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RESEARCH ARTICLE

Synthesis, Characterization, Thermal degradation and Electrical conductivity of Salicylidene- anthranilic acid- Schiff base Formaldehyde resin (R-AASA)

*Hayat Hamza Abbas and Roza Abdulrazaq Salih

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

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Abstract

A Schiff base chelating resin (Salicylidene- anthranilic acid- Schiff base Formaldehyde resin (R-AASA), was synthesized by condensing a Schiff base (AASA) derived from salicylaldehyde and anthranilic acid with formaldehyde in an alkaline medium.

The Schiff base monomer and their formaldehyde resin were characterized by elemental analysis, FTIR, UV-Visible and ^1H NMR spectroscopy. The ionic conductance (G) of the resin doped with 2,5- dimethyl benzene sulfonic acid (PXSA), p- Toluene Sulfonic acid and NaCl were studied as a function of the weight of this dopand compounds. It is noted that an increase in the conductance of the resin (R-AASA), with an increase in the weight of the dopant material, also depended on the type of the dopant compounds used for this purpose, and it followed this sequence, p- Toluene sulfonic acid > NaCl > 2,5- dimethyl benzene sulfonic acid.

This means that the highest conductance of the resin (R-AASA) occurred when it was doped with p-Toluene sulfonic acid, which equal $(9.99 \times 10^{-4}) \text{ ohm}^{-1}$ for 0.1 g.

The thermal stability of the resin (R-AASA) was studied using TGA/ DTA analysis.

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Introduction

Polyimines or Schiff base polymers, which are also called polyazines, were first reported by (Adams *et al.*, 1923). Research interest in polyazomethines continues owing to their different characteristics with chelating properties (Marcu, *et al.*, 2003 and Cazacu *et al.*, 2003), thermal stability (Racles *et al.*, 2002, Marin *et al.*, 2006), liquid crystal properties as well as intrinsic conductivity (Shukla *et al.*, 2003, Diaz *et al.*, 1999, Sun *et al.*, 1993, Aly *et al.*, 2003 and El-Shekeil and A-Aghbari, 2004). Polyazomethines are generally synthesized by polycondensation reactions, a method that has some disadvantages, among which is the necessity to ensure the special condition such as high temperature and the use in some case of a special catalyst (Grigoras *et al.*, 2001).

Recently, a new method of synthesizing polyazomethines was reported, which is oxidative polycondensation of monomers containing azomethine links (Kaya and Gut, 2004). Because of the role of oxidants such as NaOCl, H_2O_2 and air O_2 , there are some significant advantages to this method. For example, these oxidants were cheap and easily available. Phenols and Schiff base substituted phenols were polymerized easily using these oxidants (Kaya and Senol, 2003). The conducting properties of poly (2-hydroxyl-4-acryloyloxacetophnone phenylimine CO-methacrylate) and their polymer- metal complexes were studied by (Thamizharasi *et al.*, 1998). More functional oligophenols may be used to clean poisonous heavy metals in industrial wastewater. In addition Schiff base compounds had been used for the determination of transition metals in some natural food samples (FaKhari *et al.*, 2005). Therefore, the synthesis of polymer- metal complexes and azomethine polymers are very important in analytical environmental and food chemistry.

In this study the structure of the chelating resin (Salicylidene- anthranilic acid- Schiff base formaldehyde) (R-ASSA) was identified by FT-IR, UV-Visible, ^1H NMR, elemental analysis, TGA and DTA. The ionic conductance (G) of

this resin doped with many materials was studied as a function of the weight of the dopand compounds. The aim of this study was to synthesize polyazomethine and to investigate its thermal and conductivity properties.

Materials and Methods

All the chemicals and solvents were of analytical reagent grade supplied by BHD and Meck, and used without further purification.

The elemental analysis carried out by using CE-440 Elemental ANALYZER EAI EXETER ANALYTICAL, INC. FT-IR spectra by KBr pellets were recorded with a FT-IR 8400S spectrophotometer model 2000 from SHIMADZU Japan. The absorption spectra in the UV-Visible range (200-800) nm were studied with a UV-9200 BIOTECH ENGINEERING MANAGEMENT Co. LTD (UK.) UV Spectrophotometer. The ^1H NMR spectra was measured at room temperature by using an NMR spectrometer (Bruker, 300 MHz). Thermogravimetric measurements were carried out under nitrogen atmosphere using a TGA Q₅₀ V₂₀, 13 Build 39. The ionic conductance (G) was measured at room temperature by using a conductivity instrument (Konduktoskop E 365B Metrohm Herisau).

2.2. Synthesis of Schiff base monomer (AASA):

The salicylidene- anthranilic acid Schiff base (AASA) monomer is a well-known compound and was prepared according to (Iqbal *et al.*, 2006) by mixing (1.1 g, 1 mol) of salicylaldehyde with 10 ml of ethanol and then by adding to this ethanolic solution, an equimolar quantity of anthranilic acid (1 mol), magnetically stirred with the addition of 2-3 drops of concentrated H_2SO_4 , refluxed for 2h and left overnight at room temperature. The solid coloured product formed was filtered and washed with ethanol and ether consecutively. It was dried at room temperature and recrystallized with hot ethanol to give the required monomer (AASA) (Scheme 1).

