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Synthesis, Spectral and Electrical Conductance Properties of Terpolymer Resin-IV

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Abstract: *Terpolymer resin ANBAF-IV were made by combining 2-amino 6-nitrobenzothiazole, adipamide with formaldehyde at 124 □ in the presence of an acid catalyst in a 4:1:5 molar ratios. Thin layer Chromatography (TLC) was utilized to test and confirm the purity of a newly synthesized terpolymer. Elemental analysis was used to establish the compositions of terpolymer. Gel permeation chromatography was used to measure the number average molecular weight. To figure out the structure, researchers looked at electronic spectra, infrared and nuclear resonance magnetic spectra. The electrical characteristics of the ANBAF-IV terpolymer were examined over a wide range (314-403K), the activation energy of electrical conduction was calculated and the logσ vs 1000/T plot was shown to be linear over a wide temperature range.*

Keywords: Terpolymer resin, Electrical Conductivity, Condensation, Morphology, Elemental Analysis.

I. Introduction

Terpolymers are unique and versatile, which is why they are so important in the field of material research. Terpolymers have advanced at a breakneck pace, with applications in packaging, adhesives, and coatings in electrical sensors and organometallic semiconductors. Semiconductor materials are the building blocks of modern electronics, which include radios, computers, telephones, and a variety of other gadgets. Transistors, solar cells, various types of diodes, including the light-emitting diode and the silicon controlled rectifier, as well as digital and analogue integrated circuits, are examples of such devices.

Despite the fact that a wide range of conjugated organic molecules are classified as semiconductors, their carrier mobility is typically limited. This is owing to the difficulty in transferring electrons from one molecule to the next.

Phenolic resins have large number of practical application in electronic controls, insulating materials, protective adhesives, aerospace industries etc. because of their high thermal stability, heat and chemical resistance and electrical insulation properties [1, 3]. An effective approach to reduce interparticle gaps by nanofillers for making highly conductive graphite/polymer composites were reported based on the conductive tunneling mechanism [4]. Increased doping reduces the Seebeck coefficient in conventional semiconductors, and there is an optimum doping concentration for thermoelectric cooling or power production applications is an overview of the power factor (electrical conductivity times the square of Seebeck coefficient) testing findings for various electrically conductive polymers [5].

One-dimensional conductive polymers are attractive materials because of their potential in flexible and transparent electronics. Despite years of research, on the macro- and nano-scale, structural disorder represents the major hurdle in achieving high conductivities [6]. The mechanical and electrical properties of the composite with different weight percentages of nanotubes have been investigated. The high aspect ratio and the good conductivity of MWNT have been used to improve the performance of rubbery epoxy matrix nanocomposites [7]. The electrical and thermal conductivity of systems based on epoxy resin (ER) and poly (vinyl chloride) (PVC) filled with metal powders have been studied [8]. Keith J. M. et al [9] have explained the electrical conductivity of carbon / polypropylene composites tested by using single fillers included carbon black, synthetic graphite, and carbon nanotubes. Borker and colleagues [10,11] investigated the optical and electrical properties of conducting copolymers such as poly (aniline-co-n-ethylaniline) and poly (aniline-co-n-ethylaniline) (aniline-co-m-methylaniline). Solubility, spectroscopic technique, and electrical conductivity measurements were used to characterise the products. With increasing N-ethylaniline concentration, copolymer conductivity drops.Epoxy resin nanocomposites suspended with carbon nanofibers (CNFs) have been prepared and studied Rheological behaviors and electrical conductivity of epoxy resin nanocomposites suspended with in-situ stabilized carbon nanofibers [12].

