IRJSE *Int. Res. J. of Science & Engineering*, 2020; Special Issue A7: 160-164 SJIF Impact Factor 6.68
ISSN: 2322-0015
RESEARCH ARTICLE OPEN ACCESS

Study of electrical conductivity of thermally stable terpolymer resin phenyl salicylate-4,4'diaminodiphenyl ether-formaldehyde.

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Manuscript Details
Available online on http://www.irjse.in
ISSN: 2322-0015

Cite this article as:
Dewase MB, Singru RN and Siddique MIM. Study of electrical conductivity of thermally stable terpolymer resin phenyl salicylate-4,4'diaminodiphenyl ether-formaldehyde, *Int. Res. Journal of Science & Engineering*, February, 2020, Special Issue A7 : 160-164.

ABSTRACT

The resin (PS44'DADPEF) has been synthesised by the condensation of phenyl salicylate-4,4'diaminodiphenyl ether with formaldehyde in presence of 2M hydrochloric acid catalyst with different molar proportion. 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, which have been carried to elucidate the structure of the resin. The electrical conductivity of PS44'DADPEF terpolymers was measured over a wide range of temperature (303-473 K) in their pellet form. From the electrical conductivity of these terpolymers, activation energies of electrical conduction have been evaluated. The electrical conductivity of terpolymers at room temperature increases in the order PS44'DADPEF-I < PS44'DADPEF -II < PS44'DADPEF- III < PS44'DADPEF-IV. The temperature dependence of the electrical conductivity in pellets of all terpolymers is of the same type but higher values of conductivity have been obtained in terpolymers with high molar ratios of phenyl salicylate. On the basis of above studies these terpolymers can be ranked as semiconductors.

Keywords: Electrical conductivity ,Terpolymer , Semiconductor, Activation Energy..

INTRODUCTION

Polymers have long been known as insulating materials and are often used to insulate cables and electrical devices. However, there are also a number of polymers that are used as conductors. But the conductivity of these polymers is low. The terpolymers are well known for their behavior as semiconductors. The terpolymers offer novelty and versatility. The terpolymer resins can be used as high energy material, ion-exchanger, semiconductors, electronic devices ,antioxidants, fire proofing agent, optical storage data, binders, molding materials etc [1,2,3]. Electrically conducting polymer resins are undoubtedly one of the focal points of current interest in solid-state physics, engineering and chemistry. The field of semiconducting polymers has experienced dramatic advances during last decades. Due to the progress toward higher purity, processible semiconducting polymers are now available for use in 'plastic electronic device'. Plastic electronics devices include diodes, photodiodes, photovoltaic cells, sensors, light emitting diodes, lasers, field effect transistors and all polymer integrated circuits. Semiconducting dendrimers are highly branched molecular resembling to snowflakes, has the novel approach to light emitting materials, and can be used them to make red, green and blue light emitting diodes. Michael D. et al.[13] developed a technique for making high quality thin film of semiconducting polymer .The terpolymer resins are well known for their behavior as semiconductors though carrier mobility in them usually is very low [4,7,8,10]. Industrial important semiconducting material has been reported by Kanda et al [6]. The conductivity of p-cresol and melamine with formaldehyde terpolymer resins have been reported over a wide range of temperature by R. N. Singru et al [16], Dhawan and coworkers reported the conducting polymers predicted to be the futuristic materials for the development of light emitting diodes. Qiang Y.et al [15] have studied the electrical conductivity of phenol-formaldehyde resin. Numbers of groups have reported studies on the electrical conductivity and dielectric properties of composites of a variety of conducting polymers [5,9,11,12,14,17]. This article describes the synthesis, structural characterization of a new terpolymer synthesized from phenyl salicylate, 4,4'diaminodiphenyl ether with formaldehyde and its electrical conductivity measurement study.

METHODOLOGY

All chemicals used as of A.R. grade. Doubly distilled water was used in present investigation.

