

Synthesis, Characterization And Semiconducting Studies of Salicylaldehyde-Formaldehyde Melamine Copolymers

Sonali S.Pande

Department of Chemistry Shankarrao Dhawad Polytechnic,
Nagpur, India
sspande2001@yahoo.co.in

Prof.W.B.Gurnule

Department of Chemistry, Kamla Nehru College, Nagpur.
R.T.M. Nagpur University,
Nagpur, India

Abstract— Copolymer (SMF) was synthesized by the condensation of Salicylaldehyde and melamine [M] with formaldehyde [F] in presence of acid catalyst using varied molar ratios of monomers. A copolymer composition is determined on the basis of their elemental analysis and the number average molecular weight of this copolymer was determined by conductometric titration in non- aqueous medium. The intrinsic viscosity measurement in DMSO has been carried out with a view to ascertain the characteristic functions and constants. The copolymer resin was characterized by IR spectra and HNMR spectra. The electrical properties of SMF copolymers were measured over a wide range of temperature. From electrical conductivity of these copolymers, the activation energies of electrical conduction have been evaluated. On the basis of above studies, these copolymers can be ranked as semiconductors. When a voltage is applied to a thin film of this copolymer resin then they have been emitted light. This remarkable property of this copolymer resin may be used to make a wide range of semiconducting electronic devices such as transistors, light emitting diodes, solar cells and even lasers which can be manufactured by conventional inorganic semiconductors.

Keywords- Resin, Synthesis, Electrical conductivity

I. INTRODUCTION

In recent years considerable interest has been made to improve the quality of polymer by co-polymerization either by modifying methods or by introduction of variety of functional monomers. The polymer scientists are trying to polymeric resins with improved properties such as thermal stability, durability, high chemical resistivity, conductivity in the domain of desired applicability. Semiconducting polymer have been the subject of study for many decades for day to day application product for example, uses in electrical sensors and electronic devices.

Gupta et al have measured the electrical conductivity of p-hydroxybenzaldehyde- adipic acid –ethylene glycol[1].Urade et al have studied nature of resin derived from 2,6-Diaminopyridine and terphthalic acid[2]. Masram et al studied the electrical conductivity of resin derived from salicylic acid, butylenediamines and formaldehyde[3]. Singru R. studied the electronic application of 8-hydroxyquinoline-5 sulphonic acid with formaldehyde [4].Kapse et al have studied semiconducting behavior of the terpolymer derived from p-hydroxyacetophenone,quinhydrone and melamine[5].

The present study deals with the synthesis and characterization of salicylaldehyde-melamine-formaldehyde [SMF] terpolymer resin by spectral methods for the first time. The electrical conductivities of four SMF copolymer resins are studied over a wide range of temperature.

II. EXPERIMENTAL

The important chemicals like salicylaldehyde, melamine and formaldehyde used in the preparation of various new SMF copolymer resins were procured from the market and were of chemically pure grade.

A. Synthesis of SMF Copolymer resin

The SMF-I terpolymer resin was prepared by condensing Salicylaldehyde- (1.22gm, 0.1mol), melamine(1.29gm, 0.1mol), formaldehyde(11.25ml, 0.3mol) in the mole ratio of 1:1:3 in the presence of 2MHCl as a catalyst at 122+2°C for 6h in an oil bath with occasional shaking to ensure thorough mixing. The separated cream colour terpolymer resin was washed with hot water to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether to remove 4-hydroxybenzophenone- formaldehyde copolymer which might be present along with SMF terpolymer. The terpolymer resin was purified further by dissolving in 8% aqueous sodium hydroxide solution, filtered and reprecipitated by 1 drop wise addition of ice cold 1:1 (v/v) concentrated hydrochloric acid/distilled water with constant and rapid stirring to avoid formation of lumps. The process of reprecipitation was repeated twice. the terpolymer sample SMF-I thus obtained was filtered, washed with hot water, dried in air, powdered and kept in vacuum desiccator. The reaction and suggested structure of SMF-I is given in Fig. 1. In the same way the other copolymer resin viz. SMF-II, SMF-III, SMF-IV were prepared with the molar ratios 2:1:4, 3:1:5, 4:2:7.