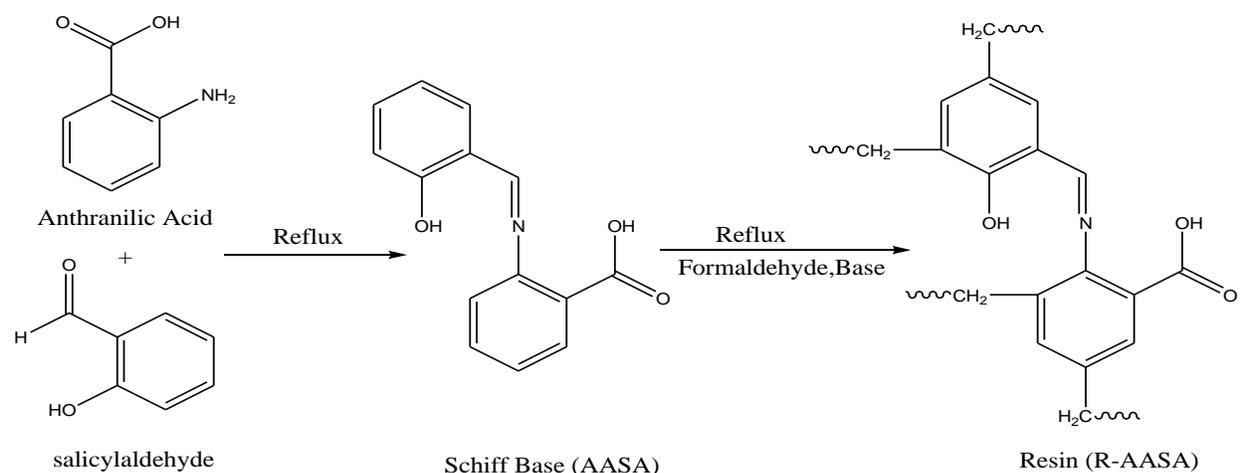
2.3. Synthesis of Salicylidene- anthranilic acid- Schiff base formaldehyde resin (R-AASA):

The Schiff base monomer (AASA) (0.01 mol) was suspended in 20 ml of water at 40°C and a minimum volume of 1M NaOH solution was then added to dissolve it. Formaldehyde (0.012 mol) was added to the alkaline Schiff base solution and the mixture was refluxed in an oil bath at 120-130°C for 2h. The resin remained soluble in the reaction mixture as a dark – brown solution. Precipitation of the polymer was carried out by neutralizing the alkaline polymer solution to (pH= 5) using 0.1 M oxalic acid solution in a similar way to the previously reported method (Soreson *et al.*, 2001, Kaya *et al.*, 2008 and Othman *et al.*, 2011).

The dark brown precipitate obtained was filtered, washed repeatedly with water followed by methanol and dried at 70 °C for 24h.

2.4. Synthesis of 2,5- dimethylbenzene sulfonic acid (PXSA):

Using a 25 ml round bottomed flask (5.2 g, 6 ml, 0.05 mol) of p- xylene was placed in 10 ml of concentrated sulfuric acid agitated gently with a swirling motion. The mixture was heated on a water bath for 10-15 min, then the flask was removed from the bath and the contents were mixed using 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 a gentle swirling motion. The warm reaction mixture was poured into a 100 ml beaker and cooled in ice. The crystalline solid was filtered by suction on a sintered glass funnel as cleared by (Kahol *et al.*, 2003).



Scheme 1: The structure of salicyldiene- anthranilic acid- Schiff base and formaldehyde resin (R-AASA)

Results and Discussion

3.1. Characterization of the synthesized compounds:

3.1.1. CHN analysis:

The elemental analysis of the ligand (Schiff base) monomer (AASA); and the resin (R-AASA) is shown in Table 1.

Table 1: Elemental analysis data of monomer (AASA) and resin (R-AASA).

Compound	Calculated/ Found		
	C%	H%	N%
AASA	69.70	4.56	5.81
	69.65	4.72	5.88
R- AASA	71.91	4.86	5.24
	71.18	4.82	5.57

