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Electrical Conductivity Study of Resin Synthesized From Salicylic Acid, Butylenediamine and Formaldehyde

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Abstract

The present paper reports the electrical conductivity study of a resin. The resin salicylic acid-butylenediamine-formaldehyde (SBDF) was synthesized by the condensation of salicylic acid and butylenediamine with formaldehyde in the presence of a hydrochloric acid catalyst with molar proportion 1:1:2.The purity of newly synthesized terpolymer has been tested and confirmed by thin layer chromatography (TLC) technique. Terpolymer resin was characterized by elemental analysis, infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and UV-Visible spectral studies. The number average molecular weight of the resin was determined by non-aqueous conductometric titration. Viscometric measurements in Dimethylformamide (DMF) have been carried out in order to ascertain the characteristics functions and constants of SBDF terpolymer. Electrical conductivity measurements have been carried out to ascertain the semiconducting nature of the terpolymer resin.

Keywords: Synthesis; characterization; number average molecular weight; electrical conductivity.

INTRODUCTION

Extensive research work has been carried out on synthesis and characterization of terpolymers in our laboratory [1-4]. The terpolymers offer novelty and versatility; hence they occupy the pivotal position in the field of material science. The progress in the field terpolymers has been extremely rapid, as they generally useful in packaging, adhesives and coatings in electrical sensors and organometalic semiconductors [5-7]. Some other applications have been reported in the field of activators, ion exchangers, catalyst and thermaly stable materials [1-4, 9-10]. Semiconductors are the most important ingredients of modern electronics. The concerted research effort was carried out to aim at developing organic materials that would posses the good electrical properties as the inorganic semiconductors. The terpolymer resins are well known for their behavior as semiconductors though carrier mobility in them usually is very low [10-12]. Kanda et al reported the rubeanato –copper semiconductive polymers and studied their AC and DC conductivity [13]. Dhawan and coworkers reported the conducting polymers predicted to be the futuristic materials for the development of light emitting diodes, antistatic and EMI materials, sensors, opto-electronic devices and rechargeable batteries due to their unique conduction mechanism and greater environmental stability [14]. This article describes the synthesis, structural characterization of a new terpolymer synthesized from salicylic acid, butylenediamine with formaldehyde and its electrical conductivity measurement study.

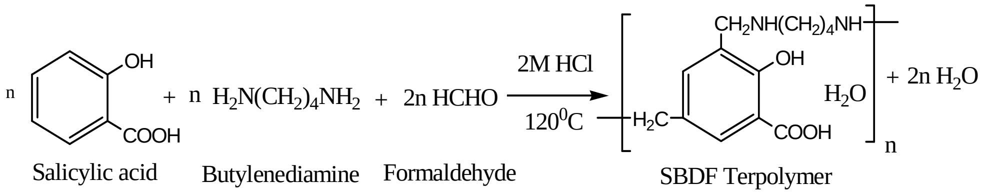
MATERIALS AND METHODS

Chemicals

All Chemicals were AR grade or chemically pure grade. Salicylic Acid, butylenediamine were purchased from Aldrich Chemical Co., USA while Formaldehyde from RANKEM, Ranbaxy, India, DMF and DMSO (HPLC grade) were used.

Synthesis of SBDF Resin:

A mixture of salicylic acid (0.05 mol), butylenediamine (0.05 mol), formaldehyde (0.05 mol) and 2M hydrochloric acid was taken in a round bottom flask fitted with water condenser and heated in an oil bath at 120^0C for 7 hours. The resinous product so obtained was repeatedly washed with cold distilled water dried in air and powdered with the help of agated mortar and pestle. The powder was washed many times with hot water to remove unreacted monomers. The air-dried powder was extracted with diethyl ether and then petroleum ether was used to remove salicylic acid- butylenediamine copolymer and other possible copolymers, which might be present along with SBDF terpolymer. It was further purified by dissolving in 8% sodium hydroxide solution, filtered and reprecipeted by gradual dropwise addition of 1:1 (v/v) hydrochloric acid with constant and rapid stirring to avoid lump formation. The SBDF resin so obtained was filtered, washed several times with hot water and dried. The purity of newly synthesized terpolymer has been tested and confirmed by thin layer chromatography (TLC) technique. (mp=148^0C)[1-4]. Analytical data for $C_{13}H_{18}N_2O_3 \cdot H_2O$ as per numerical calculations and experimental evidence are mentioned below respectively. Theoretically calculated C=58.20%, H=7.46%, N=10.44%. Experimentally found C=58.10%, H=7.51%, N=10.72%.



