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Research Article

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Synthesis and Semi conducting Behaviour of the Ter-polyligand derived from p-Hydroxyacetophenone, Quinhydrone and Melamine

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ABSTRACT

The terpolymer resin p-hydroxyacetophenone- quinhydrone -melamine was synthesized by the condensation of p-hydroxyacetophenone (0.1M), quinhydrone (0.1M) and melamine (0.1M) in the presence of polyphosphoric acid (PPA). The resin was abbreviated as PAQM-I. The structure of resin was determined by its elemental analysis, UV-VIS, IR and NMR data. The molecular weight of terpolymer was determined by non-aqueous conductometric titration technique. The molecular weight of PAQM-I was found to be 6132. The DC conductivity of sample was determined by two probe method. The conductivity of PAQM-I was found to be in range7.411 x 10^{-5} to 9.712 x 10^{-5} mho cm^{-1} for temperature range 300K-378K. The activation energy of conduction for PAQM-I was found to be 3.01 kJ mol^{-1}.

Keywords: Polycondensation, Electrical conductivity, Terpoly ligand, Semiconductors, Wilson's exponential law.

INTRODUCTION

The semi conducting property of terpolymer resin has gained sufficient ground in recent years. Electrically conducting polymer resin is undoubtedly one of the focal point current interests in solid state physics and chemistry. Their discovery has led to the emergency of not only new type of material capable of replacing metals but also new concept to explain their high conductivity. Terpolyligand containing multifunctional aromatic rings have a large number of practical applications in electronic controls, insulating materials, protective adhesives, aerospace industries etc, because of their high thermal stability, heat and chemical resistance and electrical insulation due to interesting electrical properties [1]. Various researchers were synthesized by acid catalyzed Polycondensation and studied the application of terpolymer resins of substituted Phenols and formaldehyde [2-3]. Terpolymers of salicylic acid, p-hydroxy benzoic acid, thiourea with trioxane have been reported in literature **[**4-7**].** Shah *et al* reported the microwave assisted synthesis of phenolic resin derived from salicylic acid, resorcinol and formaldehyde [8]. Sayed *et al* studied temperature dependence of electrical conductivity of salicylaldeazinate metal chelates [9]. Work on organic conducting polymer is carried out extensively due to their high conductivity, their wide applications in areas such as corrosion protection and antistatic coatings [10], in biosensors for coupling of electron transfer [11], fabrication of electrochemical windows and gas sensors [12], development of individual electronic devices and whole integrated circuits [13-14] etc. Delocalized electrons and conjugation impart semi conducting properties to the polymer resins. Dharkar *et al* studied the conductivities of melamine-aniline-formaldehyde terpolymer resins and its polychelates. The activation energy values were found to be in range of 0.847 to 1.156 eV [15]. perkin *et al* studied the electrical conductivity of phenol-formaldehyde resin [16]. Khedkar et al studied structural and semi conducting behavior of terpolymeric ligand derived from m-cresol, hexamine and formaldehyde [17].

EXPERIMENTAL SECTION

Preparation of PAQM-I

A mixture p-hydroxy acetophenone (0.1M), quinhydrone (0.1M) and melamine (0.1M) in presence of polyphosphoric acid (PPA) was stirred for 1hrs in ice bath. Then the reaction mixture was refluxed using oil bath at 128^{o}C-130^{o}C for 8 hrs with intermittent shaking. The resinous product so obtained was repeatedly washed with distilled water, dried in air and powdered .The product was extracted with diethyl ether to remove co-polymeric impurities which might be formed along with terpolymer. Product was further dissolved in 10% sodium hydroxide solution and reprecipitated by gradual drop wise addition of 1:1 hydrochloric acid with constant stirring. PAQM-I so obtained was filtered and washed several times with hot water and the dried. The synthetic details are shown in the Table1.

Table1: Synthetic details of PAQM-I

Parameters/conditions	specifications
Terpolymeric resin	PAQM-I
p-Hydroxy acetophenone	0.1M
Quinhydrone	0.1M
Melamine	0.1M
Temperature	120^{o}C-130^{o}C
Time	8 hrs
yield	68%

RESULTS AND DISCUSSION

Elemental analysis and molecular weight determination: - The terpolymer resin was analyzed for carbon, hydrogen and nitrogen content. The elemental analysis was carried out at IIT, Powai, Mumbai. The elemental analysis data are tabulated in table2.