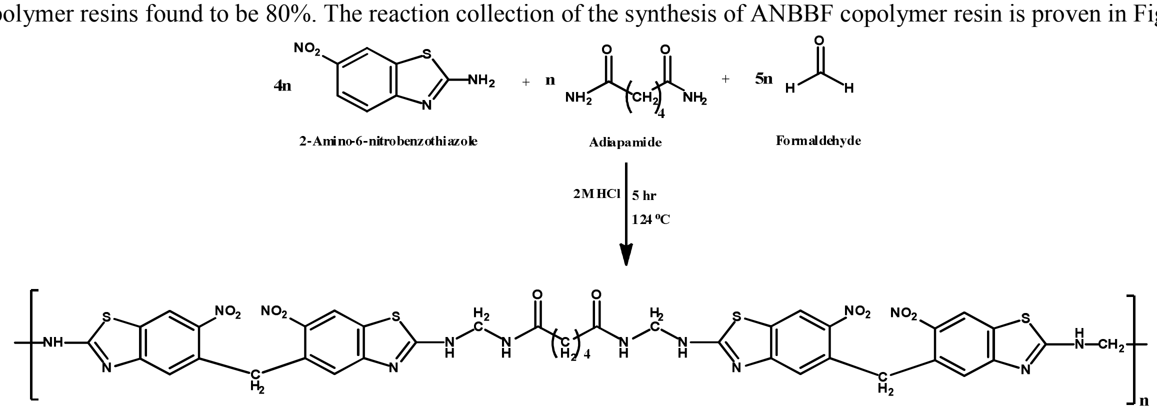
Epoxy resin/graphite nano sheet nanocomposites were fabricated and their electrical and mechanical properties were investigated and concluded that graphite sheets 30–80nm in thickness could be effectively dispersed within the epoxy resin [13]. Borole et al [14] have synthesized the terpolymer thin film poly(aniline-co-o-anisidine-co-o-toluidine) and electrical conductivity of thin films was found to be greatly affected by the nature and size of the anion present in the electrolyte. The electrical properties of 2,4-dihydroxyacetophenone-dithiooxamide-formaldehyde terpolymers were reported by Rahangdale [15]. The current research article deals with synthesis, structural characterization of a new copolymer synthesized from 2-amino 6-nitrobenzothiazole and biuret with formaldehyde and its electrical conductivity measurement study.

II. Experimental Section

The main chemicals utilized in the creation of novel ANBBF copolymer resin from the market, such as 2-amino 6-nitrobenzothiazole, biuret, and formaldehyde, were of chemically pure grade, and the purity was checked and validated by thin layer chromatography wherever necessary.

2.1 Synthesis of ANBBF Copolymer Resin

In a round bottomed flask, 2-amino6-nitrobenzothiazole (0.1mol) was dissolved in 30 mL glacial acetic acid, then biuret (0.1 mol) dissolved in 200 mL hydrochloric acid was slowly added. Dropwise additions of formaldehyde (0.2mol) dissolved in 200 mL HCl were made to the mixture, which was then refluxed for 6 hours at 124 ± 2 °C in an oil tub with constant stirring. The flask was then taken out of the oil bath and set aside to cool. With vigorous shaking, the mixture was placed into crushed ice and left overnight. To eliminate the brown colour, the product was separated, washed several times with warm water and methanol, then filtered and washed again with diethyl ether and petroleum ether. The yields of those copolymer resins found to be 80%. The reaction collection of the synthesis of ANBBF copolymer resin is proven in Fig. 1.



Copolymer (ANBAF)-IV

Figure 1: Reaction Route for the preparation of ANBAF-IV terpolymer

III. Results and Discussion

The resin sample was light brown in color, unsolvable in usually used organic solvents, but was solvable in DMF, DMSO, THF, and concentrated H_2SO_4.

3.1 Physiochemical Analysis

Elemental analysis is a way to determine the amount (typically a weight percent) of an element in a terpolymer. The newly synthesized terpolymer resins have been analysed for elements viz. carbon, hydrogen and nitrogen, at Sophisticated Analytical Instrument Facility (STIC), Kochi.

Table 1: Elemental Analysis of ANBAF-IV terpolymer

Terpolymer resins	% of C observed (Cal.)	% of H observed (Cal.)	% of N observed (Cal.)	% of O observed (Cal.)	%of S Observed (Cal)	Empirical formula of repeated unit	Empirical formula weight
ANBAF-IV	47.36 (47.56)	3.15 (3.25)	19.22 (19.91)	16.01 (16.26)	12.8 (13)	$C_{39}H_{32}O_{10}N_{14}S_4$	984

3.2 Molecular Weight Determination

The number average ($\overline{M}_n$), weight average ($\overline{M}_w$), and size average ($\overline{M}_z$), molecular weights of the terpolymer were measured by GPC (Shimadzu, Japan) using THF as a mobile phase and CLC polystyrene as a stationary phase in the column.

Table 2: Determination of Number Average, Weight Average and Size Average Molecular Weight by GPC of (ANBAF) Terpolymer Resin.