Synthesis of SBDF Terpolymer resin

Electrical Conductivity

Resin was palatalized and thin layer of colloidal graphite in acetone was applied on both sides of the pellets. The colloidal graphite on either side of pellets functioned as electrode. A typical sample holder was designed for the purpose of resistivity measurement and pellet is mounted on it. For measurement of resistivity at different temperature, a suitable electrical furnace was used. Hewlett-Packard 4192 Impendance Analyser 5Hz-13MHz was used to measure the electrical conductivity of all terpolymers resins. The temperature variations of resin were studied by placing the sample holder along with the pallet in the electric furnace that was then heated slowly. The resistances of the sample pallets were measured by two probes (terminals) method. Resistivity (ρ) was then calculated using the relation:

$$\rho \;\; = R. \text{ x } A/l$$

The DC resistivities were measured from 313 to 423 K. The electrical conductivity (σ) varies exponentially with the absolute temperature according to the well-known relationship:

$$\sigma = \sigma_0 \exp^{-Ea/kT}$$

The relationship has been modified as:

$$\text{Log } \sigma = \log\sigma_0 + \;\; -Ea/2.303kT$$

According to this relation, a plot of Log σ Vs 1/T would be linear with negative slope. From the Slope of the plots, the activation energy was calculated [10-14, 33].

RESULTS AND DISCUSSION

Characterization of Terpolymer

Molecular Weight Determination By Conductometric Titration In Non-Aqueous Medium.
The molecular weight (M_n) of the terpolymer was determined by non-aqueous conductometric titration in DMF against ethanolic KOH by using 50mg of sample. Inspection of a plot (Fig.1) revealed that there were many breaks in the plot. From this plot the first break at 180 miliequivalents and the last break at 2610 miliequivalents were noted. The calculations of (M_n) by this method is based on the following considerations [1-4, 15, 16]: (1) the first break corresponds to neutralization by the more acidic phenolic hydroxy group of all the repeating units; (2) The break in the plot beyond which a continuous increase is observed represents the stage at which phenolic hydroxy group of all the repeating units are neutralized. On the basis of the average degree of polymerization (DP) is given by the following relation.

$$DP = \frac{\text{Total meq of base required for complete neutralization}}{\text{meq of base required for smallest interval}}$$

The average degree of polymerization (DP), which is given by the following relation, is found to be 14.5 and The number average molecular weight (M_n) is 3886 as obtained by multiplying the DP by the formula weight of the repeating unit [1-4, 15, 16].

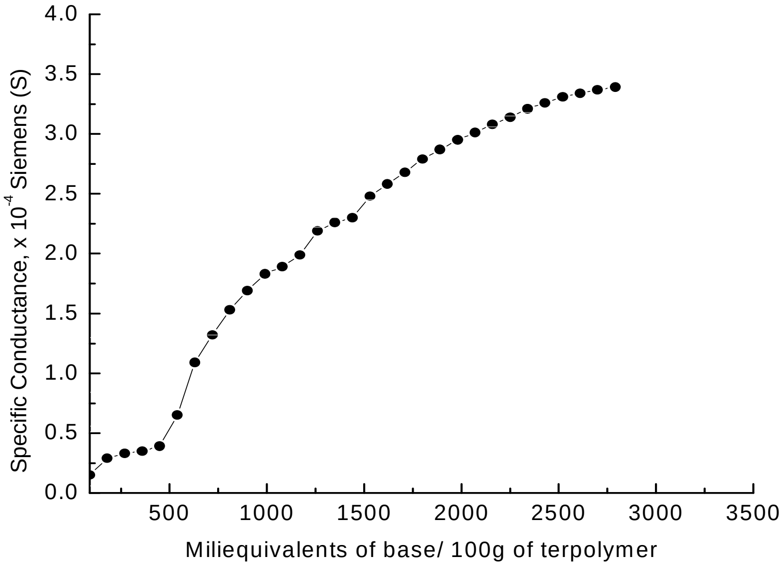


Fig.1.Conductometric titration curve of SBDF resin

Viscosity Measurements

Viscosity measurements of newly synthesized terpolymer resin have been carried out at 303 K in freshly double distilled N, N'-dimethylformamide using Tuan-Fuoss viscometer. The viscosity measurements were carried out at six different concentrations ranging from 0.5% to 3.0% in constant temperature bath. The plot of intrinsic viscosity determination is presented in fig.2. Intrinsic viscosity $[\eta]$ was determined by using Huggins and Kraemers relation [21, 22]:

$$\eta_{sp}/C = [\eta] + k_1 [\eta]^2 C \text{..................Huggins relation}$$

$$\ln \eta_r/C = [\eta] - k_2 [\eta]^2 C \text{.................Kraemer relation.}$$