Synthesis of phenyl salicylate-4,4'diaminodiphenyl ether with formaldehyde terpolymer resins;

A mixture of phenyl salicylate, 4,4'diaminodiphenyl ether and formaldehyde in molar ratio 1:1:2 in presence of 2M (200 ml) HCl as a catalyst has been prepared in round bottom flask. The resultant mixture was refluxed over an oil bath for heating at 132ºC ± 2ºC for six hours with occasional shaking to ensure thorough mixing. The resinous sticky yellow solid mass was immediately removed from the oil bath as soon as the reaction period was over and poured it into ice cold water. Yellow coloured solid mass was obtained. Similarly other three terpolymer resins namely, PS44'DADPEF-II,PS4,4'DADPEF-III and PS44'DADPEF-VI were synthesized by varying the molar ratios of the starting materials such as (2:1:3), (3:1:4) and (4:1:5) respectively with little variation of experimental conditions. The reaction is shown as below in fig.1.1.

The detailed analytical data of terpolymer PS44'DADPEF is tabulated in Table 1.1

Electrical measurement;

The DC electrical conductivity measurements of resins in solid state were carried out in a suitable sample holder designed for the purpose, by finding out the resistance of the sample, in the temperature range of 303K to 473K at constant voltage of 50 volts across the pellets prepared from terpolymer 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 Probe method. The resistivity ρ (rho) was calculated using the relation ,

$$\rho = R.\frac{A}{x}$$

Where, R= Resistance of pellet, A= Surface area of pellet, x = Thickness of pellet, and the conductivity (σ) of the resin sample is given by.

$$\sigma = \frac{l}{\rho}$$

The D.C. electrical conductivity (σ) varies with absolute temperature and the temperature dependence of conductivity was fitted to an Arrhenius type equation.

$$\sigma = \sigma_o \, . Exp^{[-\Delta Ea/KT]} \text{..................}(1)$$

Where,

σ = Electrical conductivity at temperature T

σ_o = Electrical conductivity at temperature T∞ i.e. Constant (Pre-exponential conductivity)

Δ Ea = Activation energy of electrical conductance

K = Boltzmann constant = 1.38 x 10^{-23} J/K/molecule

T = Absolute temperature

The logarithmic form of equation (1) is written as

$$\log\sigma = \log\sigma_o + \frac{-\Delta Ea}{2.303K} \cdot \frac{1}{T}$$

It is the equation of straight line. According to this equation, a plot of log σ versus 1/T would be linear i.e. straight line with the slope.

$$Slope = \frac{-\Delta Ea}{2.303K}$$

and the activation energy was estimated by

Δ Ea = -2.303 x K x slope J, (1ev = 1.6x10^{-19}J)

The measured values were plotted as a function of reciprocal of temperature. The conductivity increases with temperature; however, there are deviations at lower temperature. Arrhenius, behavior can be regarded as a good approximation to band theory related to low temperature.

RESULTS AND DISCUSSION

The prepared terpolymers were characterized by using various physical methods viz. elemental analysis, IR, NMR spectra. The number average molecular weight of the terpolymer was determined by non-aqueous conductometric titration in DMF against ethanolic KOH. The SEM photographs exhibits such spherulties which are the aggregate of crystalline present along with the some amorphous regions. The amorphous region shows secondary structural feature such as corrugations and having shallow pits. The spherulites structure of the PS44'DADPEF-I terpolymer resin, indicates the presence of crystalline structure of the polymer. But the corrugation in the surface area with deep pits, shows the amorphous nature of the terpolymers. Thus SEM micrographs of PS44'DADPEF-I terpolymer resin indicates the presence of transition structures between crystalline and amorphous.

The DC resistivity of PS44'DADPEF-I copolymer resin was measured in the temperature range of 303K to 473 K by applying a constant voltage [50 volts] across the pellet. The temperature dependence of the electrical conductivity of terpolymer is plotted in Fig.1.2. The electrical conductivity data has been summarized in Table 1.2.

