



PHOTOLUMINESCENCE STUDY OF 2-AMINO 6-NITROBENZOTHIOZOL-DITHIOOXAMIDE-FORMALDEHYDE COPOLYMER

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Abstract-

The BDF-III copolymer was synthesized by condensation polymerization method using 2-amino 6-nitrobenzothiozol, and dithiooxamide with formaldehyde in 3:1:5 molar ratios. The BDF-III copolymer has been characterized by various physicochemical methods like UV-visible, ¹H-NMR and FTIR techniques. The molecular weight and elemental composition of BDF-III copolymer was determined by nonaqueous conductometric titration method, and the elemental analysis method respectively. The surface characteristics of the copolymer were examined using SEM. The RF-501 (PC) S CE (LVD) MODEL PL spectrometer was used to evaluate the photoluminescence properties of newly synthesized copolymer. With significant input from current researchers in the field, the overall purpose of this development is to produce new polymeric material and analyze their photo luminescent properties.

Keywords: Copolymer, polymerization, titration, elemental analysis, photoluminescence.

Introduction

Nowadays, scientists have been interested to synthesized copolymers with highly conjugated chains, as they represent recent advances in polymer chemistry in recent years. Copolymers are unique and versatile, and therefore are so important in the field of material research. Since the conjugated polymer research has received a lot of attention in discovery of conjugated polymer electroluminescence in a variety of

applications, including electroluminescence, photovoltaics, and optical sensors [1][2][3]. Electroluminescence has found to be a particularly interesting application in the polymeric LEDs comprised of semiconducting polymer [4][5]. The most recent research in fluorescent polymers has focused on the arrangement and photoluminescence of fluorescent polymers, as well as the development of new engineering methodologies for the design and aggregation of fluorescent materials. Polymerization of starting monomers, using fluorescent mixes as initiators, fluorescent mixes as chain move specialists' material holding between fluorescent gathers and copolymers, and polymerization of non-fluorescent monomers can be used to make organic polymers that show fluorescence [6].

Photoluminescence is the emission of light that persists after the excitation agent has been withdrawn, as well as the fact that the colour of a material's afterglow is unrelated to the colour of the exciting light and that the process is distinct from scattering. Organic chemicals that do not generate hazardous radiation are replacing previously used photo luminescent materials. Because conjugated polymers have the potential to be used as emissive materials in light emitting diodes [7], [8], luminophores in optical devices [9], organic field-effect transistors (OFET) [10], solar cells [11] sensors [12], bio-imaging [13], and other applications, their luminescence properties are of great interest.

Photoluminescence spectroscopy is a useful method for categorizing and detecting structures, as well as analyzing optical

properties of electronic, semi-insulated, and semiconductor systems. Photoluminescence is the phenomenon in which emission of light radiation by a substance takes place that has absorbed light energy and the external energy is supplied in the form of light energy in this process. The electrons of a material absorb light of an appropriate wavelength and are stimulated, promoting them to higher energy levels, to return to the ground state, the electrons of this excited molecule or substance will emit light energy. The band gap, or the energy difference between the ground and excited electrons, is the primary factor that determines the wavelength of light required to cause photoluminescence. The electron energies in the resultant molecular orbitals are frequently higher than in the (σ) orbitals, as a result, the energy gap between the highest occupied molecular (π -bonding) orbital (HOMO) and the lowest unoccupied (π^* antibonding) orbital (LUMO) is small, resulting in semiconductor materials[14][15]. Photoluminescence with low energy input is possible due to a small band gap (1.3 - 3 eV). The p-orbital is delocalized along the length of the chain in organic π -conjugated polymers. π -conjugated semiconducting compounds make up the vast majority of organic photoluminescent materials and these are molecules with single and double or single and triple bonds that alternate.

