

Synthesis, Characterization, and Electrical Properties of Copolymer Derived from 2-Amino 6-nitrobenzothiazole, Dithiooxamide and Formaldehyde

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Abstract: The BDF-II copolymer was synthesized by reacting 2-amino 6-nitrobenzothiazole and dithiooxamide with formaldehyde in the presence of 2 M hydrochloric acid as a catalyst in 2:1:3 molar ratios. UV-visible, FTIR, and proton NMR spectral analysis were used to figure out the structure of the copolymer. The surface features of the copolymer were determined using scanning electron microscopy (SEM). The semiconducting nature of the copolymer was determined through electrical conductivity measurements. The electrical properties of the BDF-II copolymer were measured over a wide temperature range from 313-428K, the activation energy of electrical conduction was calculated, and the plot of $\log \sigma$ vs $1000/T$ was found to be linear over a wide temperature range, classifying it as a semiconductor.

Keywords: Semiconductor, Electrical Conductivity, Copolymer, Spectral Analysis, Synthesis

I. INTRODUCTION

Copolymers are polymers that are generated when two or more different types of monomers are joined. They are recognized for their adaptive usage and have been discovered to be amorphous, crystalline, or resinous. Because of its high thermal stability and electrical conductivity properties, copolymer is now widely used. Copolymers are particularly valuable in applications such as adhesives [1], high thermal resistance and ion-exchanger materials [2], and high dielectric constant for energy storage capacitor [3], coating materials [4], semiconductors [5], catalyst [6], and ion exchange resins [7]. Semiconductor materials are at the guts of recent electronics, including radios, computers, telephones, and a good range of other devices.

Transistors, solar cells, various diodes, including light-emitting diodes, silicon-controlled rectifiers, and digital and analog integrated circuits are examples of such devices. Therefore, in recent years, investigations on copolymer's semiconducting nature have made significant progress. Electrically conducting copolymers are unquestionably a popular issue in solid-state physics and chemistry. Their discovery has resulted in an urgent need for not just new types of materials capable of replacing metals, but also new concepts to explain their high conductivity. In reality, their conductivity and other qualities like thermo conduction, photoconduction, luminescence, and so on are closely related to their physical and chemical composition. In this regard, experiments were conducted to demonstrate a link between chemical structure and semiconducting property characteristics. The behaviour of the copolymers as semiconductors is well understood. Although many conjugated organic compounds are classified as semiconductors, their carrier mobility is often limited. This is owing to the difficulty in jumping electrons from one molecule to another, and hence the carrier mobility in this class of compounds increases with increasing molecular size [8][9].

Niley et.al. reported electrical conductivity of 4-hydroxyacetophenone-ethylenediamine-formaldehyde terpolymer resin [10]. R.H. Gupta and coworkers synthesized 2-hydroxyacetophenone-melamine-formaldehyde copolymer by polycondensation polymerization method and studied the electrical conductivity of synthesized copolymer which acts as industrially useful semiconducting materials [11]. Electrical conductivity of m-cresol, melamine and formaldehyde terpolymer was reported by K. M. Khedkaret al. and observed that terpolymer shows semiconducting nature at different

temperature range[12]. Sulphanilic acid-melamine-formaldehyde terpolymer was prepared by S.S.Ingle and coworkers, as the resin obeyed Wilson's law and hence it acts as semiconducting material[13]. S. S. Rahagdale, and W. B. Gurnule synthesized an industrially useful semiconducting copolymer by condensation polymerization method using 2,2'-dihydroxybiphenyl, biuret, and formaldehyde monomer[14]. The electrical conductance properties of 4-hydroxyacetophenone-catechol-formaldehyde copolymer were studied by S. K. Mahavgade[15].

The current study concentrated on the polycondensation polymerization of 2-amino 6-nitrobenzothiazole-dithiooxamide-formaldehyde (BDF) copolymer using 2M HCl as an acid catalyst. UV-Visible, proton NMR and FTIR methods were used to characterize it, and the molecular weight was calculated using a non-aqueous conductometric titration method. By using scanning electron microscopy the surface morphology of copolymer was studied. The electrical properties of copolymers were investigated to assess their semiconducting nature across a wide temperature range.

