

Copolymers of Aniline with O-Anthranilic Acid: Synthesis and Characterization

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Abstract

Chemical copolymerization of aniline with o-anthranilic acid in aqueous 1 M HCl was carried out at different molar ratios of aniline and o-anthranilic acid, and was characterized by FTIR and UV-Visible spectroscopy, elemental analysis and electrical conductivity. From FTIR and UV-Visible spectroscopy, we observed that o-anthranilic acid had been introduced into the polymer chain successfully. The percent yield of o-anthranilic acid copolymer with aniline decreases as the percent of aniline increases. An increase in the % C can be observed as the amount of o-anthranilic acid in the copolymer decrease or the amounts of aniline increase. Copolymerization of aniline with o-anthranilic acid would improve the resulting polymer via increasing the molecular weight and the conductivity as well.

Keywords

Polyaniline, Copolymerization, O-Anthranilic Acid, Conductivity

1. Introduction

Poly anilines which are soluble in aqueous solutions are particularly attractive because they can be processed in water, thus avoiding the environmental concerns associated with the use of organic solvents. It has been shown that polyanilines with sulfonic acid groups on the benzene rings [1] or on the nitrogen atoms [2]-[6] are soluble in water.

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 [7]-[10]. However, its insolubility in common solvents, which results in difficult process abilities, has restricted its applications. To improve the polymer solubility, copolymerization of aniline with aniline de-

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rivatives was proposed [11] [12].

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

2. Experimental

Reagents

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

Characterization

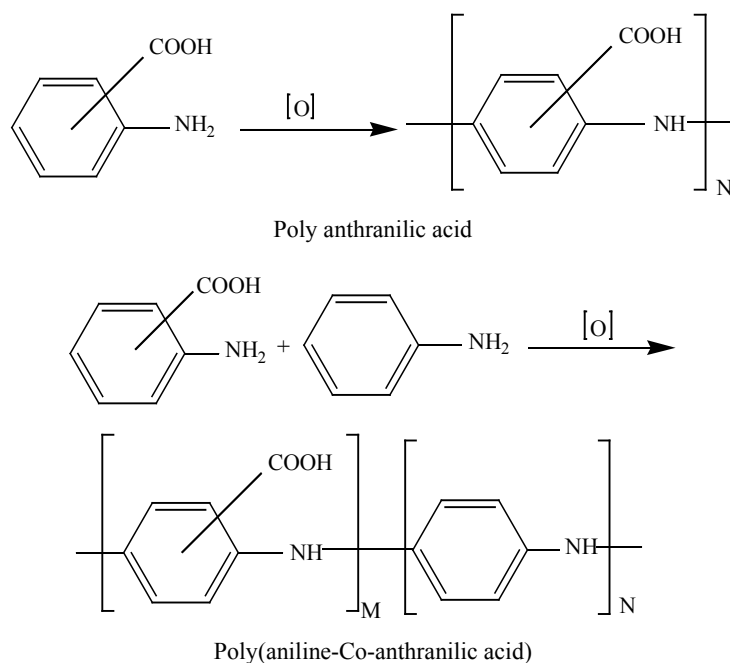
The FTIR spectra were recorded using FTIR-8201 PC (SHIMADZU) instrument by KBr pellets, and UV-Vis absorption spectra were recorded in spectrophotometer (UV-1601 SHIMADZU). The electrical conductivity was measured at room temperature by using conductivity meter (CM-30V) and The C, H, N analysis was carried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

Synthesis of copolymers

0.178 g of (AA) was dissolved in 3 ml DMF and completed to 50 ml by 0.1 M HCl. 0.08 M solution of (ANI) was prepared and then added to the solution containing (AA) and DMF. A solution of 0.1 M (APS) in 50 ml of 0.1 M HCl solution was prepared and then added to the solution containing the ANI and AA; therefore, the concentration of AA is 0.013 mol/L. At that case the molar ratio (f_1) of AA/ANI 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 ANI and APS of 0.08 and 0.1 mol/L, respectively, to give solution of different (f_1) of AA/ANI.