The amorphous polyacrylamide copolymer TPE-SP-PAM using tetraphenylethylene and spiropyran as monomers was synthesized by F. Gu and colleagues, resulting in a new exploration in the development of stimuli-responsive polymeric materials with multicolor emissions that combines photochromism and white-light emission[16]. G. Vidya and et. al developed a PPV block copolymer for blue-light emitting diodes using the Horner-Emmons condensation polymerization process[17]. Abhishek P. Kulkarni et al. synthesized five new conjugated terpolymers containing 9, 9-dihexylfluorene, 10-hexylphenothiazine (HPT) donor, and 9-fluorenone (FLO) acceptor by Suzuki copolymerization and used them to study the effects of competing energy and intramolecular charge transfer processes on the photoluminescence (PL) and electroluminescence[18]. The luminescence characteristics of metal complexes produced

from 8-hydroxy quinoline were also reported by D. Singh, V. Nishal, and their colleagues[19]. C. Kohad and colleagues also explored the photoluminescence of polymeric metal complexes synthesized using 8-hydroxyquinoline 5-sulphonic acid[20]. S. S. Rahangdaleet. al. studied photoluminescence properties of copolymer derived from 2,2'-dihydroxybiphenyl, and propylenediamine[21]. Our main focus in this paper is on the photoluminescence analysis of copolymer derived from 2-amino 6-nitrobenzothiazole, and dithiooxamide with formaldehyde in 3:1:5 molar ratios by polycondensation polymerization. A non-aqueous conductometric titration method was used to calculate the molecular weight, and the surface morphology of a copolymer was investigated using scanning electron microscopy. In the result and discussion section, the UV-Visible, proton NMR, FTIR and photoluminescence spectra were discussed.