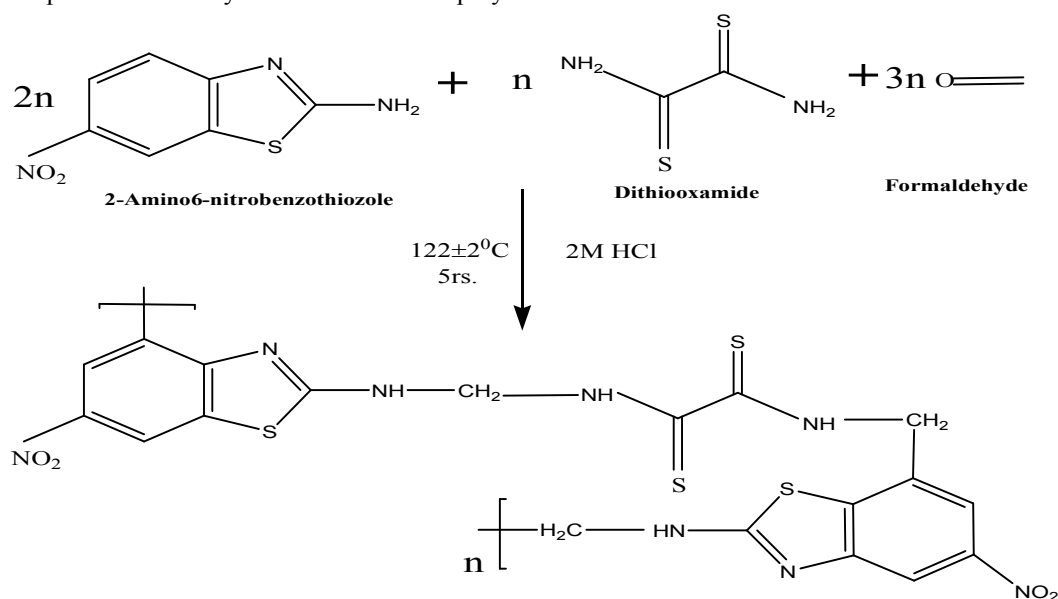
II. MATERIALS AND METHODS

2.1 Materials

Chemically pure and analytical grade chemicals and solvents were used throughout the synthesis. 2-amino-6-nitrobenzothiazole (Sigma Aldrich), Dithiooxamide (Merk India), Formaldehyde (Merk 37%), Dimethyl sulphoxide (99.8%, Fisher Scientific), Dimethyl formamide (Sigma Aldrich) (99 percent GenniChem). All of the experiments were done with double-distilled water.

2.2 Synthesis of BDF-II copolymer:

Copolymer resin (BDF-II) was synthesized by condensing 2-amino 6-nitrobenzothiazole (3.9 g, 0.2 mole), dithiooxamide(1.2g, 0.1 mole), and formaldehyde (11.25mL, 0.3 mole) in 2:1:3 molar ratios in the presence of 2 M HCl (200 mL) as a catalyst at $122\pm 2^{\circ}\text{C}$ in an oil bath for 5 hours. As soon as the reaction period was completed, the pale yellow solid product was taken from the flask. It was cleaned in cold water, dried, and powdered. To eliminate unreacted monomers, the powder was rinsed with cold water many times. It was further refined by dissolving in 8% NaOH and then filtering. The copolymer was then precipitated by drop wise addition of 1:1 (v/v) conc. HCl/water with steady stirring and filtered. The procedure was repeated several times to get the pure copolymer. The resultant polymer sample was rinsed with hot water, air dried, powdered and kept in a vacuum desiccator with silica gel. Scheme 1 shows a schematic representation of synthesis of BDF-II copolymer.



Scheme 1: Schematic representation of the synthesis of BDF-II copolymer

2.3 Characterizations

2.3.1 Physicochemical and Elemental Analysis

Vario EL III (Elementar, Germany) elemental analyzer was used to do the elemental analysis and to find out the percentage of elements present in BDF-II copolymers, such as carbon (C), hydrogen (H), nitrogen (N), and sulphur (S). The average molecular weight was calculated using conductometric titration in DMSO medium with ethanolic KOH as the titrant and 50 mg of sample. A plot of specific conductance vs milliequivalents of KOH required for neutralization of 100 g of polymer was created. The plot contained numerous breaks. The initial and last breaks were identified using this plot. This method's calculation is based on the following considerations. The average molecular weight must be calculated using the following calculation based on the average degree of polymerization.

