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Copolymers of aniline with o-anthranilic acid: Synthesis and charachterization

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ABSTRACT

Chemical copolymerization of aniline with o-anthranilic acid in aqueous 1M HCl were carried out at different molar ratios of aniline and characterized by FTIR and UV-Visible spectroscopy, Elemental analysis and electrical conductivity. From FTIR and UV-Vis. Spectroscopy, we observed that o-anthranilic acid has been introduced into the polymer chain successfully. The percent yield of o-anthanilic acid copolymer with aniline decreases as the percent of aniline increases. An increase in the % C can be observed as the amount of o-antranilc acid in the copolymer decrease or the amounts of aniline increase.

KEYWORDS

Aniline;
o-anthranilic acid;
Copolymers;
Polymer synthesis.

INTRODUCTION

Poly aniline (PA)s have considerable signifance because of their electrical and optical properties and many potential applications such as energy storage[1], electromagnetic interference shielding[2], electrochromic devices[3,4], microelectronic device[5] and sensor[6] etc. For many of these applications the solubility and processability of polyaniline are among the most impotant properties. Poly anilines which are soluble in aqueous solutions are particulary attractive because they can be processed in water, thus avoding the environmental concerns associated with the use of organic solvents. It has been shown that polyanilnes with sulfonic acid groups on the benzene rings[7] or on the nitrogen atoms[8-13] are soluble in water. Poly anilne (PA) and its derivatives are considered to be one of the most oromising classes of organic conducting polymers due to their well-behaved electrochemistry, easy protonation reversibility, excellent redox recyclability[14], good environmental stability[15], electrochromism[16], ease of doping[17] and ease of preparation. The unsubstituted PA is insoluble in common organic solvents due to the stiffness of their backbone which result from its delocalized electronic structure. Hence their synthesis is quite difficult. The copolymerization is one of the simplest method for providing the processability of conducting polymer[18].

On copolymerization of aniline with o-anthranilic acid there is a formation of material having properties intermediate to their homopolymer and more processable copolymers. In this study, at different molar ratios of aniline, a copolymer of o-anthranilic acid with aniline is prepared and charachterized using FTIR, UV-Visible, elemental analysis and electrical conductivity.

EXPERIMENTAL

Reagents

o-Anthranilic acid (AA) (Merck, Stuttgart, Germany), Aniline (ADWIC, Egypt), Ammonium persulphate (APS) (WINLAB, UK), N,N-Dimethylformamide (DMF) were used without purification.

Characterization

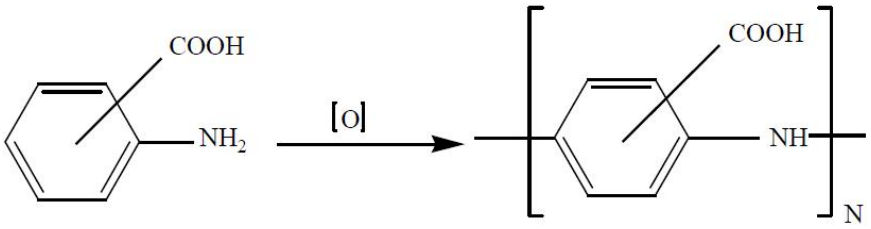
The FTIR spectra were recorded using FTIR- 8201 PC (SHIMADZU) instrument by KBr pellets, and UV-Vis absorption spectra were recorded in spectrophotometer (UV-1601 SHIMADZU). The electrical conductivity was measured at room temperature by using conductivity meter (CM-30V) and The C, H, N analysis was carried out using EA 1110 elemental analyzer.