2. Materials and Methods

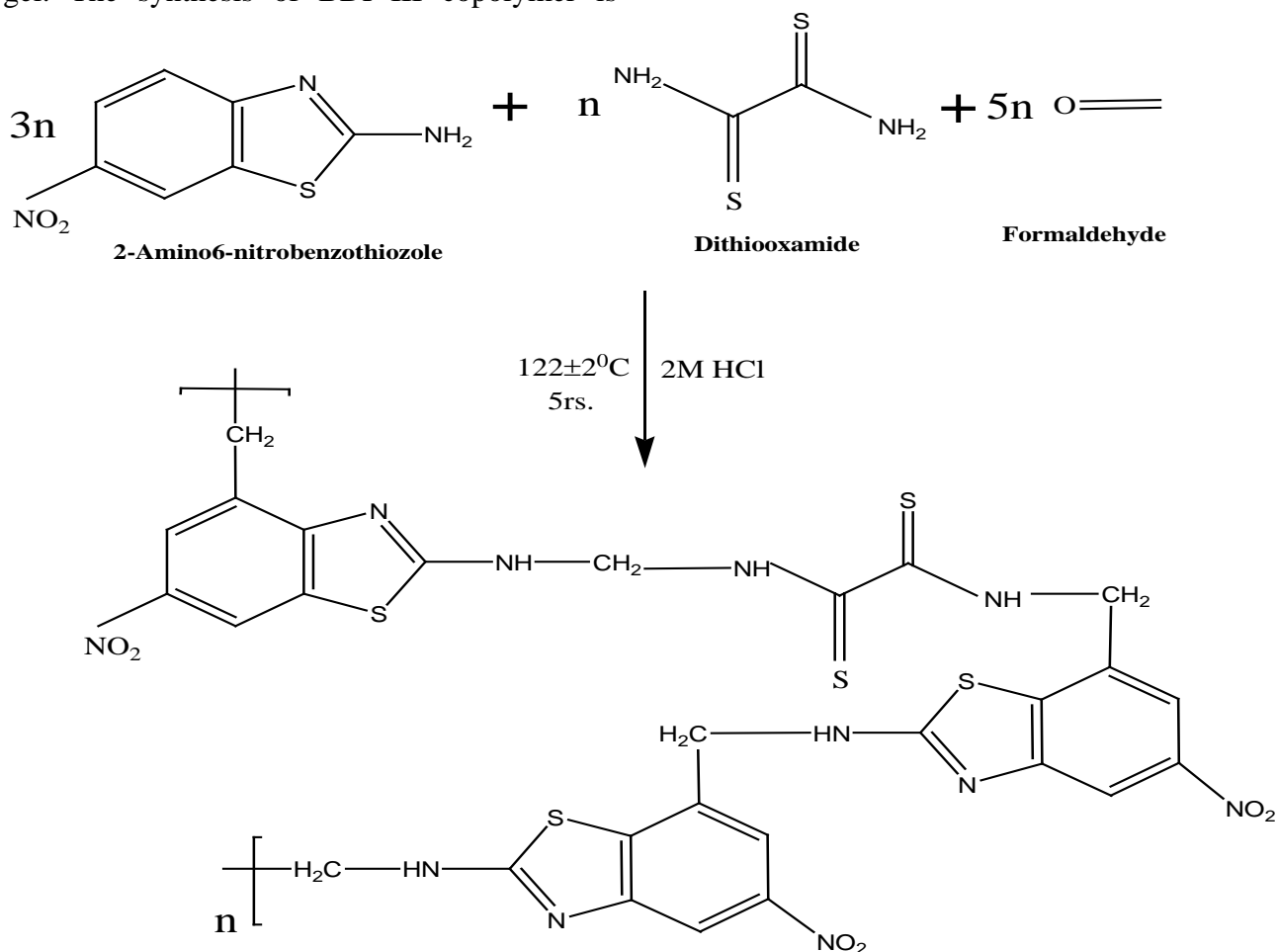
2.1 Materials

Analytical grade and chemically pure chemicals were used for 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).

2.2 Synthesis of BDF-III copolymer:

For the synthesis of BDF-III copolymer, 2-amino 6-nitrobenzothiazole (3.9 g, 0.3 mole), dithiooxamide (1.2 g, 0.1 mole), and formaldehyde (11.25 mL, 0.5 mole) were condensed in 3:1:5 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. The pale yellow solid product was removed from the flask as soon as the reaction period was completed. It was cleaned, dried, and powdered in cold water. The powder was rinsed many times with cold water to remove unreacted monomers. It was purified further by dissolving it in 8% NaOH and then filtering it. The copolymer was then precipitated by adding 1:1 (v/v) conc. HCl/water drop by drop with constant stirring and filtration. To obtain the pure copolymer, the procedure was repeated multiple times. The polymer sample was then rinsed in hot water, air dried, powdered,

and stored in a vacuum desiccator with silica gel. The synthesis of BDF-III copolymer is depicted schematically in Scheme 1.



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

2.3 Characterizations

2.3.1 Physicochemical and elemental analysis

The elemental analyzer Vario EL III (Elementar, Germany) was used to conduct the analysis and determine the percentage of elements present in BDF-III copolymers, such as carbon (C), hydrogen (H), nitrogen (N), and sulphur (S). Conductometric titration in DMSO medium with ethanolic KOH as the titrant and

50 mg of copolymer yielded the average molecular weight. A graph was made of specific conductance vs. milliequivalents of KOH required to neutralize 100 g of copolymer. There were frequent breaks in the plot. This plot was used to find the first and last breaks. Based on the average degree of polymerization, the average molecular weight must be computed using the formula below.

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

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

2.3.2 Spectral and surface analysis

A Shimadzu twin beam spectrophotometer UV-1800 was used at Shivaji Science College in Nagpur to scan the UV-Visible spectra of newly synthesized copolymer in the 200–800 nm range. The infrared spectra of BDF-III

copolymer were recorded in the range of 500–4000 cm^{-1} using a Bruker Alpha –E spectrophotometer at RUSA Centre for Bio-Actives and Natural Products, Rashtrasant Tukadoji Maharaj Nagpur University in Nagpur. Sophisticated Analytical

Instrumentation Facility at Punjab University, Chandigarh, scanned the proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra of the copolymer using a BrukerAvance-II 400 MHz NMR Spectrometer with DMSO-d₆ as the solvent. At SAIF, Karnatak University, Dharwad, the surface morphology of the BDF-II copolymer was studied at various magnifications using Jeol JSM.The RF-501 (PC) S CE (LVD)LS55 Shimadzu Model was used to record the photoluminescence properties of copolymer.