Table2. Elemental analysis and molecular weight determination of PAQM-I resin

Resin	%C		%H		%N		Mol. Formula of repeating unit	Molecular Weight of repeating unit
	Cal	Found	Cal	Found	Cal	Found		
PAQM-I	63.01	63.08	4.1	4.18	25.57	25.64	$C_{23}H_{18}N_8O_2$	438

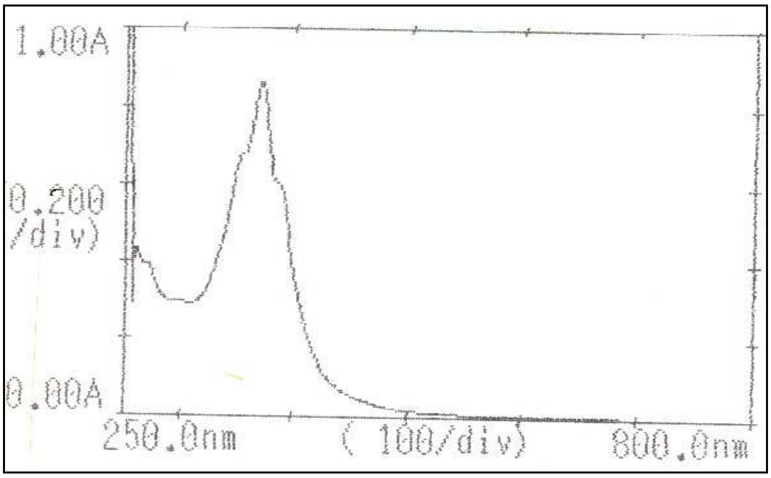

Fig. 1- UV-VIS spectra of PAQM-I resin

UV-VIS spectra of PAQM-I resin:-

UV-VIS spectra of terpolymer resin in DMSO Solvent recorded by UV-VIS Double Beam Spectrophotometer Schimadzu, Model No-1701 fitted with automatic pen chart recorder at Department of Pharmacy; RTM Nagpur

University, Nagpur.The spectrum so obtained is shown in fig1. The weak peak at 254nm assigned to n-σ*transition indicate presence of ether (–O-) group. Absorption at 371 nm was assigned to π-π* due to unsaturation. The absorption at 402nm (hump) was assigned to n–π*.

IR spectra of PAQM-I resin

IR spectra of synthesized terpolymeric resin was recorded at Department of pharmacy, RTM Nagpur University, Nagpur using FT-IR spectrophotometer Shimadzu model No-8101A. FT-IR spectral data are given in following Table3 The absorption at 3300-3350 cm^{-1} was assigned to C=N group (Imines).The sharp peak at 1686 cm^{-1} was assigned to C=O str.in α,β unsaturated cyclic ketone.The medium band at 1310 cm^{-1} was attributed to C-N str. in aromatic amine. Similarly peak at 1381cm^{-1}, 1468cm^{-1} was assigned to C-O-C str. in ether moiety. The medium band at 1655 cm^{-1} was assigned to NH def. But –NH str. peaks were not clearly observed in IR spectrum this may be due to overlapping of imines absorption for C=N str.

Table3. FT-IR spectral data [18-29]

IR (wave number in cm^{-1})	Nature of fragment assigned
3300-3350	C=N- str.
1686	C=O str.(α,β unsaturated ketone)
1655	N-H Def
1600	C=Cstr.
1381, 1468	C-H def.
1310	C-N str. Aromatic amine
1114, 1232	C-O str. in Ether moiety
837	p-Disubstituted aromatic ring