From the above Huggins and Kraemer relation, it is clear that the plots of η_{sp}/C and $\ln \eta_r/C$ versus C would be linear giving the slopes k_1 and k_2 respectively. Intercept on the axis of viscosity function gave intrinsic viscosity $[\eta]$ value in both the plots. The values of the intrinsic viscosity obtained from both the plots have been found to be in close agreement with each other[3, 15-18] The calculated values of constant k_1 and k_2 satisfy the relation $k_1 + k_2 = 0.5$ favorably which is in good agreement with the trend observed and explained by earlier workers' [3, 15-18].

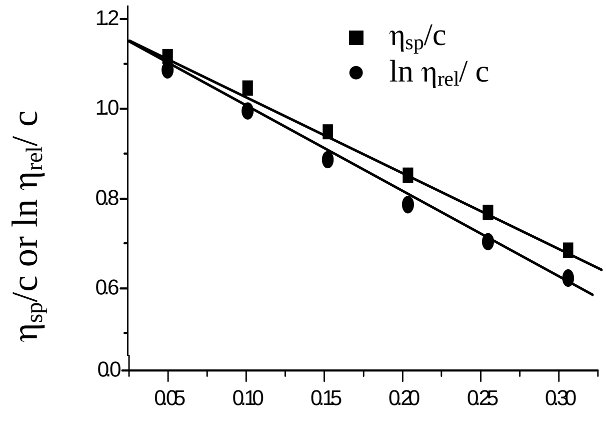


Fig. 2: Viscometric plot of SBDF resin UV-Visible Studies

The electronic spectrum of the resin was recorded in dimethylformamide (DMF) at room temperature with a UV-240 Shimadzu double beam spectrophotometer. The electronic spectrum of the SBDF terpolymer is shown in fig.3. The spectra depicted two characteristic bands in the region of 240-290 nm and 325nm. The band at 240-290 nm indicates the presence of a carbonyl (>C=O) group containing a carbon oxygen double bond in conjugation with an aromatic nucleus and was characteristic of a $\pi \rightarrow \pi^*$ transition while the latter band (less intense) may be due to $n \rightarrow \pi^*$electronic transition. The additional shift of absorption to the longer wavelength region i.e. is bathochromic shift from the basic value (237nm and 320nm, respectively) may be due to conjugation effect whereas phenolic hydroxyl group (auxochrome) is more effective for hyperchromic effect i.e. higher ε_{max} value [1-4, 19].