3.1.2. FT-IR spectroscopy:

The chemical structure of the ligand (Schiff base monomer (AASA)); resin (R- AASA), and (PXSA) were identified by FT-IR analysis using the previous analytical data available in the literature (Iqbai *et al.*, 2006, Scozzafara *et al.*, 2001 and Salih, 2010). The main functional groups and their FT-IR frequencies of the prepared compounds are presented in Table 2 and Fig. 1 and 2. They were recorded in the wave number range 4000-500 cm^{-1} by the FT-IR -4800. The FT-IR spectra of the Schiff base monomer (AASA) and of the resin (R-AASA) showed sharp peaks of strong characteristic absorption. A broad absorption band of phenolic-OH appeared at 3625 and 3365 cm^{-1} , the $\nu(\text{CH}=\text{N})$ stretching frequency appeared at 1620 and 1618 cm^{-1} and $\nu(\text{C}-\text{O}$ phenolic) at 1245-1242 cm^{-1} for AASA and R-AASA, respectively. Several absorption peaks for the $\nu(\text{C}=\text{C}$ aromatic) showed at 1566-1577 cm^{-1} . Upon condensation with formaldehyde, the IR spectra of the Schiff base resin gave broader and less intense peaks (Othmanet *et al.*, 2011). Absorption peaks 2588 cm^{-1} due to methylene linkage in the resin (R-ASSA) was observed which was absent in the Schiff base monomer (AASA) (Mohammed *et al.*, 2008). 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} are attributed 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 (Salih, 2012).

3.1.3. Electronic spectra:

The electronic spectra data of the ligand Schiff base monomer (AASA) and the resin (R-AASA) are summarized in the Table 2 and Fig. 3 and 4. The spectra of the ligand (AASA) exhibit 3 main peaks at 225.0, 255.0 and 335.0 nm. The first and second peaks were attributed to aromatic and azomethinic $\pi-\pi^*$ transition respectively. The third band in spectra of the ligand (AASA) 335.0 nm was assigned to $n-\pi^*$ transition. UV- Vis spectra of the resin (R-AASA) shows an aromatic and azomethinic $\pi-\pi^*$ transition at 220.0 and 275.0 nm respectively. The band at 335.0 nm was assigned to $n-\pi^*$ transition. The UV spectra shows specific bands for λ_{max} assigned to aromatic and azomethinic $\pi-\pi^*$ transitions at about (280 and 350) nm respectively (Silverstein *et al.*, 1981). The shifting of the $-\text{CH}=\text{N}-$ group band from 255 to 275.0 nm has been demonstrated for the formation of the polymeric conjugated π system (Kaya *et al.*, 2008).

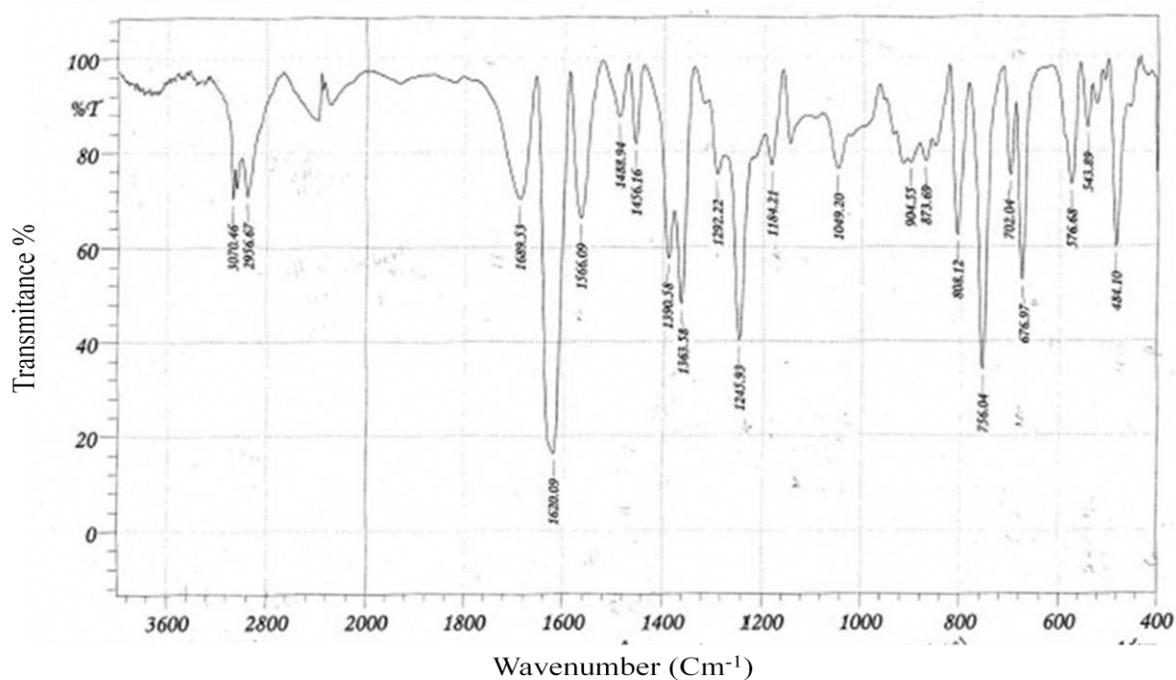


Figure 1: FT-IR of the Schiff base monomer (AASA).

