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RESEARCH ARTICLE

Synthesis and Semiconducting Behavior of Terpolymer Resin-I Derived from Sulphanilic Acid, Melamine and Formaldehyde

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Abstract: The resin-I (abbreviated as SAMF-I) was synthesized by polycondensation reaction of sulphanilic acid (0.05 M), melamine (0.05 M) and formaldehyde (0.15 M) in presence of an acid catalyst (1 M HCl). The structure of resin was determined by its elemental analysis, UV-Vis, IR data. Molecular weight of resin was determined by non aqueous conductometric titration. DC conductivity of the terpolymer was studied over a wide range of temperature. The resin was found to show semiconducting behavior since Wilson's law was obeyed. The conductivity of SAMF-I was found to be in the range 3.8×10^{-8} to 2.9×10^{-8} mho cm^{-1} for temperature range 303-423 K. The activation energy of conduction for SAMF-I was found to be 0.981 $kJmol^{-1}$.

Keywords: Polycondensation, Terpolymer, Wilson's Law, Activation energy, Electrical conductivity

Introduction

The development and foundation of modern electronics, globalization of advance technology has to be credited entirely to semiconductors. Semiconductors have a monumental impact on progress of modern electronics. New electronic semiconductor devices that are almost exponentially smaller, faster and more efficient than their immediate predecessors have been subject of interest today polymers are well known as structural materials and electrical insulators, some of them have remarkable conductivity property which has inevitable application in electronic industries. Electrical conductivity measurements have been studied to ascertain the conducting nature of the copolymer resin.

A large number of practical applications of phenolic resins have been found in electronic controls, insulating materials, protective adhesives and aerospace industries because of their chemical resistance and electrical insulation properties[1]. Shah *et al.* reported the microwave assisted synthesis of phenolic resin derived from salicylic acid,

resorcinol and formaldehyde[2]. Perkin *et al.* studied the electrical conductivity of phenol-formaldehyde resin[3]. Patel *et al.* reported the electrical resistivity of 2, 4-dihydroxyacte-phenone-urea-formaldehyde polymeric ligand and its polychelates over a wide temperature range[4]. Gurnule *et al.* studied the conducting behavior of copolymer resin[5]. The electrical property of *p*-cresol and melamine with formaldehyde polymer was measured over a wide range of temperature (313–423 K)[6]. Rahangdale *et al.*[7] carried out the study of terpolymeric resin and found that the electrical conductivity of each of the copolymer resins increases with increase in temperature. Electrical conductivity study has been done of resin synthesized from salicylic acid, butylenediamine and formaldehyde[8]. Dharkar *et al.*[9] 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. Kushwaha *et al.*[10] reported semiconducting behavior of resin derived from *p*-nitrophenol, resorcinol and formaldehyde and Kapse *et al.*[11] carried out the study of terpolymer resin *p*-hydroxyacetophenone- quinhydrone –melamine for its semiconducting property. The DC conductivity of sample was determined by two probe method[10,11].

Present paper deals with the synthesis and electrical conducting behavior of terpolymer resin obtained by acid catalyzed polycondensation of sulphanilic acid, melamine and formaldehyde.

Experimental

All chemicals were AR grade and chemically pure grade, sulphanilic acid-melamine and formaldehyde was procured from Sd fine, India. Triple distilled water was used for the entire experimental procedure.

Synthesis of sulphanilic acid-melamine-formaldehyde terpolymer resin

Sulphanilic acid-melamine-formaldehyde resin (SAMF-I) was prepared by condensing sulphanilic acid (0.05 M), melamine (0.05 M) and formaldehyde (0.15 M) in 1 M HCl (150 M), was refluxed on oil bath for 5 h at 105-110 °C with intermittent shaking. The resinous yellowish colored product so obtained was repeatedly washed with cold distilled water, dried in air and powdered. The powdered product was washed many times with hot water to remove unreacted monomers. The air dried product was extracted with ether to remove melamine and formaldehyde copolymer which might be formed as side product. It was further purified by dissolving in 8% NaOH solution, filtered and reprecipited by gradual drop wise addition of 1:1 HCl with constant and rapid stirring in order to avoid the lump formation. The SAMF-I resin so obtained was filtered, washed several times with hot distilled water, dried in air and powdered. The yield was found to be 68% of the synthesized resin[12,13]. Reaction scheme is given in Figure 1.

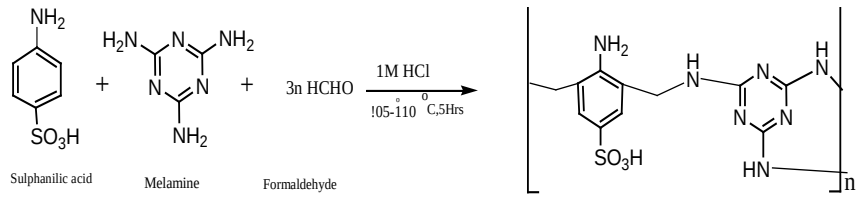

Figure 1. Reaction scheme-synthesis of SAMF-I

The detailed analytical data of terpolymer SAMF-I is tabulated in Table 1.