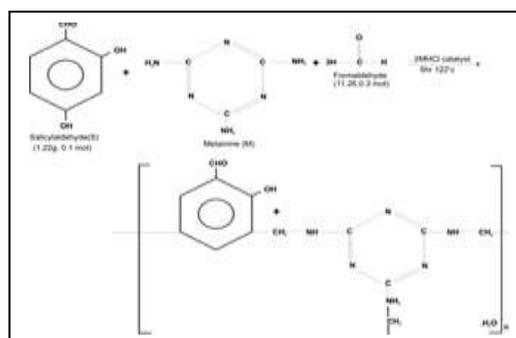


Figure.1: Preparation of SMF-1 Copolymer Resin

III. CHARACTERIZATION OF SMF COPOLYMER RESIN

A. Physicochemical and Elemental Analysis

The copolymer resin was subjected to micro analysis for Carbon, Hydrogen and Nitrogen. The number average molecular weight was determined by conductometric titration in DMSO medium using ethanolic KOH as the titrant by using 25 mg of copolymer sample. Then a plot of the specific conductance against the miliequivalents of KOH required for neutralization of 100 gm of terpolymer resin was made. Inspection of such plot revealed that there were many breaks in the plot. From this plot first break and last break were noted. On the basis of average degree of polymerization the average molecular weight has to be determined by following eq..

$$\overline{DP} = \frac{\text{Total miliequivalents of base required for}}{\text{Miliequivalent of base required for smallest interval}}$$

$$\overline{Mn} = \overline{DP}$$

The intrinsic viscosity was determined using a Tuan-Fuoss viscometer at six different concentrations ranging from 0.3% to 0.05% wt % of resin in DMSO at 30°C. Intrinsic viscosity was calculated by the Huggins eq. and Kramer's eq.

$$\eta_{sp} / C = [\eta] + K[\eta]^2 C$$

$$\ln \eta_{sp} / C = [\eta] + K' [\eta]^2 C$$

B. Spectral and surface analysis pestle and mortar

- Electronic (UV-Visible) spectra of copolymer resin in DMSO was recorded with a double beam spectrophotometer in the range of 200-850 nm. IR spectra of SMF terpolymer resin was recorded in the range of 4000-500 cm⁻¹ at SAIF, Punjab University, Chandigarh. ¹H NMR spectra was recored with Bruker Advance-II 400 NMR spectrophotometer using DMSO as solvent at SAIF, Punjab University, Chandigarh. The surface morphology was studied using scanning electron microscope at different magnification at VNIT Nagpur.

C. Conductivity Measurement

The electric electrical conductivity of SMF copolymer resin was measured over a wide range of temperature (303-423 K) in their pellet form using Auto LCR-Q meter 4910. To prepare the pellet the copolymer resin was thoroughly ground in agate pestle and mortar. The well powered copolymer was isostatically in a steel die at 10 tones/inch with the help of hydraulic press. The pellet was hard and crack free. On both sides of pellet, a thin layer of colloidal graphite in acetone was applied to ensure a good contact with the electrode. Care was also taken not to apply very high voltages to avoid any leakages across the border.

IV. SPECTRAL AND SURFACE STUDIES

The UV-Visible spectrum of all four SMF copolymer resin has been shown in Fig. 2. All the four SMF copolymer resin displayed two broad bands at 280-290 nm and 300-330 nm. The observed position of the absorption bands indicates the presence of a carbonyl group and hydroxyl group which is in

conjugation with the aromatic nucleus. The band at 300-330 nm is more intense which is accounted for a π-π* transition while the less intense band at 280-290 may be due to n-π* transition [6, 7]