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

$$\overline{Mn} = \overline{DP} \times \text{Repeat unit weight}$$

2.3.2 Spectral and Surface Analysis

UV-Visible spectra of freshly synthesized copolymer were scanned in the 200–800 nm range using a Shimadzu double beam spectrophotometer UV-1800 at Shivaji Science College in Nagpur. At RUSA Centre for Bio-Actives and Natural Products, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur, the infrared spectra of BDF-II copolymer were recorded in the range of 500–4000 cm^{-1} using a Bruker Alpha –E spectrophotometer. Using a Bruker Avance-II 400 MHz NMR Spectrometer and DMSO-d₆ as the solvent, the Sophisticated Analytical Instrumentation Facility at Punjab University, Chandigarh, scanned the proton nuclear magnetic resonance (¹H-NMR) spectra of the copolymer. The surface morphology of the BDF-II copolymer was investigated using Jeol JSM at various magnifications at SAIF, Karnatak University, Dharwad.

2.3.3 Electrical conductivity

The electrical resistivity of BDF-II copolymer was measured in a suitable sampleholder designed for the purpose, at temperatures ranging from 313 to 428 K, by applying a constant voltage across pellets made from copolymer. The measurements included the following steps.

Pellet Preparation for Resistance Measurements

The dried copolymer was thoroughly ground in an agate pestle and mortar before being pelletized isostatically in a steel die at 5 tones/inch² using a hydraulic press, then applied colloidal graphite thin layer in acetone to both sides of the pellets and dried at room temperature for 6 hours. The applied colloidal graphite layer on either side of the pellet served as an electrode, and by using multimeter, the surface continuity of the pellet was then tested.

Measurement of dimension of the pellet

Using a Traveling Microscope (comparator type), the average diameter and thickness of this pellet were measured. Actual dimensions were calculated as the average of three measurements taken in three different locations.

Sample Holder

Using brass electrodes, a simple spring-loaded sample holder was formed. The resin pellet was placed between two brass electrodes, one of which was spring-loaded and the other resting on the brass platform.

Furnace for Heating the Sample

A small furnace was used to measure resistivity at various temperatures. A rheostat was used to control the current supplied to the furnace, which was measured with an AC ammeter. A thin metal cylinder was inserted into the furnace to ensure uniform temperature. The temperature of the furnace was recorded using an Alumel-chromel thermocouple



connected to a digital multimeter that measured millivolts. For connections, the connection wires of two insulated with porcelain beads electrodes were removed.

Electrical Resistivity Testing

The pellet's resistance was measured using a BPL-India Million Megohmmeter RM 160 MK IIIA. The furnace's connection wires were connected to the instrument's terminals. By keeping the pellet in the sample holder, the corresponding resistance of the pellet was measured directly. The resistivity (ρ) was then calculated using the following relationship.

And the conductivity (σ) of the sample is

$$\rho = R \cdot \frac{A}{l}$$

given by.

$$\sigma = \frac{l}{\rho} = \frac{l}{A \cdot R}$$

According to a well-known relationship, the electrical conductivity (σ) varies exponentially with absolute temperature.

$$\sigma = \sigma_0 \cdot \text{Exp} \left[\frac{-E_a}{KT} \right] \dots\dots\dots(1)$$

Where, σ =Electrical conductivity at temperature T

σ_0 =Electrical conductivity at temperature T ∞ i.e. constant (Pre-exponential conductivity)

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

$$\log \sigma = \log \sigma_0 + \frac{-E_a}{2.303K} \cdot \frac{1}{T}$$

A plot of log σ Vs 1/T would be linear with a negative slope, according to this relationship. The activation energy(Ea) of electrical conduction was calculated using the slopes of the plots.