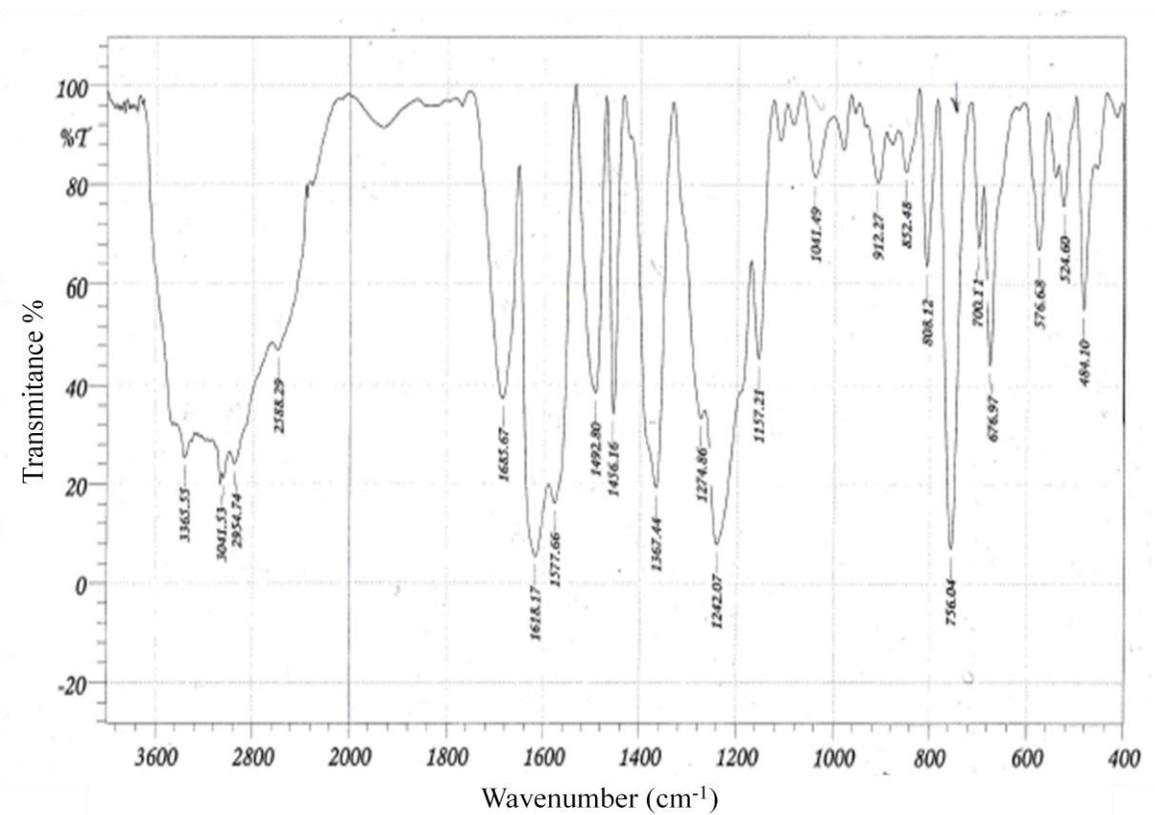


Figure 2: FT-IR of the resin (R-AASA).

Table 2: Spectral data of the prepared compounds

Compound	FT-IR frequencies (cm^{-1})						UV-Visible λ_{max} (nm)	
	-OH phen.gp.	Ar-C-H	-C-O	C=C	HC=N	-CH ₂	n- π^*	π - π^*
AASA	3625	3070	1245	1566	1620	---	335	Arom. azo. 225 255
R-AASA	3365	3041	1242	1577	1618	2588	335	220 275
PXSA	3587- 3458	2931	S=O 1024 Asy. 1190 Sym.	1488 1620				