Synthesis of copolymers

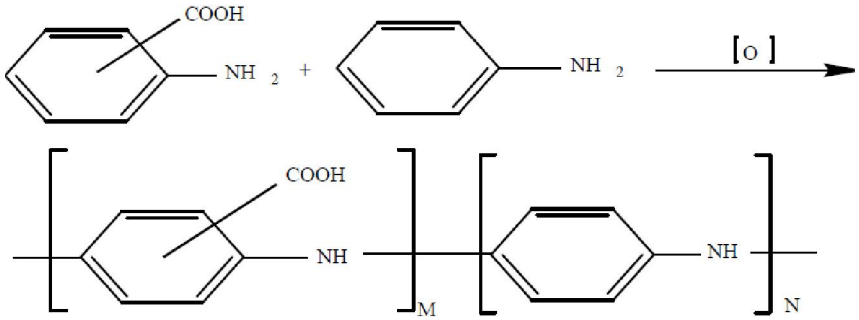
0.178 g of o- anthranilic acid (AA) was dissolved in 3 ml DMF and completed to 50 ml by 0.1 MHCl. 0.08 M solution of aniline was prepared and then added to the solution containing anthranilic acid and DMF. A solution of 0.1 M ammonium persulfate (APS) in 50 ml of 0.1 MHCl solution was prepared and then added to the solution containing the aniline and AA; therefore, the concentration of AA is 0.013 mol/L. At that case the molar ratio (f_1) of aniline/o-anthranilic acid would be 5. Different solutions were prepared in which the concentration of AA was varied from 0.0067 mol/L to 0.08 mol/L at constant concentration of aniline and APS of 0.08 and 0.1 mol/L, respectively, to give solution of different (f_1) of aniline/AA.

RESULTS AND DISCUSSION

Pol y (o-anthranilic acid, and copolymers of aniline, were synthesized according to the following reactions:



Poly anthranilic acid



Poly (aniline-Co-anthranilicacid)

FTIR spectra measurement

Figure 1 shows FTIR spectra of polyaniline (PANI)The high frequency bands at 1562 and 1477 cm^{-1} are assigned to the C=C ring stretching vibrations of the benzenoid ring and the C-N stretching of the quinoid ring, respectively. The bands 1290 and 1239 cm^{-1} correspond to the N-H bending and symmetric component of the C=C (or C-N of the benzenoid ring) stretching modes. The remaining bands at 1110 and 798 cm^{-1} could be attributed to the in -plane and out-of –plane C-H bending modes.

Figures (2,3) shows the FTIR spectra of poly (o-anthranlic acid-co aniline at f_1= 3:1 and f_1 =1:3 respectively. We observed that the FTIR spectra of copolymers show similar bands as those reported for PANI with exception of C=O absorption band 1684 and 1686 cm^{-1}, therefore, we can distinguish the copolymer with homopolymer by this charachterization band.