Table 1. Synthetic details of SAMF-I

Parameters/conditions	Specifications
Terpolymeric resin	SAMF-I
Sulphanilic acid	0.05M
Melamine	0.05M
Formaldehyde	0.15M
Temperature, °C	105-110
Time, h	5
Yield, %	68

Results and Discussion

Characterization of SAMF-I resin

Elemental analysis and molecular weight determination

The terpolymer resin was analyzed for carbon, hydrogen and nitrogen and sulphure content. The elemental analysis was carried out at National Institute of Pharmaceutical Education & Research (NIPER) Punjab University, Chandigarh India.

The number average molecular weights (Mn) of SAMF-I terpolymer was determined by non-aqueous conductometric titration in DMF using 0.1 M KOH in absolute alcohol as titrant. From the graphs of specific conductance against miliequivalents of base, first and last break were noted from which degree of polymerization (DP) and the number average molecular weight (Mn) was calculated for terpolymer resin using following equation[14].

$$DP = \frac{\text{(Total milliequivalents of the base required for last break)}}{\text{milliequivalents of the base required for first break}}$$

$$Mn = DP \times \text{Molecular weight of the repeating unit}$$

The repeating unit weight was obtained from elemental analysis. The elemental analysis and molecular weight determination data of SAMF-I resins is given in following Table 2.

Table 2. Elemental analysis and molecular weight determination of SAMF-I resin

Resin SAMF-I	%C	%H	%N	%S	DP	Mol. Weight (M_n)	M. F. of repeating unit	Mol. Wt. of repeating unit
Calculated	42.85	4.16	29.1	9.5	26	8736	$C_{12}H_{14}N_7SO_3$	336
Found	42.87	4.2	29.14	9.52				

IR spectra of SAMF-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. The broad band[15] at 3401 cm^{-1} was assigned to the O–H stretching of Ar-SO_3H. The band that appeared at 3401 cm^{-1} is due to N-H-stretching of amino group but this band seems to be merged with a broad band of –OH group of –SO_3H present in the resin[16] (Figure 2). The absorption at 2939 cm^{-1} was assigned to-CH_2- stretch shows the bridges of CH_2 in SAMF- I composite[17,18]. The inflections around 1448 cm^{-1} and 785.1 cm^{-1} suggest the presence of wagging and rocking vibrations of methylene (-CH_2-) bridges in polymeric chains[19,20]. The N–H bending vibration of primary amines is observed in the region 1650-1560.9 cm^{-1}. The secondary amine main chain was confirmed by the 1176 cm^{-1}, the convolute peak at 1340 cm^{-1} is assigned to the triazine cycle[22]. Also band at, 910 cm^{-1}, 814 cm^{-1} and 665 cm^{-1}, all of them

were assigned to –NH- bending, wagging and deformation out of plane vibrations in terpolymer resin respectively. The absorption band at1650-1580 cm^{-1} was assigned to N–H bending vibration of primary amines[14,18]. The band at 837-820 cm^{-1} was due to tetra substituted benzene ring[23]. The region 1186-1034 cm^{-1} was assigned to C–N stretch in primary and secondary amines due to weak band at 605.7 cm^{-1} and 735 cm^{-1} which were assigned to C-S str. of aromatic ring and SO_3H group[14]. A peak at 1126 cm^{-1} was due to the stretching vibrations of Ar–S bond in SO_3H composite[24]. 1327 cm^{-1} and 1165 cm^{-1} region corresponds to S=O antisymetric and symmetric stretching in sulphanilic acid[14,25]. FT-IR spectral data is given in Table 3.

Table 3. IR spectral data of SAMF-I

IR (wave number in cm^{-1})	Nature of fragment assigned
3401	O–H str.
2939	$-CH_2-$ str.
1650-1560.9	N-H bend.in pri amines
1340	triazine ring
1186-1034	C–N str. Primary/sec. amines
910 ,814,665	–NH- bend. wag. and def. out of plane vib
605.7 ,735	C-S str.
1126\	Ar–S.str.
1327 and 1165	S=O antisymetric and sym. str.
837,830	1,23,5 tetrasubstituted aromatic ring