The newly synthesized and purified BDF-III copolymer has been discovered to be yellow. The copolymer was soluble in DMF, DMSO, THF, and conc. H_2SO_4 , but insoluble in almost all other inorganic and organic solvents. It was observed that the copolymer yield was 81%. Using elemental analysis, the percentages of carbon, nitrogen, sulphur, and hydrogen in the copolymer were determined. Table 1 displays the comprehensive elemental analysis data for BDF-III copolymers, which is employed to determine the empirical formula and empirical weight. The resulting copolymer's composition was found to be quite close to the calculated values based on elemental analysis results.

3. Results and discussion

3.1 Physicochemical and elemental analysis

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

Copolymer	The empirical formula of repeating unit	Empirical formula weight	%C Found (Cal.)	% H Found (Cal.)	% N Found (Cal.)	% S Found (Cal.)
BDF-III	$\text{C}_{28}\text{H}_{21}\text{N}_{11}\text{O}_6\text{S}_5$	735	45.10(44.60)	3.15(2.97)	20.11(19.73)	11.87(12.29)

In DMSO medium, the number average molecular weight (\overline{M}_n) of the BDF-III copolymer was calculated using a nonaqueous conductometric titration method with standard potassium hydroxide (0.05M) in absolute ethanol as a titrant (Table 2). The specific conductance of each copolymer was plotted against the milliequivalents of ethanolic KOH required to neutralize 100g of each copolymer. A graph displayed the number of breaks in the plot. Figure 1 shows the first and

last breaks at 112 and 1064 milliequivalents of base, respectively. The average degree of polymerization (\overline{DP}) of the copolymer can be computed by multiplying the number average molecular weight (\overline{M}_n) with the formula weight of the repeating unit. The number average molecular weight can be easily determined using the non-aqueous conductometric titration method, according to previous research[22][23].

Table 2: Molecular weight determination of BDF-III 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{M}_n)
BDF-III	112	1064	9.5	546	5187