Terpolymer sample	Weight Average Molecular Weight (Mw)	Number Average (Mn) Molecular Weight	Size Average (Mz) Molecular Weight	The Polydispersity Index (Mw/Mn)	The Polydispersity Index (Mz/Mw)
(ANBAF)-IV	12537	12467	12589	1.0056	1.0041

3.3 Spectral Analysis

A. UV-Visible spectrum of ANBBF Copolymer Resin

Fig.2 shows the UV-Visible spectra of ANBAF-IV copolymer resin. To identify the chromophores of matter qualitatively and quantitatively Ultraviolet–visible (UV–Vis) spectroscopy is very useful.UV–Vis spectra are quite vast and normally show handiest a small wide variety of peaks. The peaks are stated as the wavelengths wherein maxima occur. The terpolymer exhibit intense absorption at λmax = 370 nm and a miles weaker absorption at λmax = 221 nm. The band at shorter wavelength corresponds to a π electron transition, whereas the longer wavelength, weaker intensity band corresponds to a transition of the nonbonding electrons at the carbonyl oxygen atom [16] .

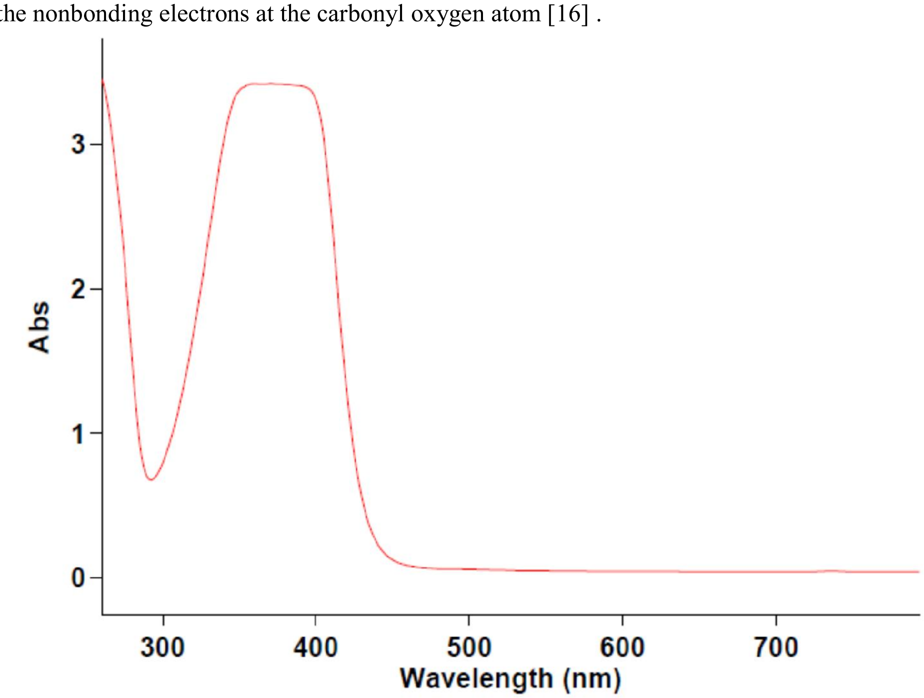


Figure 2: UV-Visible Spectra of ANBAF-IV terpolymer

B. Infra-Red Spectral Analysis

The FTIR spectra of ANBAF-IV terpolymer is presented in Fig. 3. The assignment of vibration frequency is based on the data available in the literature. A broad and strong band which appeared in the region 3534 cm^{-1}may be assigned to the stretching vibration of the NH group. The presence of nitro at 2970 cm^{-1} gives sharp and strong peak. The sharp and weak band at 3091 cm^{-1} may be due to -NH- in adipamide moiety. The strong band at1619 cm^{-1} may be assigned due to stretching vibration of Ar-CO- group. A sharp band appearing at 1449 cm^{-1} describes the presence of >C=C< (aromatic) group. The sharp and strong band observed at 1332 cm^{-1} suggest the presence of -CH_2- methylene bridge in the copolymer chain. The presence of 1, 2, 3, 4 and 5-pentasubstituted aromatic ring is recognized from weak band appearing in the region 1010-748 cm^{-1}[17].