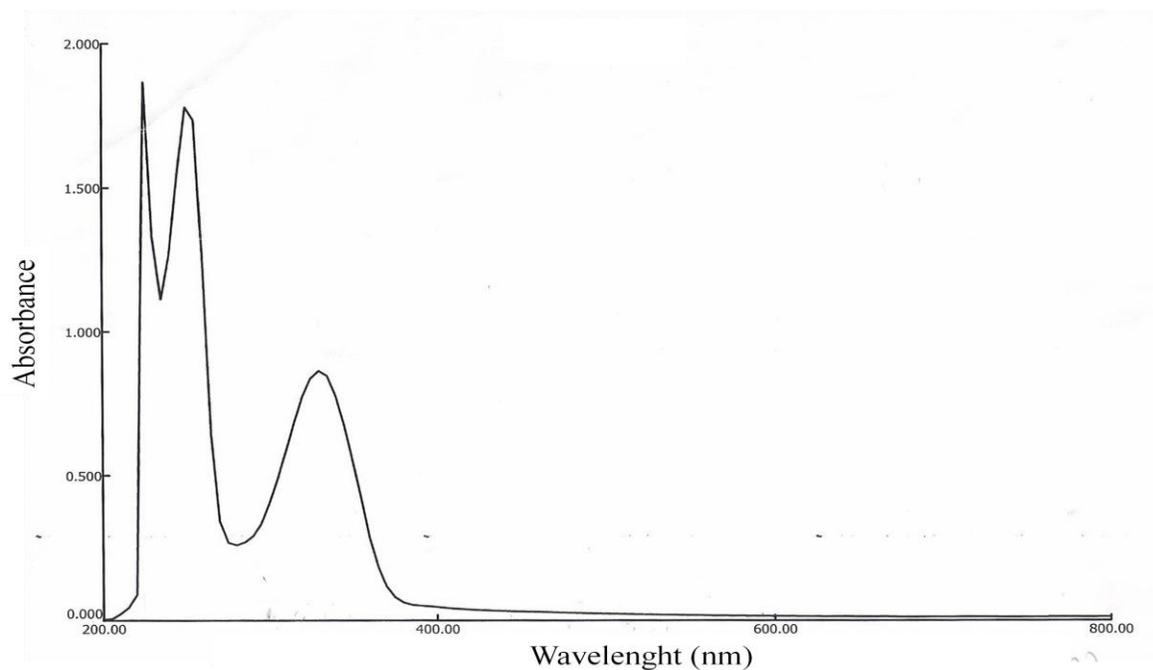


Figure 3: UV-Visible spectrum of the Schiff base monomer (AASA).

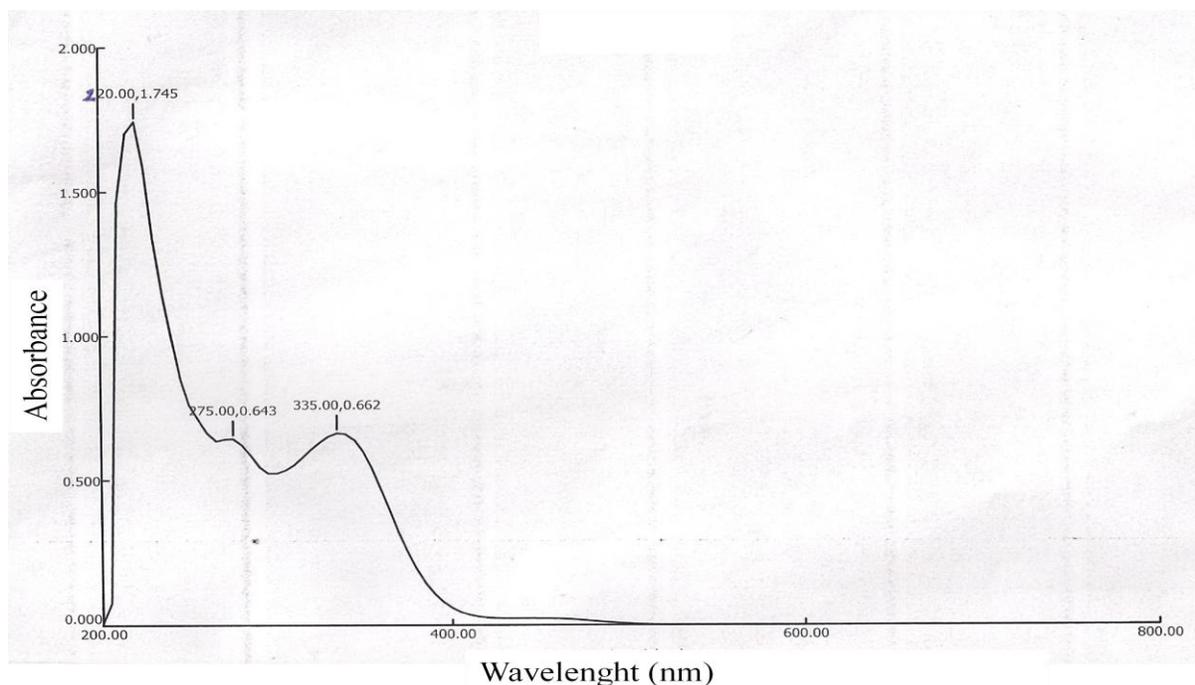


Figure 4: UV-Visible spectrum of the resin (R-AASA).

3.1.4. NMR study of the Schiff base monomer (AASA):

In the ^1H NMR spectra of the Schiff base monomer (AASA) Fig. 5 was obtained in d_6 -DMSO at room temperature using TMS as an internal standard. The signals observed at 8.964 ppm are due to the azomethine proton. The signals observed at 13.77 ppm and 9.748 ppm are due to phenol -OH and carboxylic -OH protons (Kaya *et al.*, 2008). The multiple signals around 6.947-7.642 ppm are ascribed to aromatic protons (Othman *et al.*, 2011). In the literature there were other phenol derivatives were also polymerized and described (Cazacu *et al.*, 2005 and Jain-Nig *et al.*, 2006). This ^1H NMR results are further support the IR inferences.