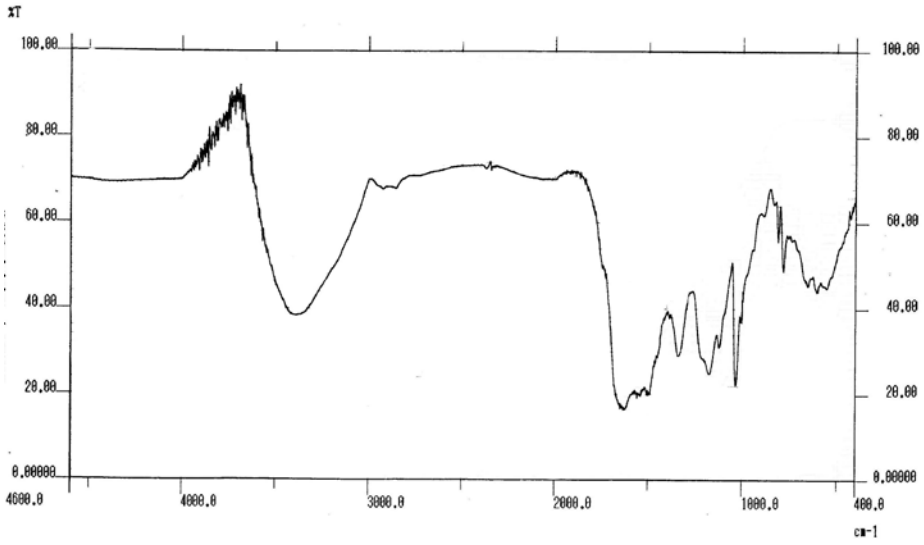

Figure 2. IR spectra of SAMF-I

UV-Vis spectra of SAMF-I resin

UV-Vis spectra of terpolymer resin in DMSO solvent was 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 UV-Vis spectra of SAMF resin is shown in Figure 3.

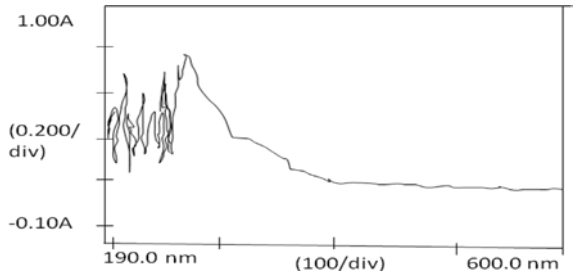

Figure 3. UV-Visible spectra of SAMF-I

UV-Vis spectrum of SAMF-1 was scanned from 190-700 nm. 213 nm was assigned to *n*-σ* transition is due to –SO_3H group. A peak at 259.5 nm was assigned to π-π* due to aromatic ring. The *n*-π* transition at 284.5 nm, this is due to the unsaturation centre present in aromatic ring or melamine ring.

Electrical conductivity of SAMF-I resins

The DC conductivity of SAMF- I resin was studied for temperature range 304 to 423 K. 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 conductance of polymeric material depends upon incalculable parameters such as porosity, pressure, method of preparation and atmosphere. Generally polymers containing aromatic nuclei and conjugated unsaturation centres in the back bone exhibit lower activation energy than those with aliphatic system[21,26,27]. The powdered sample of resin SAMF- I was palatalized by hydraulic press at pressure of 17lb $inch^{-2}$. The surface of pellet were made conducting by applying graphite paste. The diameter and thickness was measured using screw gauge. The solid state conductivity as function of temperature was recorded by two probe method.

The plot of log σ *versus*1/T was found to be linear in the temperature range under study, which indicate that the Wilson's exponential law, σ=σoexp (-Ea/kT) was obeyed. Where, k=Boltzmann constant, σ=Electrical conductivity at temperature T, σo=Electrical conductivity at temperature T→∞, Ea=Activation energy of conduction. The energy of activation (Ea) of electrical conduction calculated from the slope of the plot was found to be 0.981 kJ mol^{-1}. The electrical conductivity was found in the range of $3.80x10^{-8}$ to $2.92x10^{-8}$ mho cm^{-1} for SAMF-I resin. Electrical conductivity plots of SAMF-I resin is given in Figure 4.

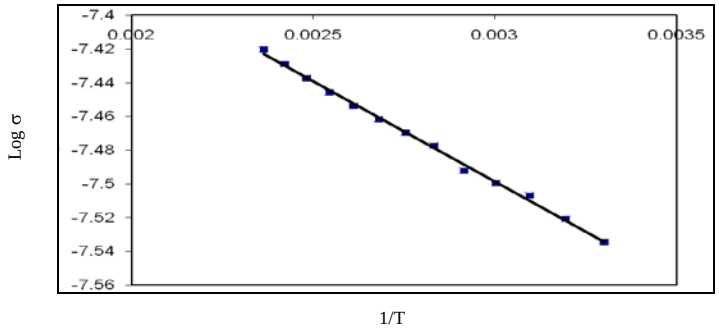

Figure 4. Electrical conductivity plot of SAMF-I

Conclusions

The data of elemental analysis, UV–Vis spectra, FTIR spectra, non-aqueous conductometric titration supports to the above tentative structure of SAMF-I terpolymeric resin. Electrical conductivity of SAMF-I terpolymeric resin increases by increasing temperature. The plot of logσ *versus* 1/T is linear, obviously satisfy Wilson law. Consequently SAMF-I show semiconducting behavior.

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