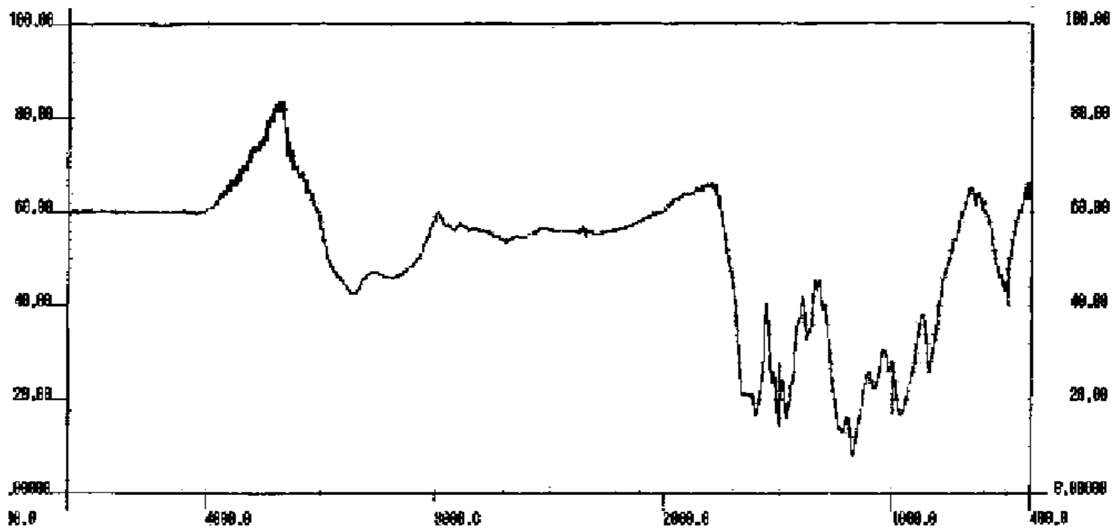

Fig. 2- IR spectra of PAQM-I resin

^{1}H NMR Spectra of PAQM-I resin:-

^{1}H NMR spectra of terpolymeric resin using DMSO -d^6 solvent was scanned by BRUKER AC II 400 NMR spectrophotometer SAIF, Punjab University, Chandigarh. The ^{1}H NMR spectral data is tabulated in Table 4. The ^{1}H NMR spectra of PAQM-I resin is shown in Figure 3.The NMR characterization of resin is based on data available in literature. In NMR spectrum of the PAQM-I resin the unsymmetrical pattern at 6.9-7.9δ was due to the aromatic proton .The singlet at 2δ was assigned to CH_3 proton in CH_3-C=N moiety. The strong signal at 4.5δ was due to -NH proton in primary amine group. The singlet at 1.2δ was attributed to proton in Cyclohexa-2, 5-diene-1, 4-diimine moiety.

Table 4: NMR spectra of PAQM-I resin [30-31]

Chemical shift(δ ppm)	Nature of fragment assigned
6.9-7.9	Aromatic protons(unsymmetrical pattern)
4.5	N-$\mathbf{H_2}$
2.0	C$\mathbf{H_3}$-C=N
1.2	Proton in Cyclohexa-2,5-diene-1,4-diimine moiety

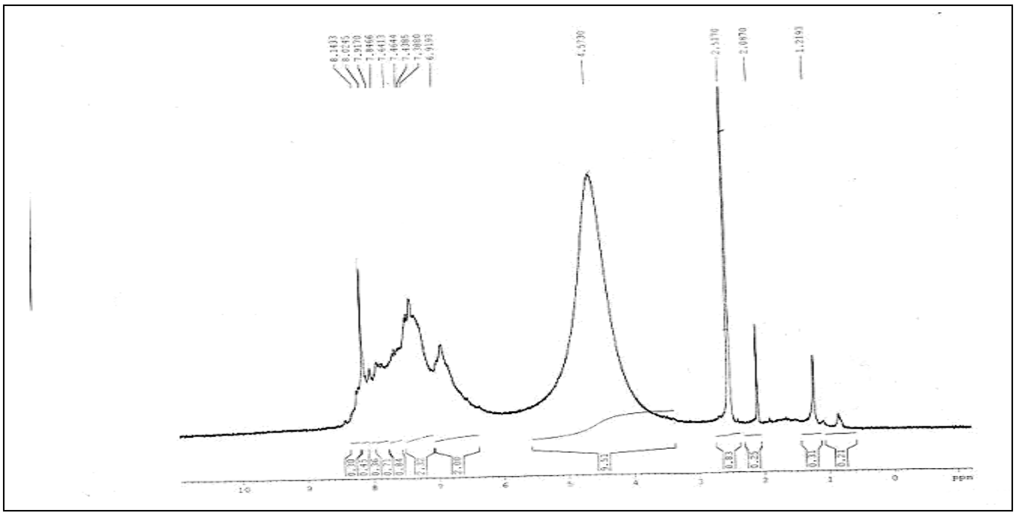

Fig. 3- ^{1}H NMR Spectra of PAQM-I resin

According to data obtained in physicochemical methods; the tentative structure of terpolymeric resin was assigned as shown in fig. 4