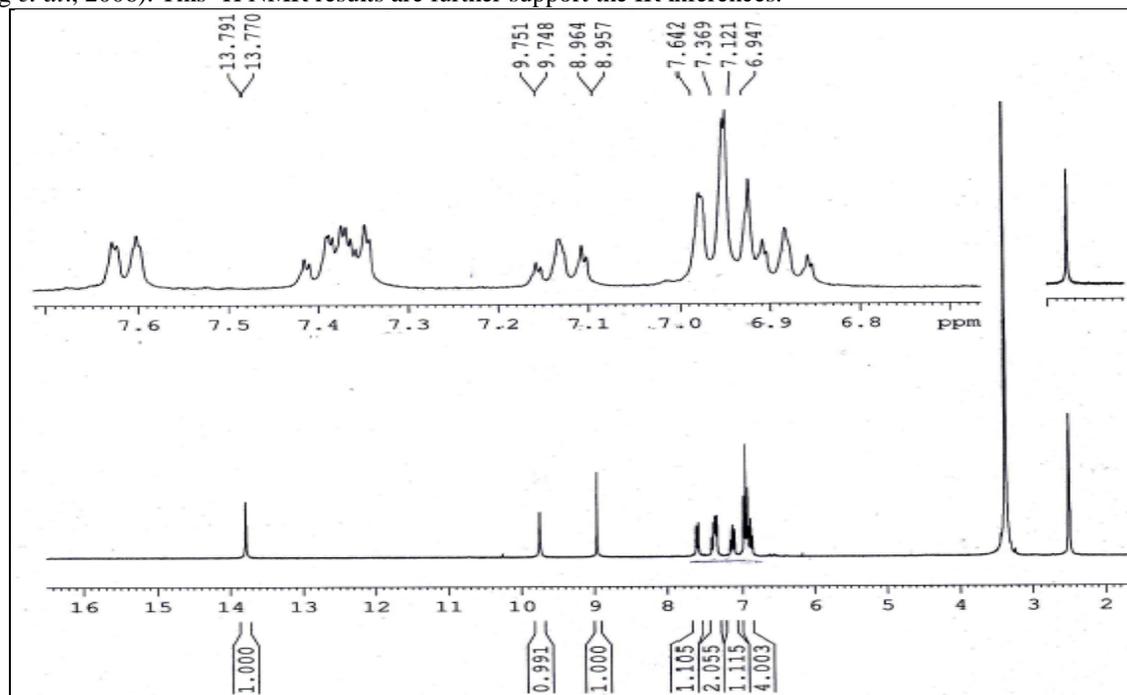


Figure 5: The ^1H NMR spectrum of the Schiff base monomer (AASA).

3.2. Thermal analyses of ligand (AASA) and resin (R-AASA):

TG/ DTG was carried out to assess the thermal stability of the Schiff base monomer (AASA) and the resin (R-AASA). The thermograms of the monomer and the resin are shown in Fig. 6 and 7 and their relative data is given in Table 3.

TG/ DTG shows the loss in weight in three stages for the monomer (AASA) and three stages for (R-AASA) between 30 and 80 °C up to 225 °C where the resin lost 5%. This could be due to the desorption of the solvent molecules from the resin present in the lattice (Samel *et al.*, 2000). Between 225 °C and 400 °C (R-AASA) lost 52% of its original weight and then gradual loss of 17% of its original weight was observed between 400 °C and 680 °C, this could be attributed to the decomposition and volatilisation of the low molecular weight fractions (Samel *et al.*, 2002). Because of the long conjugated bond system resin demonstrated higher resistance against high temperature than the monomer (Kaya *et al.*, 2008).

According to the TG analysis, both the onset of (R-AASA) was higher than the monomer and it was more stable than the monomer through to temperature and thermal decomposition. It formed carbines residue in a high amount such as 26% at 680 °C.

Table 3: TG/ DTG characterization parameters of the thermal decomposition of monomer (AASA) and resin (R-AASA).

Compound	Δm %	T_i °C	T_f °C	T_{max} °C	Residue wt %	Rate of decomp. (mg/ min.)
AASA						
Stage1	14	112.5	228	211.63		
Stage2	62	228	395	286.58	-----	0.73
Stage3	24	395	680	535		
R-AASA						
Stage1	75	100	225	212.5		
Stage2	52	225	400	298.11	26	0.67
Stage3	1	400	680	535		