III. RESULTS AND DISCUSSION

3.1 Physicochemical and elemental analysis

Copolymer	The empirical formula of repeating unit	Empirical formula weight	%C Found (Cal.)	% H Found (Cal.)	% N Found (Cal.)	% S Found (Cal.)
BDF-II	C ₁₉ H ₁₄ N ₈ O ₄ S ₄	546	42.12(41.80)	2.59(2.88)	20.43(19.87)	23.44(22.90)

Table 1: The physicochemical and analytical data of the BDF-II copolymer

It was discovered that the newly synthesized and purified BDF-II copolymer is yellow. The synthesized copolymer was soluble in DMF, DMSO, THF, and conc. H₂SO₄ solvents, but it is insoluble in almost all other inorganic and organic solvents. The copolymer yield was discovered to be 84%. The percentage of carbon, nitrogen, sulphur, and hydrogen in the copolymer was determined using elemental analysis. Table 1 shows the BDF-II copolymers detailed elemental analysis data, which is used to assign the empirical formula and empirical weight. The composition of the copolymer obtained was found to be in good agreement with the calculated values based on elemental analysis data.

The BDF-II copolymer's number average molecular weight (\bar{M}_n) was determined in DMSO medium using a nonaqueous conductometric titration method with standard potassium hydroxide (0.05M) in absolute ethanol as a titrant which was shown in Table 2. A plot of specific conductance versus milliequivalents of ethanolic KOH required to neutralize 100g of each copolymer was created. The number of plot breaks was revealed by a plot. The first break was

at 112 milliequivalents of base, and the last break was at 1064 milliequivalents of base, as shown in Figure 1. By multiplying the average degree of polymerization (\overline{DP}) by the formula weight of the repeating unit, the number average molecular weight (\overline{Mn}) of the copolymer can be calculated. Previous research has shown that determining the number average molecular weight using the non-aqueous conductometric titration method is simple [16][17].

Table 2: Molecular weight determination of BDF-II copolymer

Polymer	1 st phase of neutralization	The final phase of neutralization (Meq/100g sample)	Degree of polymerization (\overline{DP})	Empirical weight (gm)	Number average molecular weight (\overline{Mn})
BDF-II	112	1064	9.5	546	5187

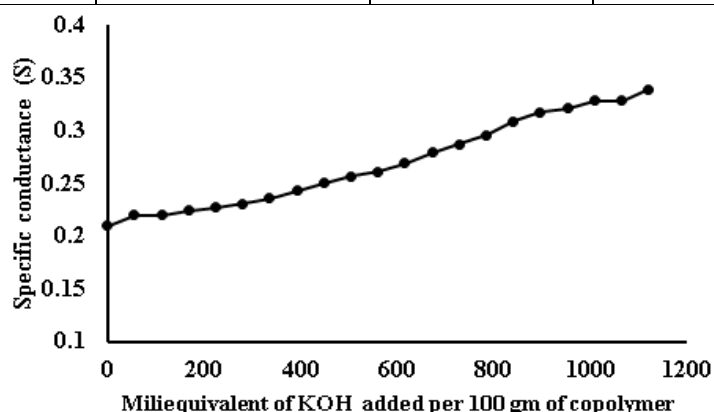


Figure 1: Conductometric titration curve of BDF-II copolymer

3.2 Spectral and Surface Analysis

Figure 2 shows the UV-visible spectrum of the BDF-II copolymer, which was recorded in DMSO solvent at a scanning rate of 100 nm min⁻¹ in the 200-800 nm region. In the UV-visible spectra of the newly synthesized BDF-II copolymer, the presence of chromophore groups like C=S, NO₂, >C=N, C=C in conjugation with the aromatic nucleus, i.e. benzothiazole ring and -NH auxochrome groups, results in two distinct bands with varying intensities at 253 nm and 344 nm. Because of the $\pi \rightarrow \pi^*$ allowed transition, the absorption band at 253 nm is less intense, whereas the absorption band at 344 nm is more intense due to the $n \rightarrow \pi^*$ transition. As a result, the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions confirm the presence of aromatic nuclei and -NH groups, respectively. The bathochromic shift i.e. a shift toward a longer wavelength from the basic values 240 nm and 310 nm could be due to the combined effect of conjugation, while the -NH group (auxochrome) is responsible for the hyperchromic effect (higher ϵ_{max} value) [18][19].