3. Results and Discussion

Poly(*o*-anthranilic acid) and copolymers of aniline were synthesized according to the following reactions:



3.1. FTIR Spectra Measurement

Figure 1 shows FTIR spectra of polyaniline (PANI). The high frequency bands at 1562⁽⁴⁾ and 1477⁽⁵⁾ 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⁽⁶⁾ and 1239⁽⁷⁾ cm⁻¹ correspond to the N-H bending and symmetric component of

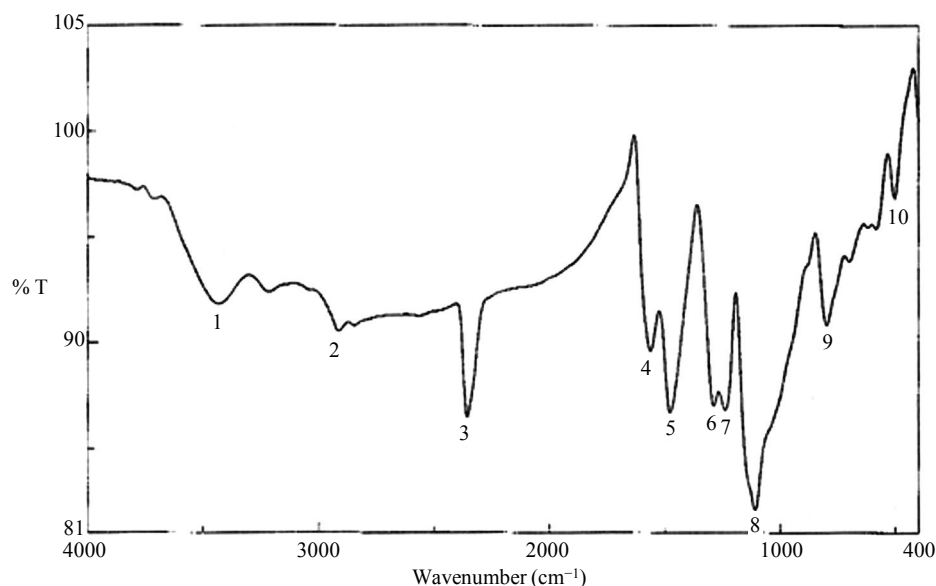


Figure 1. FTIR spectra of PANI.

the C=C (or C-N of the benzenoid ring) stretching modes. The remaining bands at $1110^{(8)}$ and $798^{(9)}$ cm^{-1} could be attributed to the in-plane and out-of-plane C-H bending modes.

Figure 2 and **Figure 3** show the FTIR spectra of poly(o-anthranilic 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 $1684^{(4)}$ cm^{-1} (**Figure 2**) and $1686^{(4)}$ cm^{-1} (**Figure 3**), therefore, we can distinguish the copolymer with homo polymer by this characterization band. It means that AA had been introduced into the polymer chain successfully.

3.2. UV-Vis Spectra Measurement

The UV-Vis spectra of poly(o-anthranilic acid-aniline) copolymer at different mole fractions of aniline and o-anthranilic acid are shown in **Figure 4** and tabulated in **Table 1**.

Two absorption bands at 348 and 512 nm. That are attributed to benzenoid ($\pi-\pi^*$ transition) and quinoid rings, respectively. The $\pi-\pi^*$ transitions are related to the extension of the conjugation along the polymer backbone. These bands show shift from 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 group's effect with the increase of the torsion angle between close phenyl rings with respect to polyaniline causing a different copolymer conformation.

3.3. Yield and Conductivity Measurements

Table 2 Shows the yield and the conductivity of o-anthranilic acid and its copolymers with aniline at different molar ratios (f_1) using DMSO.

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 observed a slightly increase in the conductivity as the amount of o-anthranilic acid decreases.

3.4. 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 PAA in acidic medium and copolymers of AA with ANI at several mole ratio of AA/ANI. A relatively increase in the % C can be observed as the amounts of o-anthranilic acid in the copolymer decrease or the amounts of aniline increase.

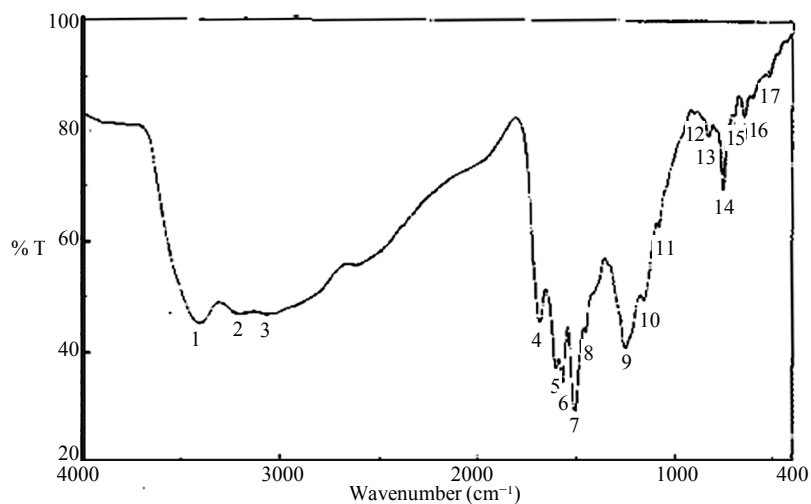


Figure 2. FTIR spectra of poly(o-anthranilic acid-co-aniline) at $f_1 = 3:1$.

