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Synthesis, identification and study of electrical conductivity of the doped poly aniline

Roza A. Salih

Chemistry Department, College of Science, Basrah University, Basrah, Iraq

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Abstract Poly aniline and poly aniline doped with 2,5-dimethyl benzene sulfonic acid (PXSA), 4-hydroxy-m-benzene disulfonic acid (PDSA), 3-chloro-4-hydroxybenzene sulfonic acid (OCPSA) were prepared. The polymers are identified by FT-IR and UV-vis spectroscopy. The ionic conductivities of poly aniline and poly aniline doped with 2,5-dimethyl benzene sulfonic acid (PXSA), 4-hydroxy-m-benzene disulfonic acid (PDSA), 3-chloro-4-hydroxybenzene sulfonic acid (OCPSA) were studied as a function of weight of the dopant compounds. It is noted that an increase of the conductance of poly aniline by doping with OCPSA, and became equal to $0.001321 \Omega^{-1}$ for 1 g higher than the conductance for the poly aniline when it is doped with OCPSA.

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1. Introduction

Poly aniline (PAn) in the emeraldine base form is rendered conductivity through doping by its exposure to protonic acids. The doping or protonation occurs by a general reaction of poly aniline with protonic acids in the form $H^+ M^-$, where M^- is the counter ion (Kahol et al., 2003; Gosh et al., 1999). The polymer chains search for the lowest attainable energy conformation and orientation suitable “lattice matching” between the periodic polymer structure and that of the host tends to maximize the host guest interactions (Wu et al., 1996).

E-mail address: rozachemistry@yahoo.co.uk

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The process that transforms insulating polymers to excellent conductors is through the formation of charge transfer complexes between the electron donors such as sodium or potassium (n-doping reduction) or by electron acceptors such as I_2 , AsF_5 , or $FeCl_3$ (p-doping oxidation) with the polymers. The doped polymer backbone becomes positively or negatively charged with the dopant forming oppositely charged ions (Na^+ , K^+ , I_3^- , I_5^- , AsF_6^- and $FeCl_4^-$).

In contrast to the other electrically conductive polymers, poly anilines may be doped with protons. Also, poly aniline is available as powder, film, or fibrils (Kryszeewski, 1980; Heeger et al., 1990; Paloheimo et al., 1995).

The correlations suggest that PAn is reversibly doped into three forms: (1) reduced form, (2) a radical cation intermediate form, and (3) oxidized form. PAn is the first known conducting polymer that is stable in an aqueous solution for all these three forms. The radical cation form is highly conductive. The oxidized and reduced forms, however, are insulating (McManus et al., 1985; Ozdemir et al., 2006; Hino et al., 2006).

Fundamental interest in poly aniline stems from the possibility of investigating physics in different states, such as “Fermi glass” state, the “granular metal” state, or as a “disordered metal” close to the metal–insulator transition state. Poly anilines technological significance arises due to its ability to be formed into films and fibers (Kahol et al., 2003).

2. Materials and methods

2.1. Synthesis of poly anilines

PAn particles were synthesized using conventional oxidation polymerization of aniline to produce a fine emeraldine hydrochloride form. A solution of 1.2 mol aniline monomer in 800 ml of 1 M HCl was chilled and stirred for 2 h. Then polymerization was initiated at -5°C by a prechilled solution of 0.72 mol ammonium peroxy sulfate in 400 ml of 1 M HCl. The reaction was maintained for an additional 2 h to complete the reaction and produce the emeraldine hydrochloride form of PAn.

A small amount of 1 M NaOH was finally injected into the reactor to precipitate the PAn particles. After washing with distilled water, several times and measuring the pH, this precipitate was filtered and washed with distilled water and ethanol to remove the unreacted monomer and oligomer. Products were dried for 1 day using a freeze-drying process type Freeze E1, from (VIRTIS Inc.) (Lee et al., 2001). The polymer was then identified by UV–vis and FT-IR techniques (Salih, 2007).

2.2. Synthesis of 2,5-dimethyl benzene sulfonic acid (PXSA)

In a 25 ml round bottomed flask 5.2 g (6 ml, 0.05 M) of *p*-xylene was placed and 10 ml of concentrated sulfuric acid was added with gentles swirling agitation. The mixture was heated on water bath for 10–15 min, then the flask was removed from the bath and the contents were mixed with a circular motion every 2 min. The reaction was completed when the xylene layer on the surface of the acid has disappeared. The mixture was cooled at room temperature and 5 ml of H_2O was added cautiously with gentle swirling. The warm reaction mixture was poured into a 100 ml beaker and cooled in ice. The crystalline solid was filtered with suction on a sintered glass funnel (Kahol et al., 2003).

2.3. Synthesis of 4-hydroxy-*m*-benzene disulfonic acid (PDSA)

In a dry 500 ml flat-bottomed flask was placed 31 g (0.33 M) of phenol and then mixed with 116 g of concentrated sulfuric acid. The mixture was heated in a boiling water bath for 3 h with mechanical stirring. Then the mixture was cooled at room temperature or below by immersing the flask in ice water and a solution of 95 g of NaOH in 235 ml water was added slowly, the solid salt was separated (Kahol et al., 2003).