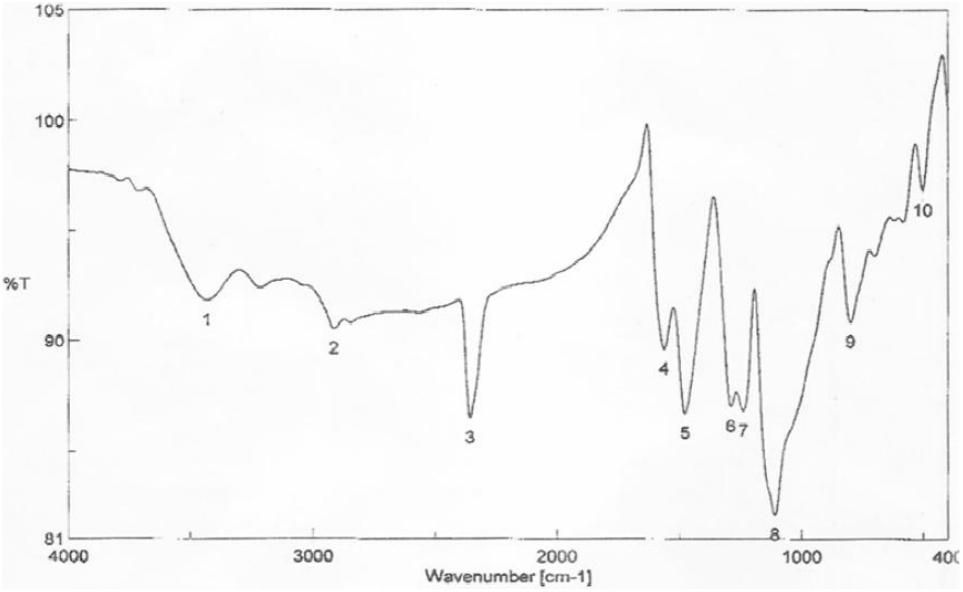


Figure 1 : FTIR spectra of PANI

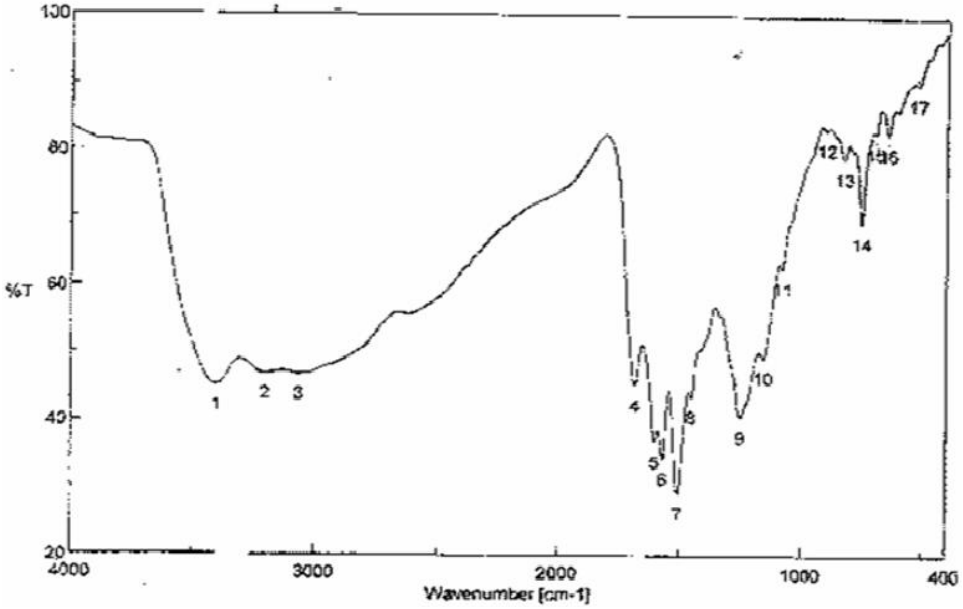


Figure 2 : FTIR spectra of Poly (o-anthranilic acid – Co – aniline) at f_1 =3:1

It means that AA had been introduced into the polymer chain successfully.

UV- Vis spectra measurement

Figure 4 shows the UV-Vis spectra of poly (o-anthranilic acid – aniline) copolymer at different mole fractions of aniline. Two absortion bands at 348 and 512 nm. That are attributed to benzenoid(π- π* transition) and quinoid rings, respectively. The π- π* transitions are related to the extension of the conjugation along the polymer backbone. These bands show shift from 350, 348 nm for o-anthranilic acid to lower values for the different mole fractions of the copolymers. Indicating a decrease in the extension of conjugation with respect to polyaniline, this decrease may be attributed to the carboxylic acid groups effect with the increase of the torsion angle between close phenyl rings with respect to polyaniline causing a different copolymer conformation.

Yielmd and Conductivity measurements

We observed the percent yield of o-anthranilic acid copolymer with aniline decreases as the percent of aniline increases as shown in Figure 5. Also, we ob-