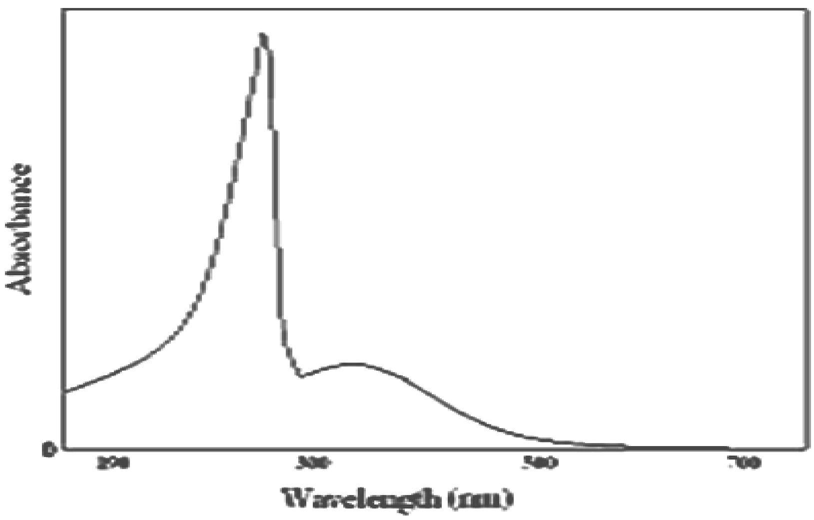


Fig.3: Electronic spectra of SBDF resin Infra Red Studies

Infrared spectra in the region 400-4000cm^{-1} were recorded on a Perkin-Elmer with KBr pellets. The IR spectrum of the newly synthesized salicylic acid butylenediamine formaldehyde terpolymer resin is depicted in fig 4. The assignment of vibrational frequencies is mainly based on the data available in the literature. A broad band appeared at 3237.3 cm^{-1} [1-4,21-23] may be due to the stretching vibrations of phenolic hydroxyl group exhibiting intermolecular hydrogen bonding which exists between -OH group of different polymer chains. The band observed at 3013.7 cm^{-1} may be due to the stretching vibrations of –NH (imide) [1-4, 21-23]. The inflections around 1443.6 cm^{-1}, 1295.4 cm^{-1} and 785.4 cm^{-1} suggest the presence of bending, wagging, rocking vibrations of methylene ($-CH_2-$) bridges in polymeric chains [20,22,24,26]. The medium broad band at 1613.6cm^{-1} may be ascribed to aromatic ring. The broad band at 1660.7 cm^{-1} may be due to the stretching vibrations of >C=O [1-4]. The broad bands at 1483.9 cm^{-1}, 759.3 and 696.2 cm^{-1} are due to –NH- bending, wagging and deformation out of plane vibrations in terpolymer resin respectively [1-4, 21-23]. The band at 1383.4 cm^{-1} may be due to phenolic >C-O stretching modes of vibration [1-4, 20-23]. The presence of band at 893.6 cm^{-1} to 1210.7 cm^{-1} suggests that the aromatic ring is 1, 2, 3, 5-substituted. This fact is further supported by the presence of band at 853.2 cm^{-1} for tetra-substituted benzene ring [1-4, 20-23].

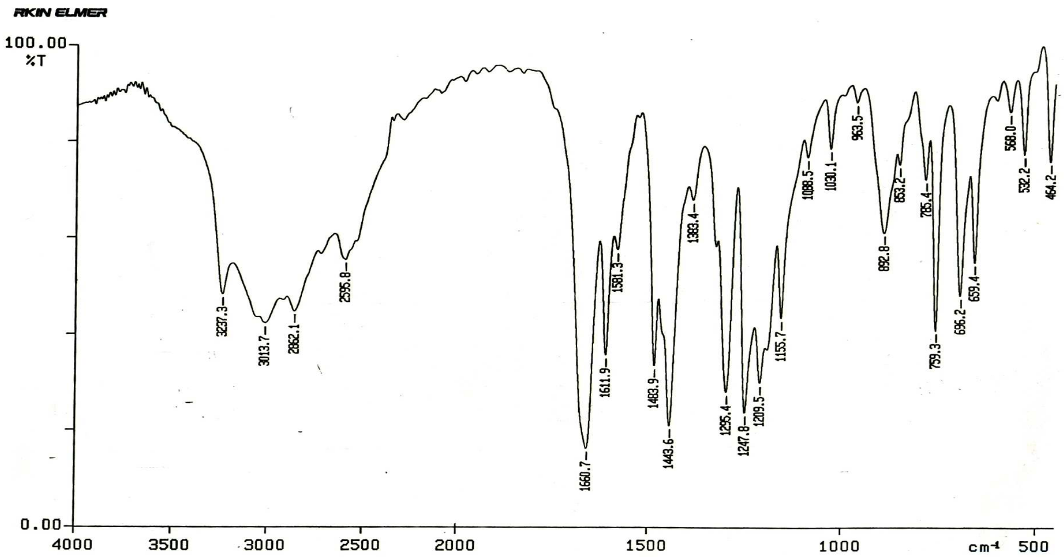


Fig. 4: Infrared spectra of SBDFresin

NMR Studies

The NMR was scanned at 300MHz with duterated dimethylsulfoxide (DMSO) solvent The NMR spectrum of the SBDF terpolymer shown in fig.5 exhibited signals in the region of 7.69 δ (ppm), which may have been due to the proton of the aromatic ring (Ar-H), and the signals in the region 7.81 δ (ppm) may have been due to the phenolic-OH proton in hydrogen bonding (Ar-OH) [1-4, 24, 25]. The signals displayed at 7.41 δ (ppm) may have been due to the carboxylic proton of Ar-COOH. The presence of a broad signal around 6.89 δ (ppm) may have been due to the presence of –NH bridges [1-4, 24-25]. A methylene proton $Ar-CH_2-N$ moiety was inferred by the appearance of a weak singlet signal at 3.89 δ (ppm) [1-4, 24-25].