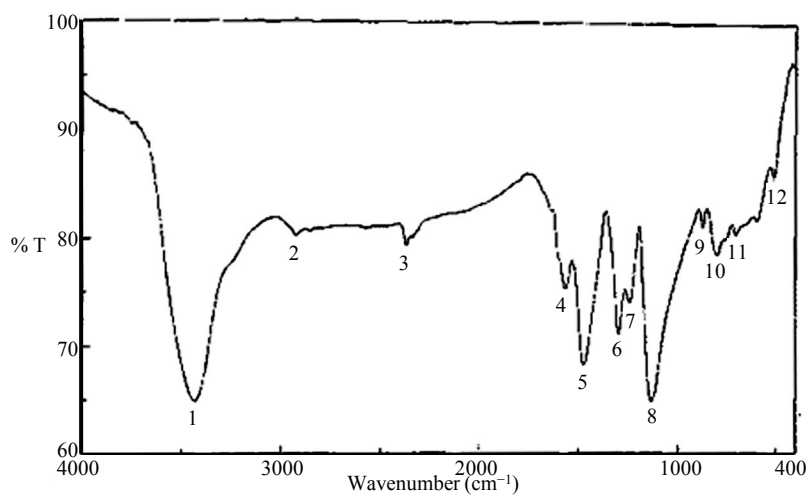


Figure 3. FTIR spectra of poly(o-anthranilic acid-co-aniline) at $f_1 = 1:3$.

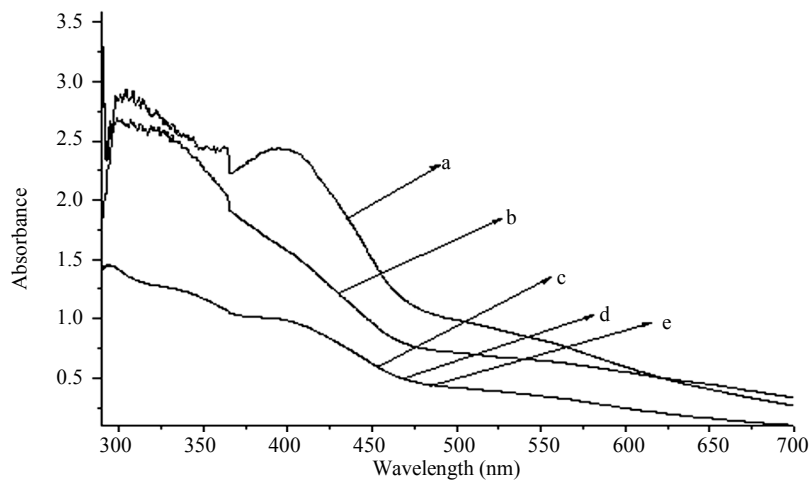


Figure 4. Uv-Vis absorption spectra of copolymer of o-anthranilic acid with aniline at different molar ratios using DMSO as a solvent (f_1) a = 3:1, b = 2:1, c = 1:1, d = 4:1, and e = 1:3.

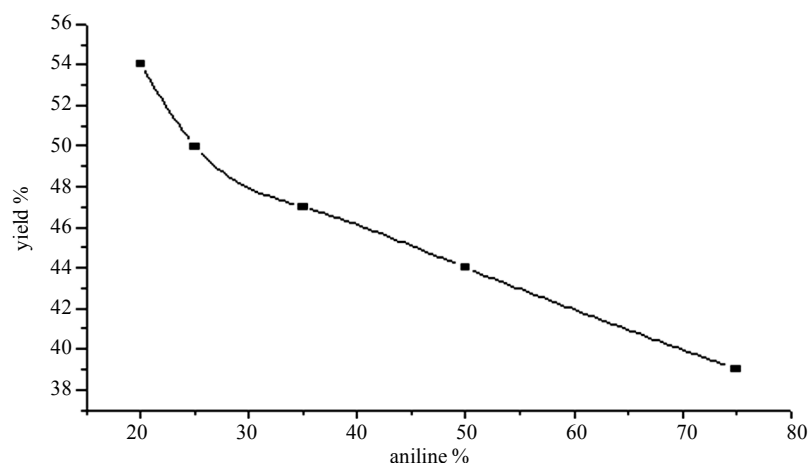


Figure 5. Percent yield of o-anthranilic acid copolymer with aniline.