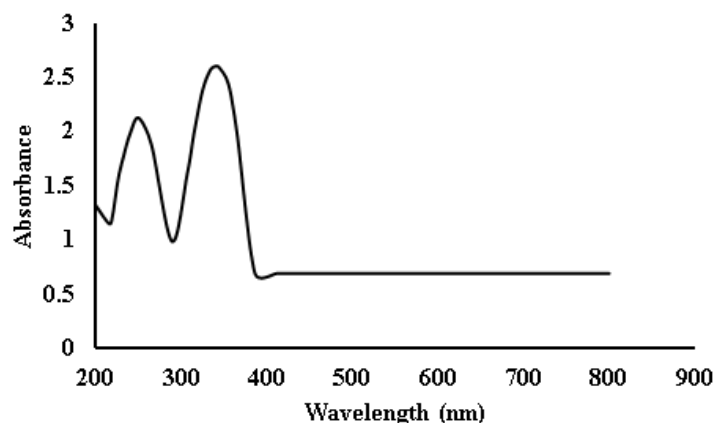


Figure 2: UV-Visible spectra of BDF-II copolymer

The newly synthesized BDF-II copolymer's FTIR spectra are shown in Figure 3. Band frequencies and group assignments for the copolymer are based on previous research[20][21]. The band that formed at 3614cm^{-1} was caused by the $-\text{NH}$ asymmetric and symmetric vibrations. Stretching vibrations of the thio ($\text{C}=\text{S}$) group produce the band at 1511cm^{-1} . Sharp and medium absorption bands in the range of 1195 to 886cm^{-1} result from the 2, 6, 8-trisubstituted benzothiazole copolymer ring. The $-\text{CH}_2$ asymmetrical and symmetrical vibrations in the BDF-II copolymer were confirmed by an absorption band that appeared between 2945cm^{-1} . At 2914cm^{-1} , the aromatic ring's $-\text{CH}$ stretching vibrations reach their peak. The band at 1442cm^{-1} suggests a $-\text{CH}_2$ bending vibration in the copolymer's $\text{N}-\text{CH}_2-\text{N}$ bridge. The presence of the $\text{C}-\text{S}-\text{C}$ group is confirmed by the band at 744cm^{-1} , whereas the $\text{C}=\text{N}$ stretching mode of the thiazole ring is responsible for the band at 1653cm^{-1} . The band obtained at 1493cm^{-1} is due to $-\text{NO}_2$ group of benzothiazole ring.