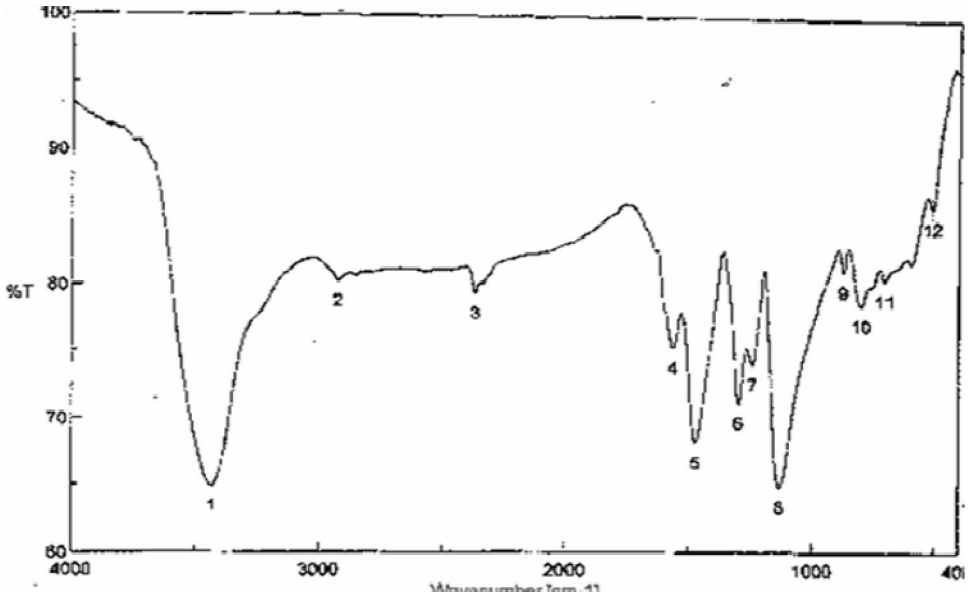


Figure 3 : FTIR spectra of Poly (o-anthranilic acid – Co – aniline) at f_1=1: 3

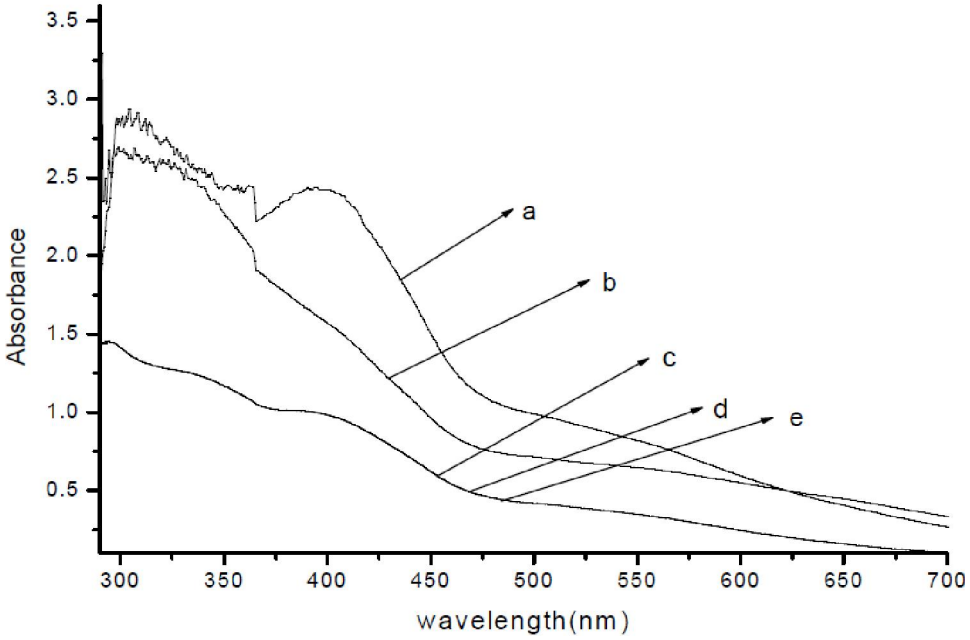


Figure 4 : UV-Vis absorption spectra of copolymer of o-anthranilic acid with aniline at different molar ratios using DMSO as a solvent; (f_1) a = 3:1, b = 2:1, c = 1:1, d = 4:1, e =1: 3

served a slightly increase in the conductivity as the amount of o-anthranlic acid decreases.

Elemental analysis

The elemental analysis was carried out in order to know about the composition of the polymer with various elements such as C, H, N, and S present in the polymer matrix. TABLE [3], shows the calculated and observed percent values of C, H, N and S for poly o-anthranilic acid and copolymers of o-anthranilic acid with aniline at several mole fraction of aniline. An increase in the % C can be observed as the amounts of o-anthranilic acid in the copolymer decrease or the amounts of aniline increase.

CONCLUSION

O-anthranilic acid copolymer with aniline can be synthesized by chemical oxidation using ammonium persulfate as the oxidizing reagent at different molar ratios of aniline. The FTIR spectra of copolymers show