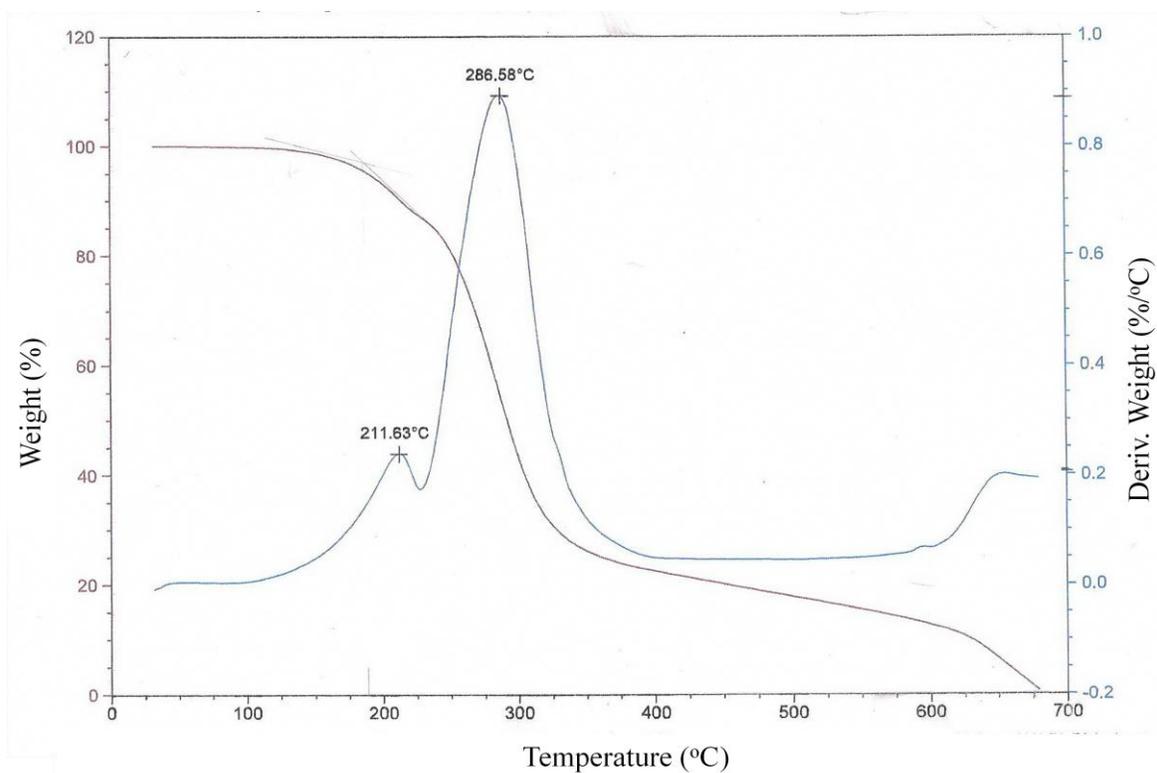


Figure 6: The TG/ DTG thermograms of the Schiff base monomer (AASA).

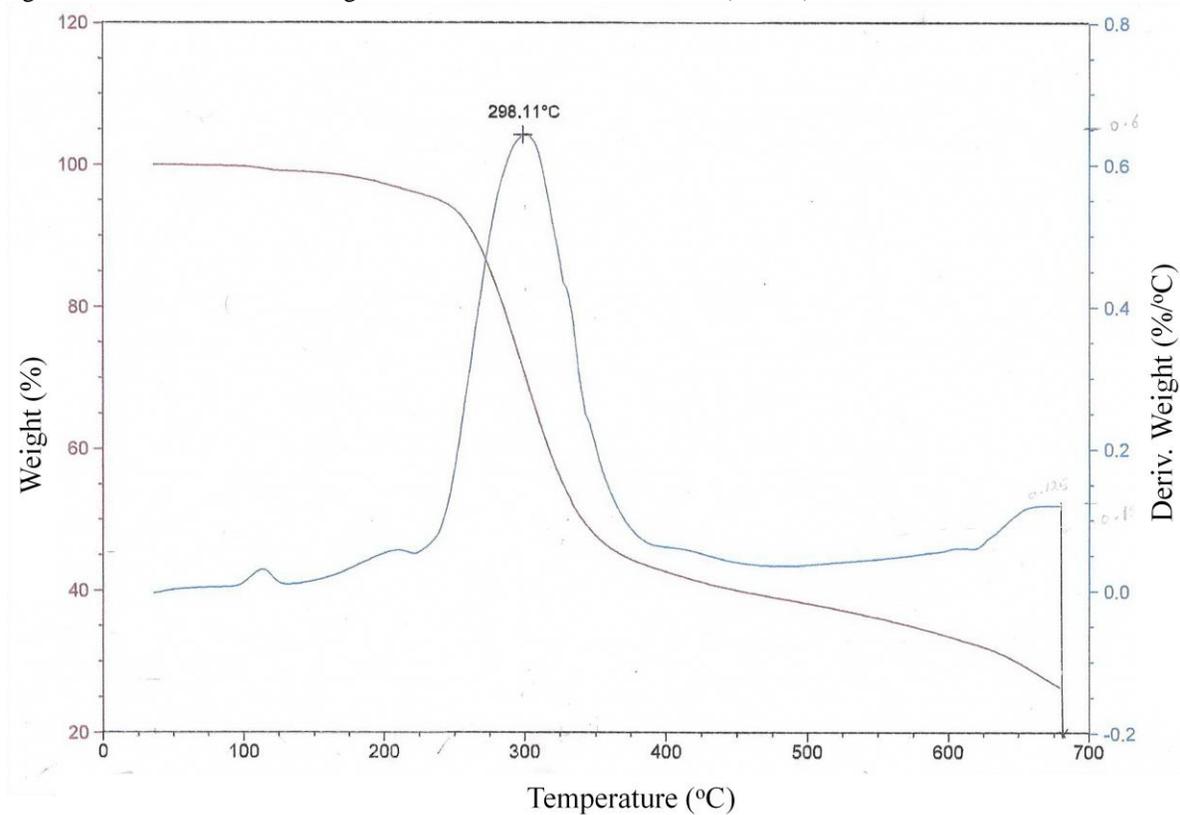


Figure 7: The TG/ DTG thermograms of the resin (R-AASA).