The evaluation of activation energy data shows that the values of electrical conductivity of PS 44'DADPEF terpolymer resins vary between 6.31 x 10^{-12} to 1.56 x 10^{-8} ohm^{-1} cm^{-1} at 303K and 4.35 x 10^{-7} to 3.96 x 10^{-4} at 403K. The sequence of electrical conductivity is found to be PS 44'DADPEF -I < PS 44'DADPEF -II < PS 44'DADPEF -III < PS 44'DADPEF -IV. This sequence of electrical conductivity shows that as molar ratio of the reacting monomers increase the electrical conductivity is found to be increased. This means that electrical conductivity may depend upon the concentration of the reacting monomers. As the number of aromatic salicylate ring increases in the structure of repeat unit of terpolymer, which increase the π electrons, conjugation and delocalization, in the structure which may increase the conductivity due to decreasing the forbidden energy gap between valance band and conduction band. From activation energy data it shows that, the order of thermal activation energy is just the reverse of electrical conductivity. The sequence of thermal activation energy is PS 44'DADPEF-I > PS 44'DADPEF -II > PS 44'DADPEF -III > PS 44'DADPEF -IV i.e. as molar ratio of reacting monomers increases, the thermal activation energy decreases. This is due to the fact that the magnitude of activation energy depends upon the number of π electrons present in the semiconducting material, more the number of π bonds, lower is the magnitude of activation energy and vice-versa. Dunlop [16] has been reported that the parameters such as level of protonation, porosity, pressure counter ion, method of preparation, atmosphere etc. do not affect the activation energy but its magnitude depends on the number of π electrons present in the semiconducting material therefore it is fairly reproducible. Thus the low magnitude of activation energy may be due to the presence of large number of π electrons. The results are also in good agreement with earlier co-workers.

Table 1.1 Analytical data of terpolymer PS44'DADPEF

Terpolymer	Carbon % Found (calcd.)	Hydrogen % Found (calcd.)	Nitrogen % Found (calcd.)	Molar ratio	Yield %	Melting point K	Empirical formula of repeat unit	Empirical formula weight
PS4,4'DADPEF -I	73.80 (73.18)	5.24 (5.03)	6.38 (6.20)	1:1:2	70	423	$C_{27}H_{23}N_{2}0_{4}$	439
PS4,4'DADPEF -II	73.98 (73.23)	4.96 (4.10)	4.21 (3.95)	2:1:3	80	443	$C_{41}H_{33}N_{2}0_{7}$	665
PS4,4'DADPEF - III	74.07 (73.74)	4.83 (4.13)	3.14 (3.10)	3:1:4	85	448	$C_{55}H_{43}N_{2}0_{10}$	891
PS4,4'DADPEF - IV	74.13 (74.02)	4.75 (4.20)	2.51 (2.48)	4:1:5	80	460	$C_{69}H_{53}N_{2}0_{13}$	1117

Table 1.2. Electrical Conductivity Data of PS 44'DADPEF Terpolymer Resins

Terpolymers	Electrical Conductivity		ΔT	ΔE
	303 K	403 K	(K)	(J)
PS 44'DADPEF -I	6.31×10^{-12}	4.35×10^{-7}	100	1.8774×10^{-19}
PS 44'DADPEF- II	7.94×10^{-11}	3.97×10^{-6}	100	1.8235×10^{-19}
PS 44'DADPEF-III	1.07×10^{-9}	5.18×10^{-5}	100	1.8201×10^{-19}
PS 44'DADPEF-IV	1.56×10^{-8}	3.96×10^{-4}	100	1.7934×10^{-19}