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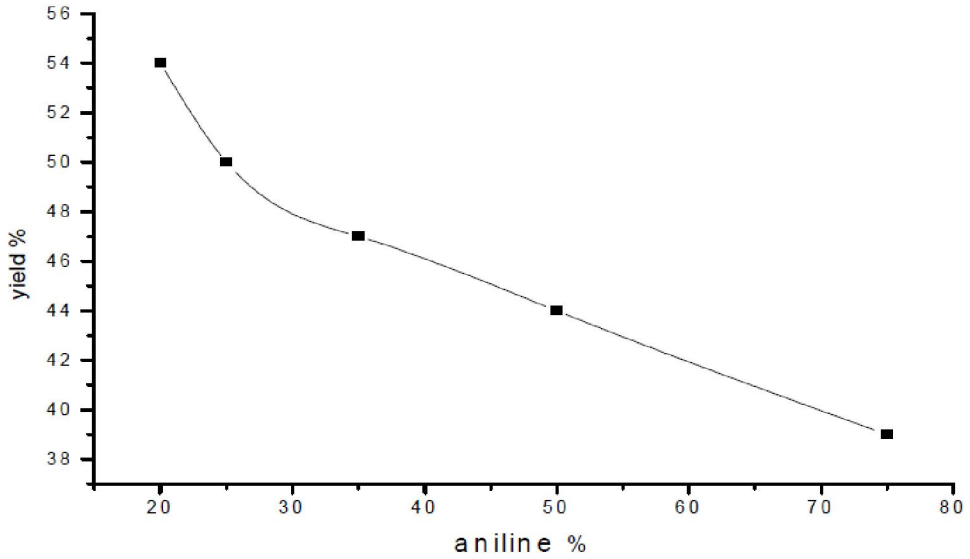

Figure 5 : Percent yield of o-anthranilic acid copolymer with aniline

TABLE 1 : UV-Vis of o-anthranilic acid in acid its copolymer with aniline at different molar ratios (f_1) using dimethylsulfoxide solvent (DMSO).

Polymer	(f_1) of o-anthranilic acid / aniline	Benzenoid	λ_{max}.(nm) Quinoid
o-anthranilic alkaline acid medium	—	348	512
o-anthranilic acid – Co- aniline	4:1	298	413
o-anthranilic acid – Co- aniline	3:1	306	535
o-anthranilic acid – Co- aniline	2:1	308	520
o-anthranilic acid – Co- aniline	1:1	298	419
o-anthranilic acid – Co- aniline	1:3	300	410

TABLE 2 : Yield and conductivity of o-anthranilic acid and its copolymers with aniline at different molar ratios (f_1) using DMSO.

Polymer	Yield (%)	Conductivity (S cm^{-1})
o-anthranilic acid in alkaline medium	75.2 %	$1.89 * 10^{-5}$
Copolymer of o-anthranilic/aniline at $f_{1=4:1}$	54.1 %	$3.41 * 10^{-5}$
Copolymer of o-anthranilic/aniline at $f_{1=3:1}$	50.21 %	$3.62 * 10^{-3}$
Copolymer of o-anthranilic/aniline at $f_{1=2:1}$	47.4 %	$3.78 * 10^{-3}$
Copolymer of o-anthranilic/aniline at $f_{1=1:1}$	44.6 %	$4.28 * 10^{-2}$
Copolymer of o-anthranilic/aniline at $f_{1=1:3}$	39.32 %	$5.23 * 10^{-2}$

TABLE 3 : Elemental analysis of poly (o-anthranilic acid) (AA) and their copolymer with aniline (A) at different molar ratios (f_1)

Sample	C%		H%		N%		S%	Total%
	Found	Cal.	Found	Cal.	Found	Cal.	Found	
o-anthranilic acid in alkaline medium	48.99	62.34	5.52	3.55	9.47	10.39	0.26	64.24
AA / A at f_1 = 4:1	50.80	62.92	5.45	3.34	9.24	14.03	0.40	65.89
AA / A at f_1 = 2:1	50.92	65.48	5.68	3.71	8.73	13.36	2.23	67.56
AA / A at f_1 = 1:1	53.52	69.17	4.02	4.24	7.82	12.41	0.48	65.84
AA / A at f_1 = 1:3	51.08	76.03	5	5.23	9.76	10.64	1.20	67.04

similar bands as those reported for PANI with exception of C =O absorption band 1684 and 1686cm^{-1}. The shift for o-antharnilc acid to lower values for the different mole fractions in UV-Vis spectroscopic may

be attributed to decrease in the extension of conjugation with respect to poly aniline due to the carboxylic acid effect cause an increase of the torision angle between close phenyl rings with respect to polyaniline causing copolymer conformations. An increase in the conductivity as the amount of o-anthanilic acid decreases as well as increase in the % C in the copolymer.

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