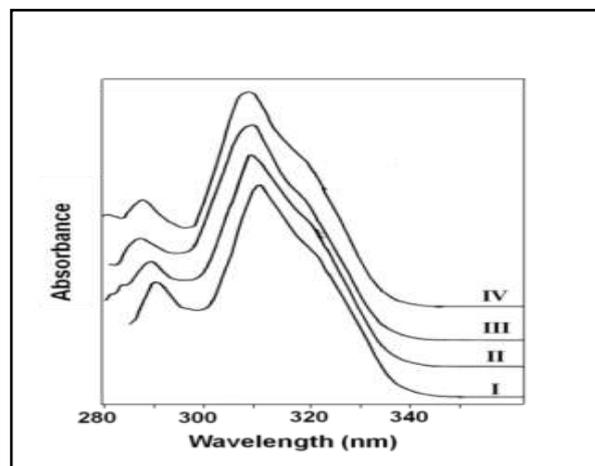


Figure. 2 UV-visible Spectra of SMF Copolymer Resins

A. Infrared Spectra

The IR spectra of all four SMF copolymer resins are presented in fig 3. IR spectra revealed that all four SMF terpolymer resin give rise to nearly same pattern of spectra. A broad band appeared at the region 3418-3420 cm⁻¹ may be assigned to stretching vibration of phenolic -OH group exhibiting intramolecular hydrogen bonding[8]. The band at 3245-3249 cm⁻¹ is due to stretching of -NH. The band at 1606-1607cm⁻¹ may be due to aromatic ring substituted. The band at 1602-1604 cm⁻¹ may be due to aromatic ring (substituted). The band at 1342, 1278 may be due to CH₂ bending,

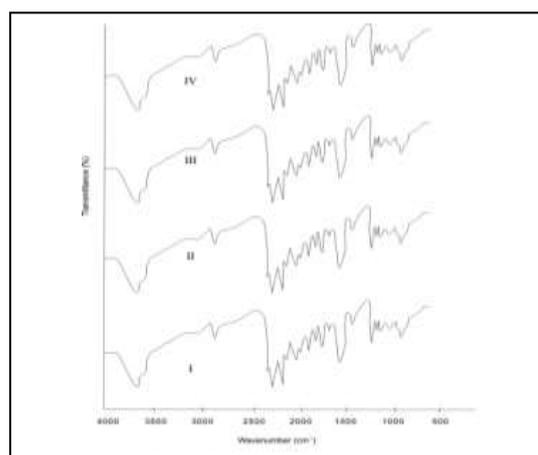


Figure. 3. Infra Red Spectra of SMF Copolymer Resins

B. Nuclear Magnetic Resonance spectroscopy

¹H NMR spectra of all SMF terpolymer resin are shown in fig 4. The medium signal at 2.52-2.54 ppm may be due to methylene proton of Ar-CH₂ bridge. The signal in the range of

9.90-9.98 ppm may be due to phenolic hydroxyl group[9,10]. The singlet in the region 7.33-7.34 ppm may be due to proton of -NH bridge. The weak multiplate signal in the region at 8.10-8.15 ppm may be due to aromatic proton of A r-H.

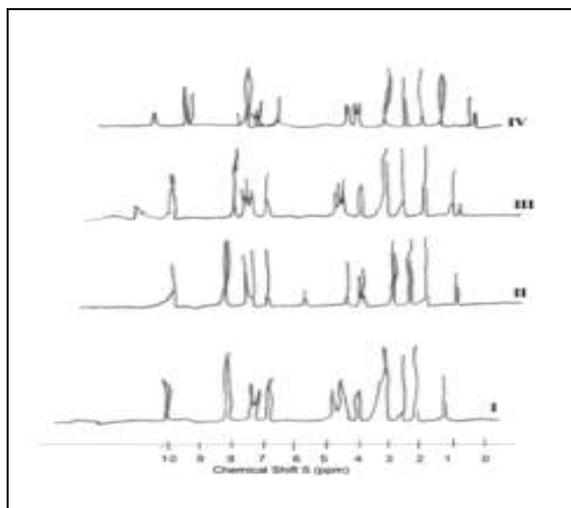


Figure. 4 ¹H NMR Spectra of SMF Copolymer Resin

C. Nuclear Scanning electron microscopy (SEM)

Surface analysis has found great use in understanding the surface features of the materials. The morphology of the reported sample was investigated by scanning electron micrograph at different magnification which is shown in fig 5. for SMF. It gives the information of surface topography and defect in the structure. The morphology of polymer resin shows spherulites and fringed model. The spherules are complex polycrystalline formation having as good as smooth surface. This indicates the crystalline nature of SMF copolymer resin. The morphology of copolymer shows a fringes model of the crystalline amorphous structure. Thus by SEM micrograph morphology of the resin shows the transition between crystalline and amorphous nature, when compared to other resin, the SMF terpolymer resin is more amorphous in nature, hence shows higher metal ion exchange capacity.