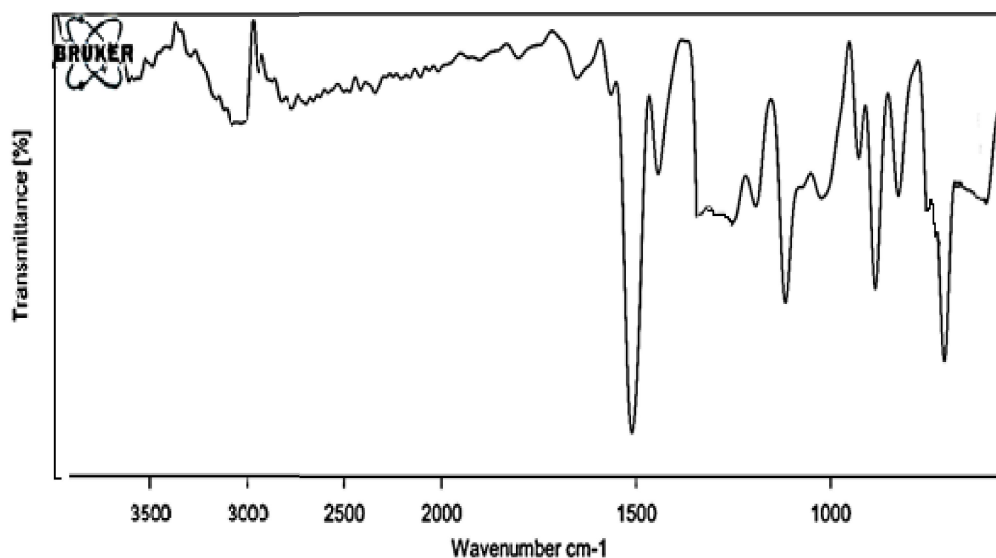


Figure 3: FTIR spectra of BDF-II copolymer

BDF-II copolymer NMR spectra were scanned in $\text{DMSO}-d_6$ solvent, as shown in Figure 4. Literature was used to examine the signals in the proton NMR spectra of the BDF-II copolymer[22][23]. The singlet signal at 8.31ppm is caused by the $-\text{NH}$ proton of the benzothiazole ring. At 4.60ppm , the singlet signal is attributed to the thioimide's $-\text{NH}$ proton. The copolymer's methylene protons are responsible for the 2.54ppm signal. The weak multiple signals that appeared in the range of 7.21 - 8.15ppm are caused by all of the protons in the aromatic ring. The $\text{N}-\text{CH}_2-\text{N}$ bridge proton is responsible for the singlet signal seen at 3.41ppm .

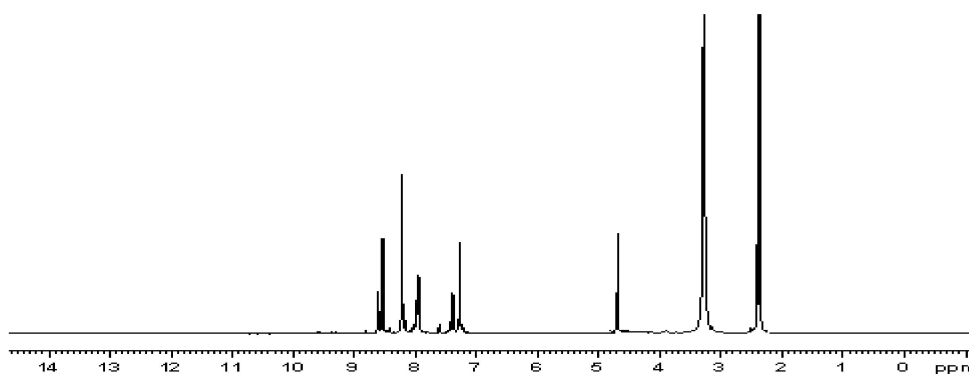


Figure 4: ^1H -NMR spectra of BDF-II copolymer

Surface analysis has proven to be a valuable tool for determining material surface properties. At various magnifications, Figure 5 shows a scanning electron micrograph of the morphology of the newly synthesized BDF-II copolymer. In the copolymer morphology, spherules and fringed models can be seen. Because of their complicated polycrystalline structure, spherules have a smooth surface. This shows that the BDF-II copolymer is crystalline. A fringes model is sometimes used to depict the amorphous-crystalline structure. It also includes a model of amorphous-crystalline structure fringes. The degree of crystalline character is determined by the monomer's acidic nature. The copolymer has a more amorphous appearance, with a closed packed surface with deep pits and reactive active sites buried in the copolymer matrix. Air voids may have caused a few holes and cracks that have been discovered[24][25].

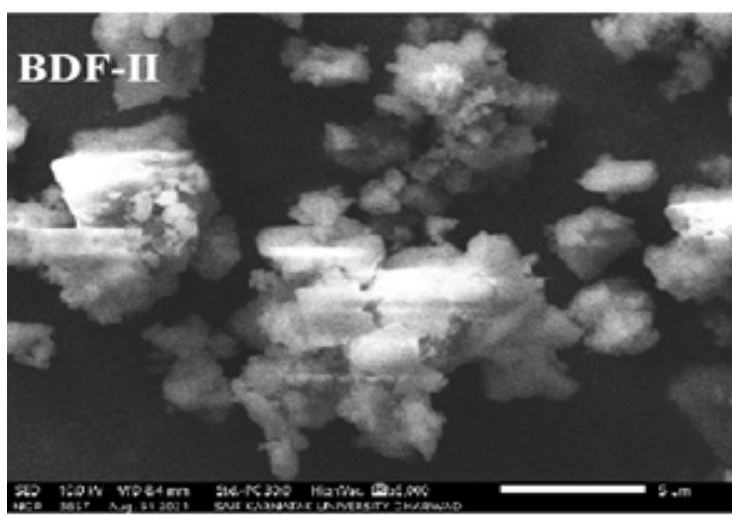


Figure 5: SEM micrograph of BDF-II copolymer

3.3 Electrical Conductivity

By applying a constant voltage (50 volts) across the pellet, the DC resistivity of BDF-II copolymer was measured in the temperature range of 313 to 4280 K. Figure 6 shows the electrical conductivity of copolymer as a function of temperature. The following conclusions are drawn from electrical conductivity data.