2.4. Synthesis of 3-chloro-4-hydroxybenzene sulfonic acid (OCPSA)

An amount of 12.6 g of O-chloro phenol and 10 ml of concentrated sulfuric acid were stirred together on a water bath for

about 30 min. The mixture was cooled to 0°C , and then was converted into the sodium salt by adding NaOH (Kahol et al., 2003).

The fine powder of emeraldine hydrochloride form was dispersed in 1 M aqueous solution of functionalized aromatic sulfonic acids like 2,5-dimethyl benzene sulfonic acid, 4-hydroxy-*m*-benzene disulfonic acid, 3-chloro-4-hydroxybenzene sulfonic acid under vigorous stirring for 24 h. After the doping reaction, the solution was filtered and the collected material was washed with 1 M aqueous solution of functionalized aromatic sulfonic acid (Kahol et al., 2003).

2.5. Spectroscopy

Ultraviolet and visible spectra: The compounds were identified by UV–vis spectrum. The spectra were recorded on Ultraviolet (UV) Helios Alpha spectrophotometer 200–800 nm, UVA No. 102024 in H_2O solvent with quartz cell.

Infrared spectrum: FT-IR spectra were recorded on FT-IR 8400S spectrophotometer model (2000) from SHIMADZU Japan, and the spectra were recorded as KBr pellets.

2.6. Electrical conductivity

The ionic conductance (G) of solutions of the prepared compounds in DMF was measured at room temperature, by using conductivity instrument (Konduktoskop E 365B Metrohm Herisau).

3. Results and discussion

3.1. Identification of the synthesized compounds

3.1.1. Infrared spectroscopy (IR)

The chemical structures of the synthesized compounds (PXSA, PDSA, and OCPSA) were identified using FT-IR analysis. Table 1 shows the absorption bands of the active groups. The main functional groups and their FT-IR frequencies for the prepared compounds are presented in Table 1.

For the compound (PXSA), the peak at 2931 cm^{-1} is assigned to aromatic (C–H) stretching, whereas those at 1488 and 1620 cm^{-1} to aromatic ring (C=C), stretching vibrations. The peak at 1024 cm^{-1} is due to (S=O) asymmetrical stretching.

The peak at 1190 cm^{-1} is due to (S=O) symmetrical stretching, the peak at 823 cm^{-1} is due to (C–H) aromatic ring. For the compound (PDSA), the peak at 3456 cm^{-1} to (O–H) stretch, and the peak at 1126 cm^{-1} due to (S=O) symmetrical stretching, the peak at 1631 and 1604 cm^{-1} due to (C=C) aromatic ring, the peak at 622 cm^{-1} is due to O–H out of plane deformation.

For the compound (OCPSA) the peak at 3473 cm^{-1} is due to O–H stretch in phenols, and the peak at 1039 cm^{-1} due to (S=O) asymmetric stretching, the peak at 1166 cm^{-1} due to (S=O) symmetrical stretching, the peak at 1425 cm^{-1} and the peak at 1629 cm^{-1} due to (C=C) aromatic ring stretching vibrations, the peak at 829 cm^{-1} due to (C–H) aromatic, the peak at 605 cm^{-1} due to (O–H) out of plane deformation, the peak at 673 cm^{-1} due to (C–Cl) Silverstein et al., 1981.

Table 1 The main functional groups and their FT-IR frequencies of the compounds (in cm^{-1}).

C-Cl	O-H	C-H	S=O	C=C	C-H	O-H	Samples
		823 out of plane bending	1024 (Asymmetrical)	1488 1620	2931	3587 3458	PXSA
	622	622 out of plane bending	1190 (Symmetrical) 1126 (Symmetrical)	1631 1604		3456 3417	PDSA
673	605	829	1039 (Asymmetrical) 1166 (Symmetrical)	1425 1629		3473 Phenols	OCPSA

3.1.2. Ultraviolet-visible spectroscopy (UV)

The chemical structures of the prepared compounds (PXSA, PDSA, and OCPSA) were identified using UV-vis analysis.