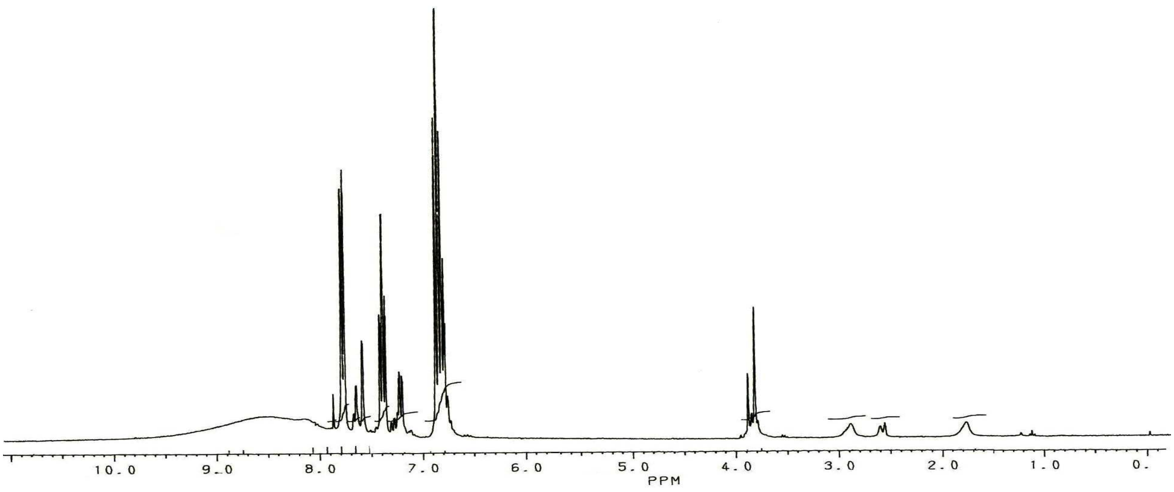


Fig. 5: NMR spectra of SBDF resin

Electrical Conductivity For SBDF Resin

The temperature dependence of the electrical conductivity of the terpolymer is shown in fig.6. The electrical conduction of polymeric material depends upon incalculable parameters such as porosity, pressure, method of preparation, atmosphere etc; activation energy (Ea) is not affected by these parameters and, therefore, it is fairly reproducible [26-29]. The magnitude of activation energy depends on the number of electrons present in semiconductor materials. The more the number of Л – electrons lowers the magnitude of activation energy and vice versa. Generally polymers containing aromatic nuclei in the backbone exhibit lower activation energy than those with aliphatic system.

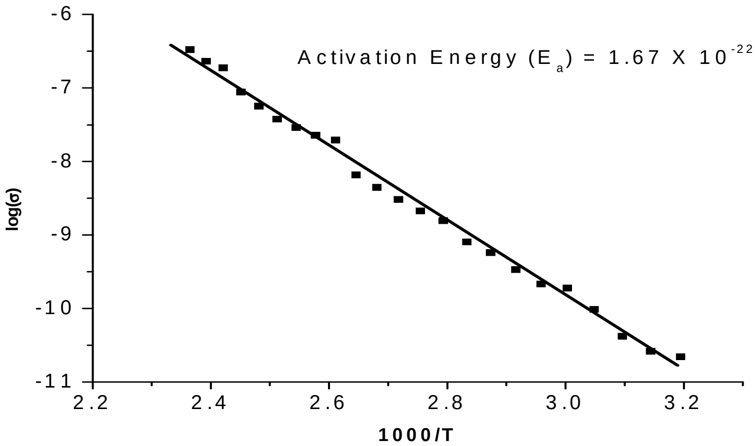


Fig.6: Electrical Conductivity Plot of SBDF Resin

Thus, the low magnitude of activation energy may be due to the presence of large number of Л-electrons in the polymer chain. This is in good agreement with the most probable structure proposed for the newly synthesized resin under investigation [10-14,26-29].The SBDF terpolymer shows the electrical conductivity in the range of 2.20 x10^{-11} to 3.33x10^{-7}Siemen and the plots of log σ versus 1/T is found to be linear in the temperature range under study, which indicate that the Wilson's exponential law $\sigma = \sigma o \exp (\Delta E/kT)$ is obeyed. The energy of activation (Ea) of electrical conduction calculated from the slopes of the plots is found to be in the range of 1.67 x 10^{-22} J/K.

CONCLUSION

A resin SBDF based on condensation reaction of Salicylic acid and butylenediamine with formaldehyde has been prepared by simplest route. SBDF resin is soluble in diethyl ether, DMSO,DMF, aqueous KOH/NaOH (8% solution) and found to be acid resistant in hot condition also.

Electrical conductivity of the resin increases with increase in temperature. Hence, the resin may be ranked as semiconductors. The concerted research effort was carried out to aim at developing organic materials that would possess the good electrical properties as the inorganic semiconductors.

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