/Cm
poly 2 – methyl aniline – co – 2 – amino benzoic acid at (60°C)	25	0.01×10^{-2} S/Cm

FT-IR Spectroscopy

Figure 6 shows the IR spectra of poly(2–methyl aniline–co–2–aminobenzoic acid) at different temperatures, the characteristic bands are :1163, 1684, 1209 and 756 cm^{-1} . The band at 1163 cm^{-1} corresponds to the –CH$_3$ group in poly 2–methyl aniline while the band at 1684 cm^{-1} is related to (C=O stretching). The band at 1209 cm^{-1} is related to (-CH bending) and that at 756 cm^{-1} is related to (out of plane-CH bending). As we mentioned before the copolymers prepared at 0 °C have relatively more 2–methyl aniline units, while as the temperature rises more amino benzoic acid group will be predominated
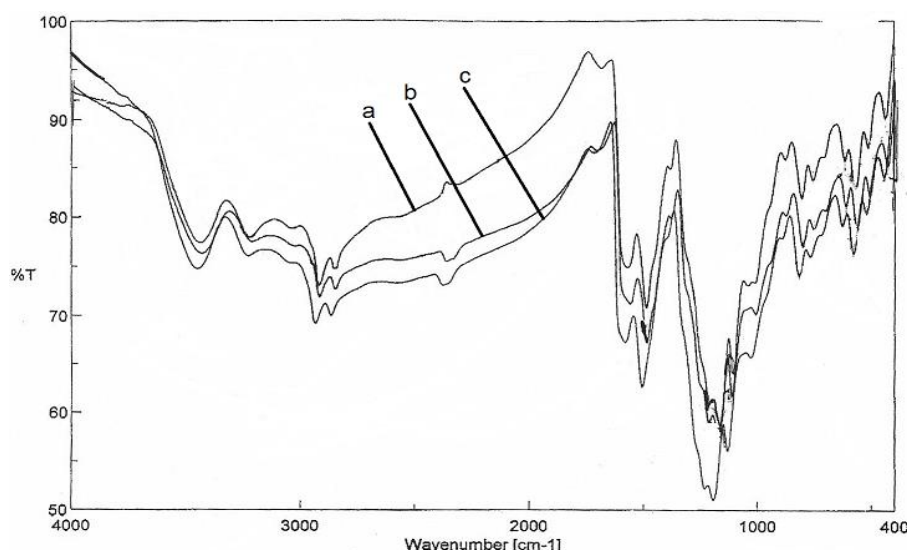

Figure 6: IR spectra of poly(2-methyl aniline–co-2-amino benzoic acid) at a)room temperature)60° C , c) 0° C.

UV-Visible spectroscopy

Figures (7 and 8) show the UV-Vis spectra of poly(2–methyl aniline–co–2–amino benzoic acid) copolymer at different temperatures. The absorption maxima for 2 – methyl aniline and 2 – amino benzoic acid copolymer at room temperature is 312 nm while two absorption peaks are shown for the copolymer at 0 °C and 60 °C which are 312 ,787 cm^{-1} and 315,608 cm^{-1}, respectively. As shown previously in Fig .4 the UV-Vis spectra of poly (2 – methyl aniline) shows a band at 612 nm since shift in the copolymer at   0°C and 60°C is observed as shown in Fig. 8. It may be because of the poor conjugation along the copolymer chain where amino benzoic acid units isolate 2–methylaniline blocks a long the polymer chain, the coplanarity of the ʌ system was lost and charge delocalization was reduced between the chains.
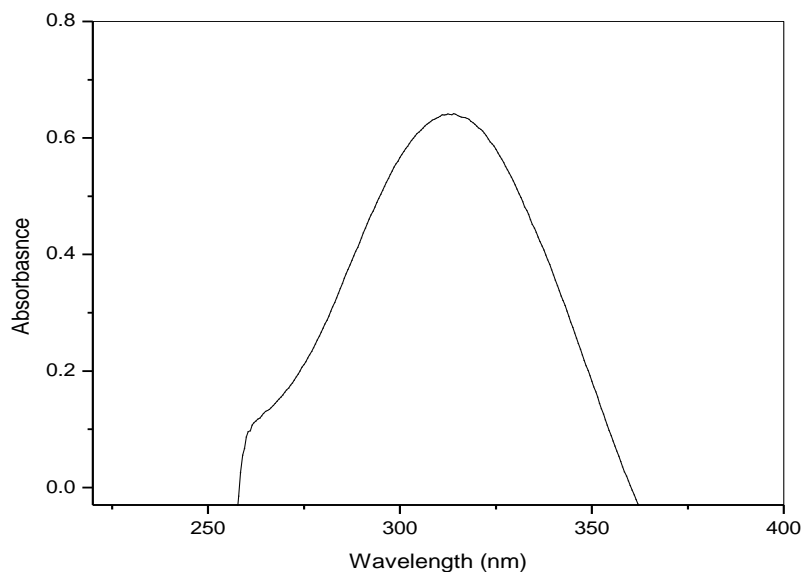
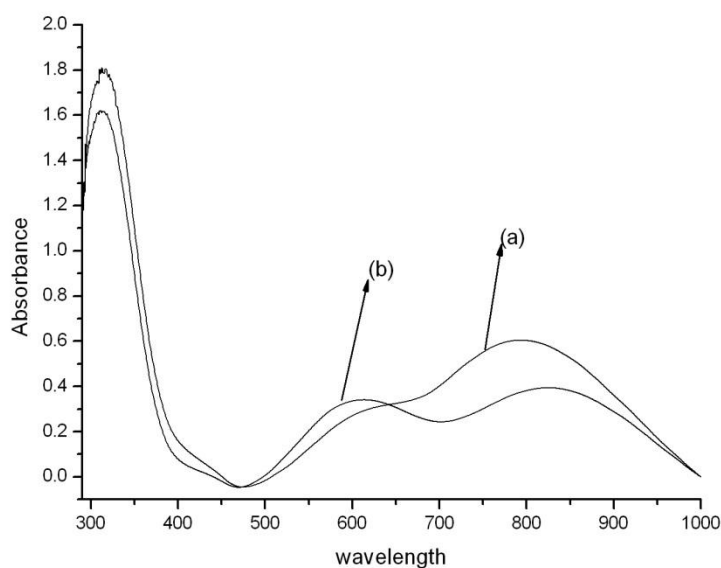**Figure 7: UV-Visible spectra of poly (2 – methyl aniline – co – 2 – amino benzoic acid) at room temperature.**

Figure 8: UV-Visible spectra of poly (2–methyl aniline–co–2–amino benzoic acid) at (a) 0°C , (b) 60°C)

CONCLUSION

Poly(2-methyl aniline-co-aniline) was synthesized at different molar ratios of the monomers. The solubility of aniline improved by the addition of 2 – methyl aniline where the copolymerization show a large resemblance to poly (2–methyl aniline) due to higher amount of 2 – methyl aniline in the mixture. At higher molar ratio of 2– methyl aniline the conductivity was minimized. Poly(2-methyl aniline-co-2-amino benzoic acid) was synthesized at different temperatures: room temp., 0°C, and 60°C. It was observed that the relatively high yield and conductivity at room temperature in comparison to the other temperatures .This may be attributed to the higher rate of polymerization of poly(2-methyl aniline) at room temperature and the higher conductivity may be became from the homogenous protonation of imine nitrogen and more order chain conformation of the copolymers. FTIR, Uv-Vis (CHN) elemental analyses were very useful to predict the composition of the copolymers.

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