3.3. Measurement of the electrical conductivity:

The ionic conductance (G) of the prepared compounds was measured in the THF (Tetrahydro Furan) solvent. The influence of the weight of the dopant material on the conductivity of the chelating resin (R-AASA) is shown in Fig. 8 (a, b, c). It is apparent that the conductivity of the chelating resin (R-AASA) increases as the weight of the dopant material increases. In Fig 8 (a), it should be noted that the conductivity is higher and is equal $9.99 \times 10^{-4} \text{ ohm}^{-1}$ for 0.1 g using p- toluene sulfonic acid as a dopant material, while, in Fig. 8 (b), it can be seen that the highest conductivity was equal to $9.82 \times 10^{-6} \text{ ohm}^{-1}$ for 0.1 g using 2,5- dimethylbenzene sulfonic acid (PXSA) as a dopant material, in Fig. 8 (c), the ionic conductivity was stable in the value of $0.85 \times 10^{-5} \text{ ohm}^{-1}$ for 0.02- 0.1 g using NaCl as a dopant material, so that the sequence of conductivity is p- Toluene sulfonic acid > NaCl > 2,5- dimethylbenzene sulfonic acid (PXSA) for 0.1 g of the dopant sample, while from Fig. 8(a, b, c) it is observed that the conductivity is found to be increased with increasing weight. This increase in conductivity could be due to the increase in efficiency of the charge transfer between the chelating resin (R-AASA) and the dopant.

The long side chain exerted a strong steric effect on the doping process (Salih and Mater, 2012), making it more difficult for 2,5- dimethylbenzene sulfonic acid to protonate the amine group. This could have resulted from the decreasing of the doping level of the chelating resin (R-AASA), when it was doped with this dopant material. As a result, the chelating resin (R-AASA) has lower conductivity compared to when it is doped with p- Toluene sulfonic acid which has the highest conductivity.

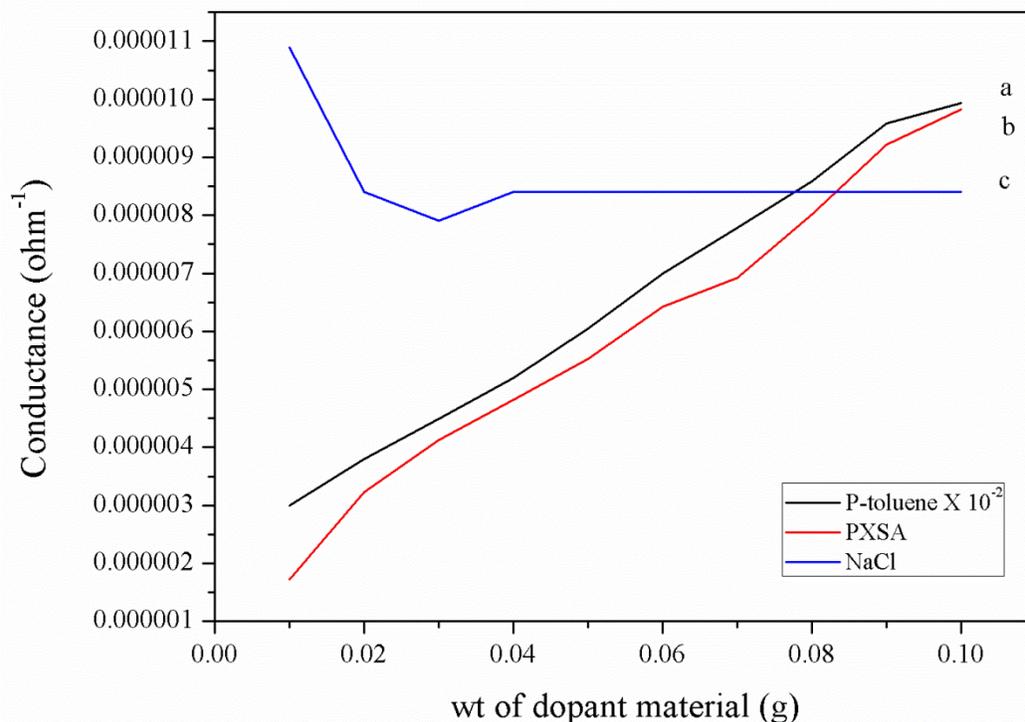


Figure 8: Effect of (a) p- toluene sulfonic acid, (b) PXSA and (c) NaCl on conductance of the resin (R-AASA).

Conclusion

The phenolic Schiff base condensed readily with formaldehyde in alkaline medium to form resin (R-AASA). 2,5- dimethylbenzene sulfonic acid (PXSA), p- Toluene sulfonic acid and NaCl were used as dopants during the polymerization process. Room temperature conductivity is found to be higher in p- Toluene sulfonic acid. The studied resin showed good thermal stability.

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