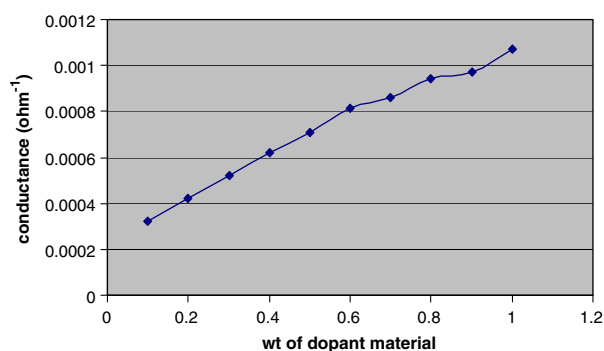
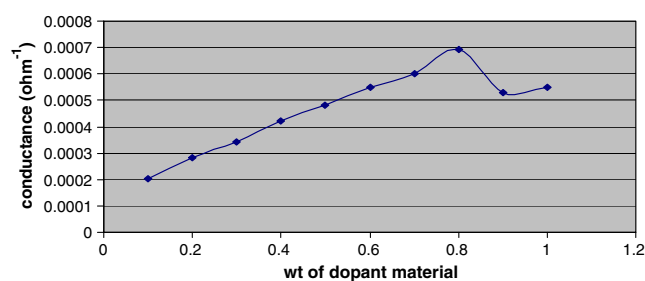
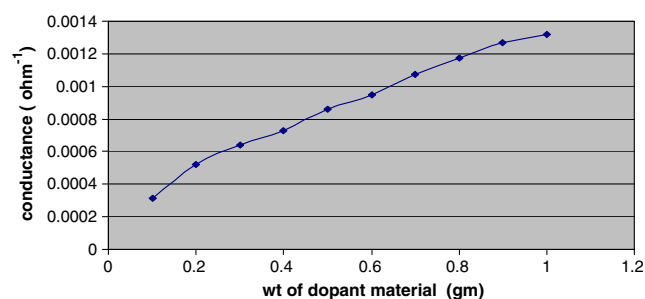
The UV-vis spectrum of the compound PXSA has three bands, the first at 290.50 nm and the second at 356 nm associated with the $n \rightarrow \pi^*$ transition in (S=O) group. The transition responsible for absorption in S=O compounds can be traced to the lone pairs of electrons on the O atom, the Lewis concept of a “lone pair” of electrons is represented in the molecular orbital theory by a pair of electrons in an orbital confined largely to one atom and not appreciably involved in a bond formation. One of these electrons may be excited into an empty π^* orbital of the S=O group which gives rise to a $n \rightarrow \pi^*$ transition (290 nm) because $n \rightarrow \pi^*$ transitions in S=O are symmetry forbidden, the absorptions are weak.

The UV-vis of the compound PDSA has two bands, the first at 296 and the second at 360 nm associated with the $n \rightarrow \pi^*$ transition in (S=O) group. The transition responsible for absorption in S=O compounds can be traced to the lone pairs of electrons on the O atom.

The UV-vis spectrum of the compound OCPSA has one band at 295 nm associated with the $n \rightarrow \pi^*$ transition in (S=O) group, therefore, the transition due to electron unconjugated in the oxygen atom, thus the transition takes in the molecules composed of double bonds of such an atom, for example S=O groups (Atkins, 2001).

3.1.3. Measurement of the electrical conductivity

The ionic conductances (G) of the prepared compounds were measured in the DMF solvent. The influence of weight of dopant material on the conductivities of the poly aniline is shown in Figs. 1–3. It is apparent that the conductivity of the poly aniline increases as the weights of the dopant material increases. In Fig. 1 it should be noted that the conductivity was higher and is equal to $0.001 \Omega^{-1}$ in 1 g, while in Fig. 2 it

**Figure 1** Effect of PXSA on conductance of poly aniline.**Figure 2** Effect of PDSA on conductance of poly aniline.**Figure 3** Effect of OCPSA on conductance of poly aniline.

can be seen that the highest conductivity was equal to $0.0007 \Omega^{-1}$ in 0.8 g. In Fig. 3 it should be noted that the highest conductivity was equal to $0.001321 \Omega^{-1}$ in 1 g.

The electrical conductivity depends mainly on the number and mobility of the charge carriers and can be correlated with the chemical composition and morphology type. The conductivity of PAn was higher than that of the other polymers in their self-doped and doped forms. Poly PAn doped with OCPSA had highest electrical conductivity in its self-doped, with respect to PAn.

The long side chain exerted a strong steric effect on the doping process, making it more difficult for PDSA to protonate the nitrogen group. The conductivity decreased with an increase in the side group of PDSA. This could have resulted

Table 2 Room temperature conductivity values of poly aniline doped with different organic sulfonic acid.

Dopant material	Higher conductivity (G)	Weight of dopant material (g)
PXSA	0.001	1
PDSA	0.0007	0.8
OCPSA	0.001321	1

from the decreasing doping level from PAN to PDSA. It may be that with the bonding of the side group, the distance between the two main chains increased, and this made interchain polaron or bipolaron doping more difficult.

The values of room temperature conductivities of poly aniline doped with organic sulfonic acid are listed in Table 2. Among the different organic sulfonic acid for doping purpose, the sequence of conductivity is OCPSA > PXSA > PDSA.

4. Conclusion

The poly aniline was synthesized by chemical polymerization method, 2,5-dimethyl benzene sulfonic acid (PXSA), 4-hydroxy-m-benzene disulfonic acid (PDSA), 3-chloro-4-hydroxybenzene sulfonic acid (OCPSA) were used as dopants during the polymerization process. Spectroscopic and conductivity of the dopant sample are found to be affected by the type of the dopant sample used for doping purpose. Room temperature conductivity is found to be higher in 3-chloro-4-hydroxybenzene sulfonic acid (OCPSA) doped the polymer than that doped with 2,5-dimethyl benzene sulfonic acid (PXSA), 4-hydroxy-m-benzene disulfonic acid (PDSA).

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