Table 1. UV-Vis of o-anthranilic acid in acidic medium and its copolymer with aniline at different molar ratios (f_1) using Dimethyl sulfoxide solvent (DMSO).

Polymer	(f_1) of AA/ANI	Benzenoid	λ_{\max} (nm) Quinoid
O-anthranilic acid in acidic 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 \cdot cm $^{-1}$)
O-anthranilic acid in acidic 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 PAA and their copolymer with ANI at different molar ratios (f_1).

Sample	C %		H %		N %		S %	Total %
	Found	Cal.	Found	Cal.	Found	Cal.	Found	
O-anthranilic acid in acidic medium	48.99	62.34	5.52	3.55	9.47	10.39	0.26	64.24
AA/ANI at $f_1 = 4:1$	50.80	63.92	5.45	3.34	9.24	14.03	0.40	65.89
AA/ANI at $f_1 = 3:1$	52.77	63.84	4.53	3.47	8.21	13.79	0.67	66.18
AA/ANI at $f_1 = 2:1$	53.92	65.48	5.68	5.68	8.73	13.36	2.23	67.56
AA/ANI at $f_1 = 1:1$	53.52	69.17	69.17	4.02	7.82	12.41	0.48	65.84
AA/ANI at $f_1 = 1:3$	54.08	76.03	76.03	5	9.76	10.64	1.20	67.04

4. 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 and o-anthranilic acid. The FTIR spectra of copolymers shows similar bands as those reported for PANI with the exception of C=O absorption band 1684 and 1686 cm^{-1} . The shift for o-anthranilic 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 PANI due to the carboxylic acid effect because an increase of the torsion angle among close phenyl rings with respect to PANI causes a different copolymer conformation. An increase in the conductivity as the amount of o-anthranilic acid decreases as well as increase in the % C in the copolymer.

References

- [1] Yue, J. and Epstein, A.J. (1991) Electrochemical Polymerization of Aromatic Amines: IR, XPS and PMT Study of Thin Film Formation on a Pt Electrode. *Macromolecules*, **24**, 4441-4445.
- [2] Angelopoulos, M. (1992) Application of Intrinsically Conducting Polymers. Presented at the NATO ARW, Champain, VT.
- [3] Leclerc, M., Guay, J. and Dao, L.H. (1989) Synthesis and Characterization of Poly(alkylanilines). *Macromolecules*, **22**, 649- 653.
- [4] Chavalier, J.W., Begeron, J.Y. and Dao, L.H. (1992) Synthesis, Characterization, and Properties of Poly(N-alkylanilines). *Macromolecules*, **25**, 3325-3331.
- [5] Leclerc, M., Guay, J. and Dao, L.H. (1988) Conducting Polymer Derived from 4-Aminobiphenyl. *Journal of Electroanalytical Chemistry*, **251**, 31-39.
- [6] Bergeron, J.Y., Chavalier, J.W. and Dao, L.H. (1990) Water-Soluble Conducting Poly(aniline) Polymer. *Journal of the Chemical Society, Chemical Communications*, Issue 2, 180-182.
- [7] Nguyen, M.T., Kassi, P., Miller, J.L. and Diaz, A.F. (1994) Influence of Polymerization Conditions on the Properties of Poly(2-methylaniline) and Its Copolymer with Aniline. *Macromolecules*, **27**, 3625-3631.
- [8] Prevost, V., Petit, A. and Pla, F. (1999) Studies on Chemical Oxidative Copolymerization of Aniline and o-Alkoxy-sulfonated Anilines I. Synthesis and Characterization of Novel Self-Doped Polyanilines. *Synthetic Metals*, **104**, 79-87.
- [9] Stejskal, J., Sapurina, I. and Trchova, M. (2010) Polyaniline Nanostructures and the Role of Aniline Oligomers in Their Formation. *Progress in Polymer Science*, **35**, 1420-1482.
- [10] Soares, B., Celestino, M., Magloli, V. and Khastgir, D. (2010) Synthesis of Conductive Adhesives Based on Epoxy Resin and Polyaniline. DBSA Using the *in Situ* Polymerization and Physical Mixing Procedures. *Synthetic Metals*, **160**, 1981-1986.
- [11] Volkov, A., Tourillon, G., Lacaze, P.C. and Dubois, J.E. (1980) Electrochemical Polymerization of Aromatic Amines: IR, XPS and PMT Study of Thin Film Formation on a Pt Electrode. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, **115**, 279-291.
- [12] Yue, J., Wang, Z.H., Cromak, K.R., Epstein, A.J. and MacDiarmid, A.G. (1991) Effect of Sulfonic Acid Group on Polyaniline Backbone. *Journal of the American Chemical Society*, **113**, 2665-2671.