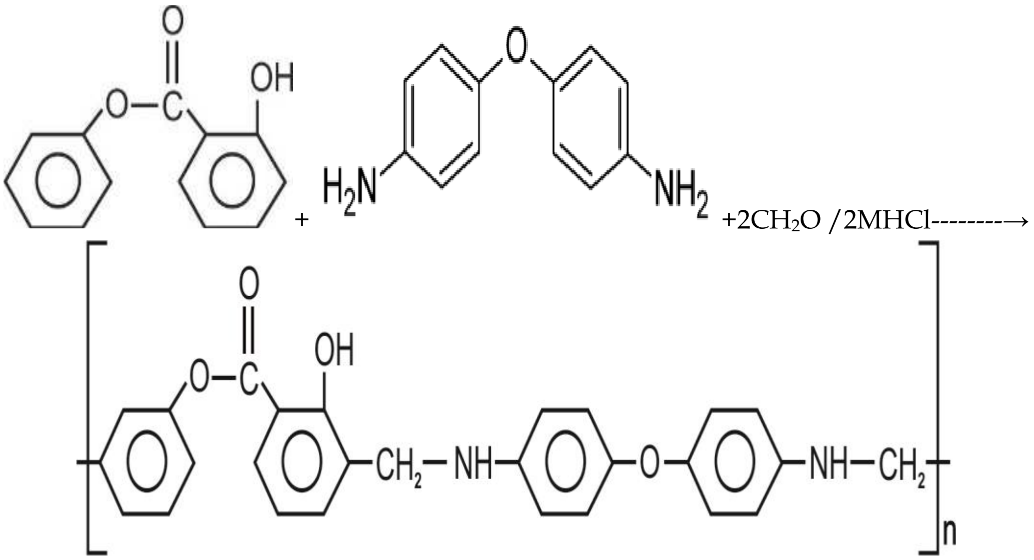

Fig. 1.1 Reaction and Structure of Representative PS44'DADPEF-I Terpolymer Resin

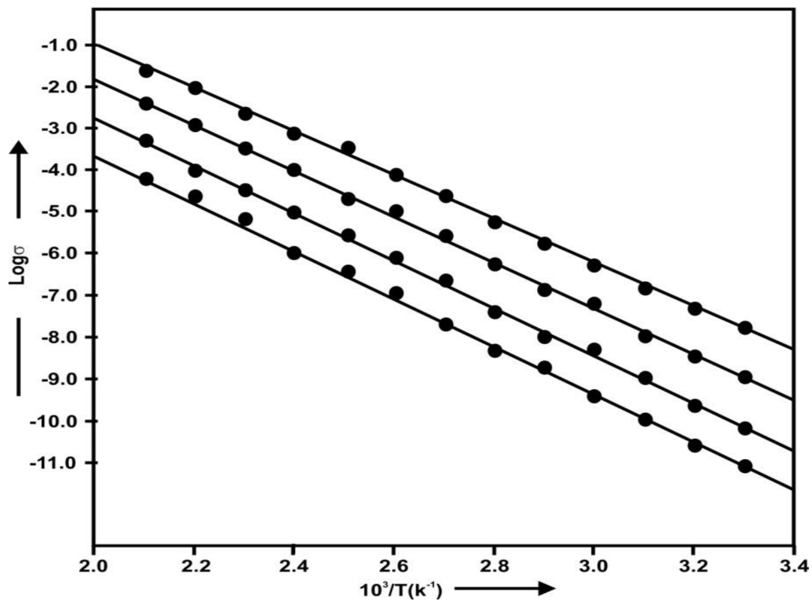

Fig.1.2 Electrical Conductivity Plots of PS 44'DADPEF Terpolymer Resins

CONCLUSION

Newly synthesized terpolymer resins PS 44'DADPEF has been prepared by simplest route and soluble in diethyl ether, DMSO,DMF, aqueous KOH/NaOH (8% solution) and found to be acid resistant in hot condition also. The temperature dependence of electrical conductivity shows that conductivity increases with temperature, however there are deviations at lower temperature due to moisture contained. As the conductivity is found very low even at higher temperature in the range of 10^{-12} to 10^{-2} ohm^{-1} cm^{-1}, it indicate that PS 44'DADPEF terpolymer resins have low charge carrier intramolecular transfer. These indicate the semiconducting nature of the PS 44'DADPEF terpolymer resins. The concerted research effort was carried out to aim at developing organic materials that would possess the good electrical properties as the inorganic semiconductors.

Acknowledgement: The authors are thankful to the Principal and Head, Department of Chemistry, Government Science College , Gadchiroli for providing necessary laboratory facilities.

Conflicts of interest: The authors stated that no conflicts of interest.

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