1. At room temperature, the electrical conductivity of BDF-II copolymers ranges from 3.74×10^{-9} to 6.45×10^{-6} Siemen.
2. In the temperature range under study, the plots of $\log \sigma$ versus $1/T$ are found to be linear, indicating that Wilson's exponential law $\sigma = \sigma_0 \cdot \text{Exp}[-E_a/KT]$ is obeyed.
3. The energy of activation (E_a) of electrical conduction is 14.04×10^{-23} J/K, as calculated from the slopes of the plots.
4. As the temperature rises, the electrical conductivity of the copolymer increases. As a result, BDF-II copolymer could be classified as a semiconductor.

Uncalculated parameters influence the polymeric sample's resistance[26]. These parameters, such as porosity, pressure, method of preparation, and atmosphere, do not affect the activation energy, making it fairly reproducible[27]. The number of Π - electrons present in the semiconducting material determines the magnitude of the activation energy. The magnitude of energy of activation (E_a) decreases as the number of Π - bonds increases. Aromatic nuclei in the backbone of polymers have a lower activation energy than aliphatic polymers. As a result, the presence of a large number of Π - electrons could explain the low activation energy magnitude.

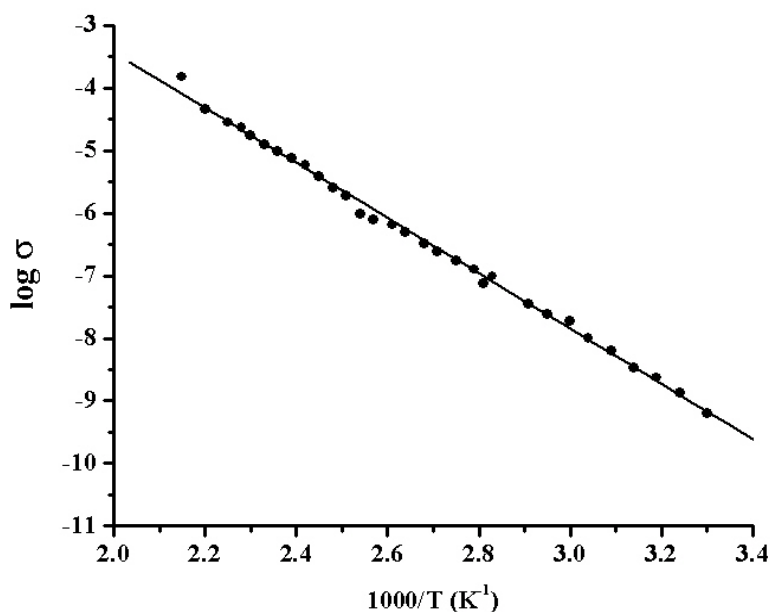


Figure: 6 Electrical conductivity plot of BDF-II copolymer

IV. CONCLUSION

The BDF-II copolymer was made by polymerizing 2-amino 6-nitrobenzothiazole and dithioamide with formaldehyde in the presence of an acid catalyst using polycondensation polymerization in 2:1:3 molar ratios. Elemental analysis, UV-Visible, FT-IR, ¹H-NMR spectral analyses, and physicochemical analysis were used to determine the copolymer's proposed structure. Scanning electron microscopy confirmed the semicrystalline nature of the copolymer. Electrical conductivity of BDF-II copolymer at room temperature ranges between 4.53×10^{-10} to 8.12×10^{-7} Siemen, according to results of copolymer electrical conductivity tests. In the temperature range under investigation, the plots of $\log \sigma$ vs $1000/T$ were found to be linear when the equation $\sigma = \sigma_0 \cdot \text{Exp}[-E_a/KT]$ is followed. As the temperature rises, the electrical conductivity of each resin rises. As a result, these copolymers have the potential to be classified as semiconductors. The goal of the coordinated research effort was to develop organic materials with similar electrical properties to inorganic semiconductors. The resistance of the polymeric material is determined by incalculable factors such as porosity, pressure, preparation methods, and atmosphere, but these factors do not effect on the activation energy, which is fairly reproducible.

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