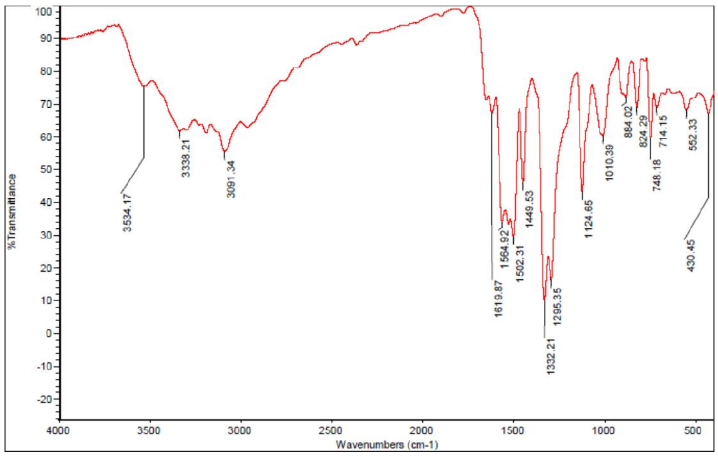


Figure 3: IR Spectra of ANBAF-IV terpolymer

C. ^{1}H NMR Spectra

The ^{1}H-NMR spectra of ANBAF-IV copolymer is depicted in Fig. 4. The spectrum reveals different pattern of peaks, since each of them possesses a set of protons having different proton environment. The weak multiplicity signals (unsymmetrical pattern) in the region δ 7.4 ppm which is due to aromatic proton (Ar-H). A significant singlet signal appearing at δ 5.1 ppm is attributed to tiazole proton. The medium triplet signal observed at δ 7.5 ppm may be due to amido proton Ar-CH_2-NH- of copolymer chain. The proton of methylenic bridge Ar-CH_2- NH- may be recognized from doublets signal which appears in the region δ 4.8 ppm. The presence of quartet peaks in the region δ 2.5 ppm reveals the presence of methylene proton of Ar-CO-CH_2- [18]

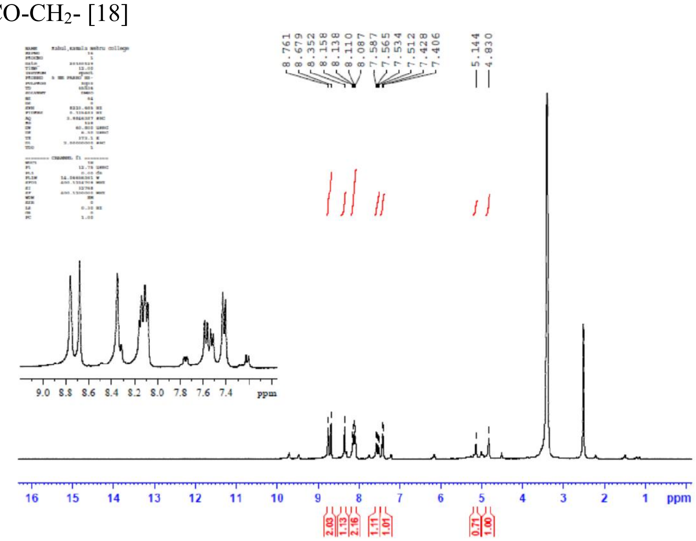


Figure 4: ^{1}H NMR Spectra of ANBAF-IV terpolymer

D. Scanning Electron Microscopy

The surface morphology of ANBAF-IV copolymer resin was studied by scanning electron micrograph at different magnification which is presented in Fig. 5. It gives information about surface topography and defects in the structure. The investigated copolymer appeared to be dark brown in color. At lower magnification it shows spherules in which the crystals are arranged more closely in smaller surface area. It indicates the crystalline nature of resin and this property exhibits low ion exchange capacity for higher hydrated size metal ion. At higher magnification it shows more amorphous character with less close packed surface having deep pits. The amorphous nature of the resin indicates higher ion exchange capacity for metal ion. Thus resin is crystalline as well as amorphous or transition between crystalline and amorphous, showing less or more good ion exchange capacity [19].