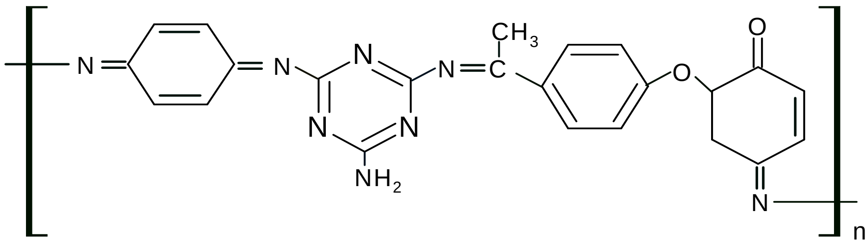

Fig. 4- Tentative structure of PAQM-I

Electrical conductivity for PAQM-I resin

The electrical conductance of polymeric material depends upon incalculable parameters such as porosity, pressure, method of preparation and atmosphere. Activation energy is not affected by these parameters and therefore, it is fairly reproducible. The magnitude of activation energy depends on the number of loosely bound electrons present in semi conducting materials. Resins are well known for their behavior as semiconductors through carrier mobility in them usually is very low. Generally polymers containing aromatic nuclei in the back bone exhibit lower activation energy than those with aliphatic system.

The powdered sample of PAQM-I resin was palatalised by hydraulic press at pressure of 17 lb inch^{-2}.The surface of pallet was made conducting by applying graphite paste. The diameter and thickness was determined using screw gauge. The solid state conductivity as function of temperature was recorded by two probe method. The specific conductance of this resin was calculated by value of specific resistance. The electrical conductivity as a function of temperature of the polymer was studied.

The electrical conductivity (σ) varies exponentially with absolute temperature as shown in following Wilson's equation [31-38],

$$\sigma = \sigma^o \exp^{(-\Delta E/kT)} \quad \text{----------------------- (1)}$$

Where, k = Boltzmann constant,
σ =electrical conductivity at temperature T;
σ^o= electrical conductivity at temperature $T \rightarrow \infty$;
ΔE=Electrical conductivity energy of electrical conduction.

Above equation (1) has been modified as,

$$\text{Log } \sigma = \text{Log } \sigma^o - [Ea/2.303kT] \quad \text{----------------------- (2)}$$

The plot of Log σ versus 1/T is shown in fig. 5

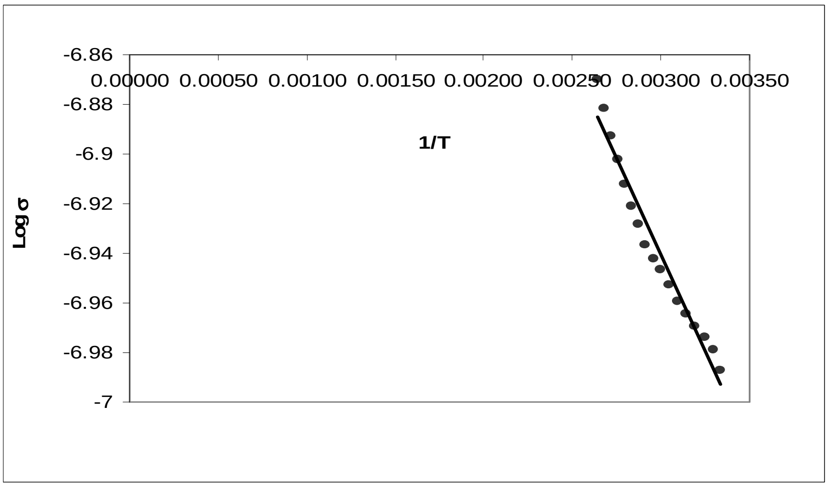

Fig. 5- Electrical conductivity plot of PAQM-I

The DC conductivity of PAQM-I resin was studied for temperature range 300K-378K.The electrical conductivity for PAQM-I was found in the range of 7.411 x 10^{-5} to 9.712 x 10^{-5} mho cm^{-1} in mentioned temperature range. The energy of activation (Ea) of electrical conduction calculated from the slopes of the plot was found to be 3.01 $kJmole^{-1}$ of PAQM-I resin.

CONCLUSION

The data of elemental analysis, Uv–Vis spectra, FT-IR spectra, ^{1}H NMR spectra, supports to the above tentative structure of PAQM-I terpolymeric resin. Electrical conductivity of PAQM-I terpolymeric resin increases with increase in temperature. The plot of log σ versus1/T is found to be linear in the temperature range under study, which indicates that the Wilson's exponential law is obeyed. Hence this terpolymer may be ranked as semiconductor for temperature range 300-378 K. The low activation energy of conduction of resin may be due to presence of large number of delocalized π-electrons in the polymer chain. This is in good agreement with the tentative structure of ter-polyligand.

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