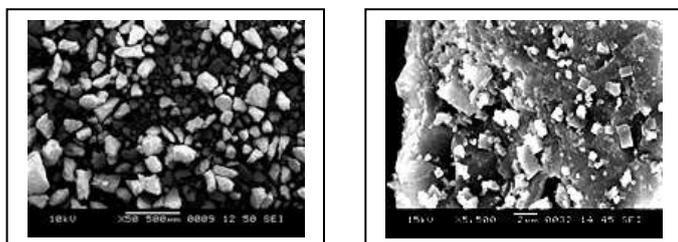


Figure. 5. SEM Micrograph of SMF-I Copolymer resin

D. Electrical conductivity for SMF copolymer

The electrical conductance of polymeric material depends on incalculable parameters porosity, pressure, method of synthesis 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 semiconducting materials. Resins are well known for their behavior as semiconductors

through carrier mobility in them is low. Generally polymers with aromatic nucleus exhibit lower activation energy than those with system aliphatic system. The electrical conductivity (σ) varies exponentially with the absolute temperature according to well known relationship, $\sigma = \sigma_0 \exp(-E_a/K)/T$
 σ =Electrical conductivity at temperature (T)
 σ_0 =Electrical conductivity at temperature (∞) (preexponential conductivity)

E_a =Activation energy of electrical conduction.

K =Boltzmann Constant (1.3817×10^{-23} J/K).

T = Absolute temperature.

This relation has been modified as,

$$\log \sigma = \log \sigma_0 + (-E_a/ 2.303 K) 1/T$$

According to this relation

a plot of $\log \sigma$ vs. $1/T$ is plotted which is shown in Fig.6. The

plots are linear with negative slope.

This indicates the semiconducting nature of the resin. The values of activation energy and electrical conductivity for SMF copolymer resin are given in table 1.

TABLE I. ELECTRICAL CONDUCTIVITY DATA OF SMF COPOLYMER RESINS

Copolymers	Electrical Conductivity		ΔT (K)	ΔE (J/K)
	313 K	423 K		
SMF-I	3.88×10^{-10}	9.05×10^{-7}	313 – 423	13.06×10^{-23}
SMF -II	3.51×10^{-9}	1.07×10^{-6}	313 – 423	12.71×10^{-23}
SMF-III	2.09×10^{-8}	8.71×10^{-5}	313 – 423	10.17×10^{-23}
SMF -IV	1.14×10^{-7}	1.22×10^{-4}	313 – 423	9.53×10^{-23}

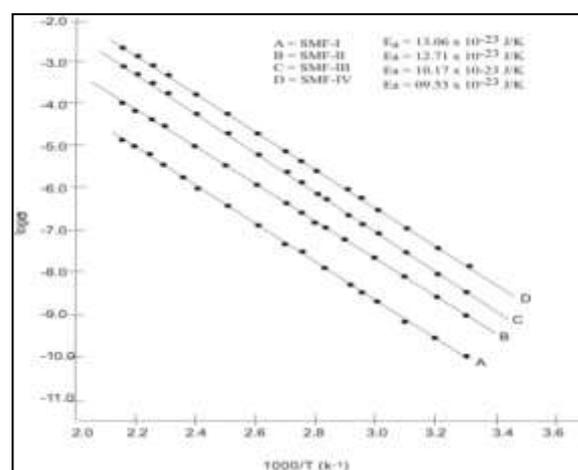


Figure. 6. Electrical Conductivity of SMF Copolymer Resin

The sequence of electrical conductivity is found to be SMF-I<SMF-II<SMF-III<SMF-IV. As the number of rings increases in the structure of repeat unit of copolymer ,increase the π electrons, conjugation and delocalization which may

increase the electrical conductivity due to increasing the forbidden energy gap between valence band and conduction band. The order of thermal activation energy is just reverse of electrical conductivity SMF-I>SMF-II>SMF-III>SMF-IV

V. CONCLUSIONS

1. A Copolymer SMF, based on the condensation reaction of Salicylaldehyde and melamine with formaldehyde in the presence of acid catalyst was prepared.
2. The electrical conductivity of each of these copolymer resin increases with the increasing temperature. Hence these copolymers may be ranked as semiconductors.
3. The energy of activation is found to be in the order SMF-I>SMF-II>SMF-III>SMF-IV and electrical conductivity is found to be in the order be SMF-I<SMF-II<SMF-III<SMF-IV.

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