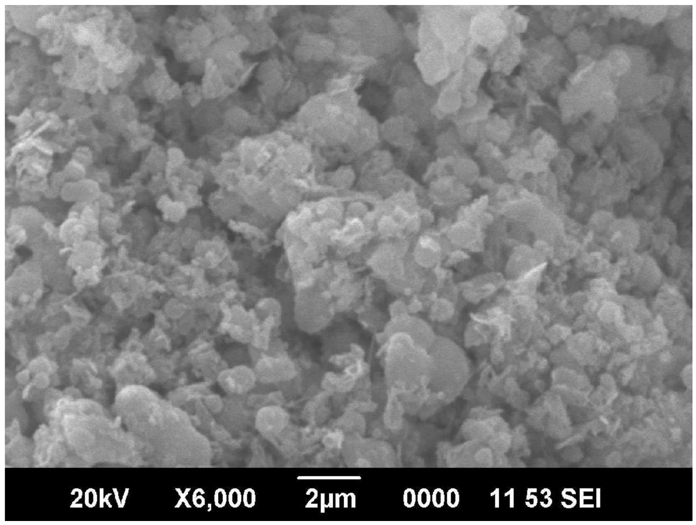


Figure 5: SEM Image of ANBAF-IV terpolymer

E. Electrical Conductivity Measurement of Terpolymer ANBAF-IV

The DC resistivity of a (ANBAF-IV) terpolymer resin was measured in the temperature range of 314 to 429 K by applying a constant voltage (50 volts) across the pellet. The experimental results of electrical conductivity of (ANBAF-IV) terpolymer are incorporated in Table 3 to 4. The temperature dependence of the electrical conductivity of these terpolymer is plotted in Fig.6.1. From the results of electrical conductivity data following conclusions are drawn.

- The electrical conductivity of (ANBAF-IV) terpolymer at room temperature lies in the range of 2.58 x 10-11 to 2 x 10-10 Siemen.
- In the temperature range under consideration, the plots of log σ versus l/T is found to be linear, indicating that Wilson's exponential law $\sigma = \sigma_0 \exp(\Delta E/kT)$ is obeyed.
- When calculated from the slopes plots, the energy of activation (Ea) of electrical conduction is found to be in the range of 8.67 x 10-20 to 11.48 x 10-20 J/K.
- In the temperature range under consideration, the plots of logσ vs l/T are found to be linear, indicating that Wilson's exponential law is valid. Each of these Copolymer resins' electrical conductivity increases as the temperature rises. As a result, these terpolymer resins could be considered semiconductors.
- The electrical conductivity of (ANBAF-IV) terpolymer resin at room temperature varies from of 1.30 x 10-11 to 1.21 x 10-10 Siemen [20].
- The energy of activation is found to decrease in the order: (ANBAF)-I>(ANBAF)-II >(ANBAF)-III>(ANBAF)-IVand electrical conductivity is found to increase in the order: (ANBAF)-I<(ANBAF)-II<(ANBAF)-III<(ANBAF)-IV.

It supports the fact that more the number of π bonds (more the π electrons), lower the magnitude of activation energy and vice-versa.

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Table 3: Estimation of Energy of Activation of Conduction of (ANBAF-IV Terpolymer Resin

Diameter of the pellet =1.433

Surface Area of the pellet (A) = 1.613

Thickness of the pellet (l) =0.189

A/l = 8.534

Temp (K)	1000 /T (k^{-1})	Resistance in Ohm 'R'	Resistivity ρ= RA/l (ohm cm)	Conductivity σ=l/ ρ (ohm cm)$^{-1}$or S	Log σ
314	3.1847	5.50×10^{8}	4.9946×10^{9}	2.0021×10^{-10}	-9.6985
319	3.1347	4.60×10^{8}	4.1773×10^{9}	2.3993×10^{-10}	-9.6199
324	3.0864	3.90×10^{8}	3.5416×10^{9}	2.8235×10^{-10}	-9.5492
329	3.0395	3.20×10^{8}	2.9059×10^{9}	3.4412×10^{-10}	-9.4632
334	2.9940	2.62×10^{8}	2.3792×10^{9}	4.2030×10^{-10}	-9.3764
339	2.9498	2.05×10^{8}	1.8616×10^{9}	5.3717×10^{-10}	-9.2698
344	2.9069	1.65×10^{8}	1.4983×10^{9}	6.6742×10^{-10}	-9.1756
349	2.8653	1.38×10^{8}	1.2531×10^{9}	7.9802×10^{-10}	-9.0979
354	2.8248	9.86×10^{7}	8.9539×10^{8}	1.1168×10^{-9}	-8.9520
359	2.7855	7.92×10^{7}	7.1922×10^{8}	1.3903×10^{-9}	-8.8568
364	2.7472	6.93×10^{7}	6.2932×10^{8}	1.5890×10^{-9}	-8.7988
369	2.7100	6.12×10^{7}	5.5576×10^{8}	1.7993×10^{-9}	-8.7444
374	2.6738	5.09×10^{7}	4.6222×10^{8}	2.1634×10^{-9}	-8.6648
379	2.6385	4.50×10^{7}	4.0864×10^{8}	2.4471×10^{-9}	-8.6113
384	2.6041	3.60×10^{7}	3.2691×10^{8}	3.0589×10^{-9}	-8.5144
389	2.5706	3.20×10^{7}	2.9059×10^{8}	3.4412×10^{-9}	-8.4632
394	2.5380	2.50×10^{7}	2.2702×10^{8}	4.4048×10^{-9}	-8.3560
399	2.5062	2.32×10^{7}	2.1068×10^{8}	4.7465×10^{-9}	-8.3236
404	2.4752	2.00×10^{7}	1.8162×10^{8}	5.5060×10^{-9}	-8.2591
409	2.4450	1.70×10^{7}	1.5437×10^{8}	6.4779×10^{-9}	-8.1885
414	2.4154	1.55×10^{7}	1.4075×10^{8}	7.1047×10^{-9}	-8.1484
419	2.3866	1.30×10^{7}	1.1805×10^{8}	8.4709×10^{-9}	-8.0720
424	2.3584	1.05×10^{7}	9.5351×10^{7}	1.0487×10^{-8}	-7.9793
429	2.3310	9.64×10^{6}	8.7541×10^{7}	1.1423×10^{-8}	-7.9422

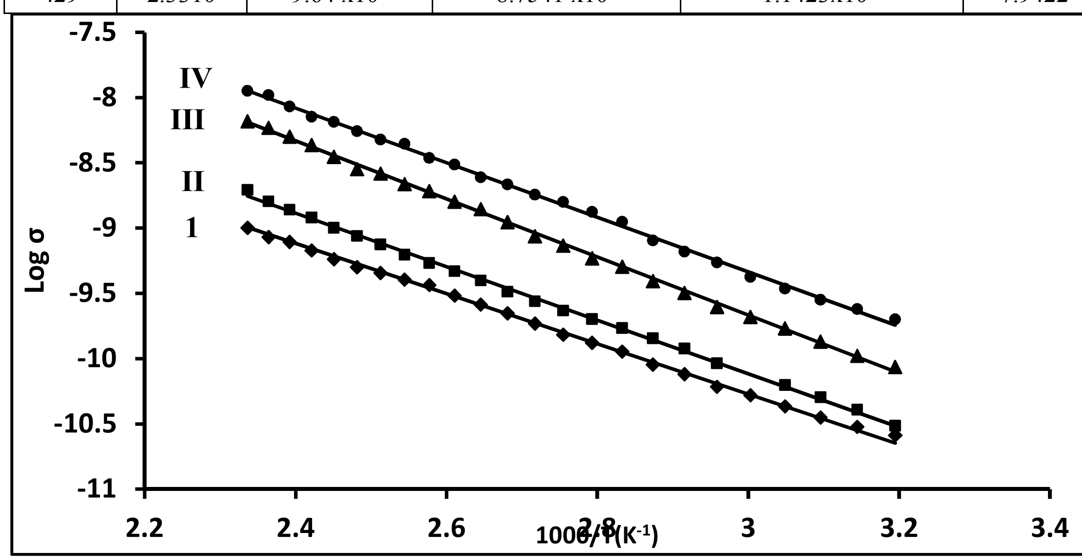

Figure 6: Electrical Conductivity Plot of ANBAF-IV terpolymer

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Table 4: Electrical Conductivity Data of (ANBAF-IV) Terpolymer Resin

Terpolymer	Electrical Conductivity		ΔT (K)	ΔE (J/K)
	314 K	429 K		
(ANBAF)-IV	2.00 x 10^{-10}	1.14 x 10^{-8}	314 – 429	8.67 x 10^{-20}

IV. Conclusion

Terpolymer resin ANBAF-IV were made by combining 2-amino 6-nitrobenzothiazole, adipamide with formaldehyde at 124 ℃ in the presence of an acid catalyst in a 4:1:5 molar ratios. Thin layer Chromatography (TLC) was utilized to test and confirm the purity of a newly synthesized terpolymer. Elemental analysis was used to establish the compositions of terpolymer. Gel permeation chromatography was used to measure the number average molecular weight. To figure out the structure, researchers looked at electronic spectra, infrared and nuclear resonance magnetic spectra. The electrical characteristics of the ANBAF-IV terpolymer were examined over a wide range (314-429K), the activation energy of electrical conduction was calculated and the logσ vs 1000/T plot was shown to be linear over a wide temperature range**.** Electrical conductivity of the resin increases with increase in temperature. Hence, the resin may 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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