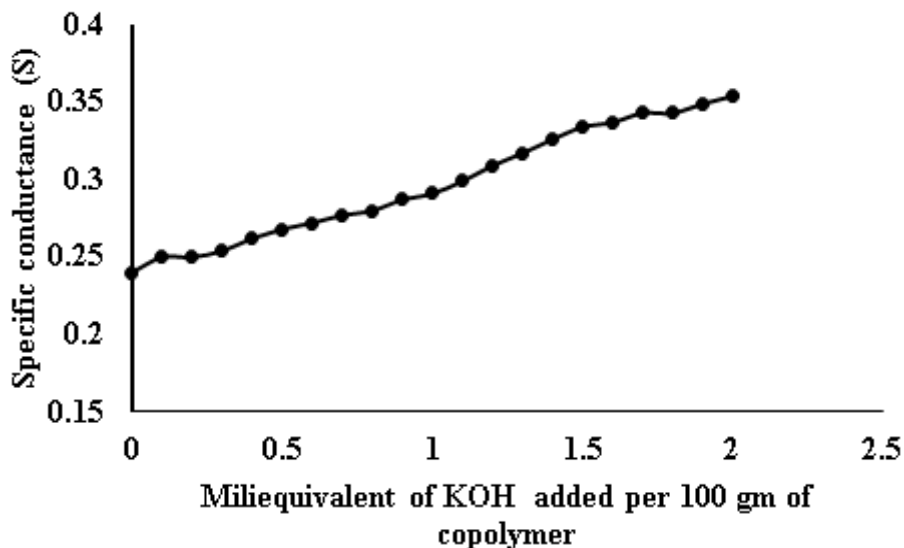


Figure 1: Conductometric titration curve of BDF-III copolymer

3.2 Spectral and surface analysis

The UV-visible spectrum of the BDF-III copolymer was recorded in DMSO solvent at a scanning rate of 100 nm min^{-1} in the 200-800nm range, as shown in Figure 2. The presence of chromophore groups in conjugation with the aromatic nucleus, such as C=S, NO_2 , $>\text{C}=\text{N}$, and C=C., i.e. benzothiazole ring and -NH auxochrome groups, results in two different bands with varied intensities at 260nm and 350nm in the UV-visible spectra of the newly synthesized BDF-III copolymer. The absorption band at 260nm is less intense because to the $\pi \rightarrow$

π^* allowed transition, whereas the absorption band at 350nm is more intense due to the $n \rightarrow \pi^*$ transition. As a result, the presence of aromatic nuclei and -NH groups is confirmed by the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. The bathochromic shift, or shift toward a longer wavelength from the basic values of 240 nm and 310 nm, could be owing to the combined impact of conjugation, whilst the hyperchromic effect (higher max value) is caused by the -NH group (auxochrome)[24][25].

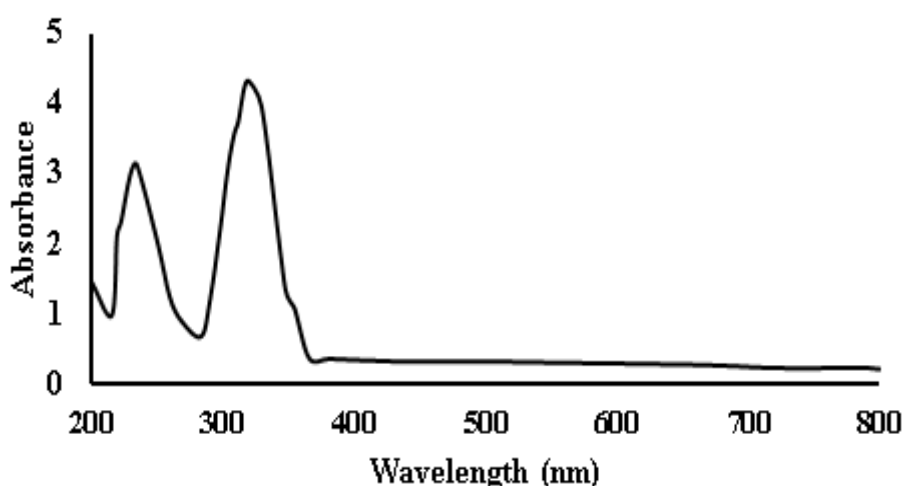


Figure 2: UV-Visible spectra of BDF-III copolymer

Figure 3 shows the FTIR spectra of the newly produced BDF-III copolymer. The copolymer's band frequencies and group assignments are based on earlier studies[26][27].The -NH asymmetric and symmetric vibrations caused the band to

develop at 3614 cm^{-1} . The band at 1513 cm^{-1} is produced by stretching vibrations of the thio (C=S) group. The 2, 6, 8-trisubstituted benzothiazole copolymer ring produces sharp and mild absorption bands in the range of 1195 to 885 cm^{-1} . An absorption

band that developed between 2947cm^{-1} corroborated the $-\text{CH}_2$ asymmetrical and symmetrical vibrations in the BDF-III copolymer. The aromatic ring's $-\text{CH}$ stretching vibrations reach their maximum at 2917cm^{-1} . A $-\text{CH}_2$ bending vibration in the copolymer's $\text{N}-\text{CH}_2-\text{N}$ bridge is

suggested by the band at 1443cm^{-1} . The band at 747cm^{-1} confirms the presence of the $\text{C}-\text{S}-\text{C}$ group, whilst the band at 1654cm^{-1} is due to the thiazole ring's $\text{C}=\text{N}$ stretching mode. The $-\text{NO}_2$ group of the benzothiazolering is responsible for the 1495cm^{-1} band.

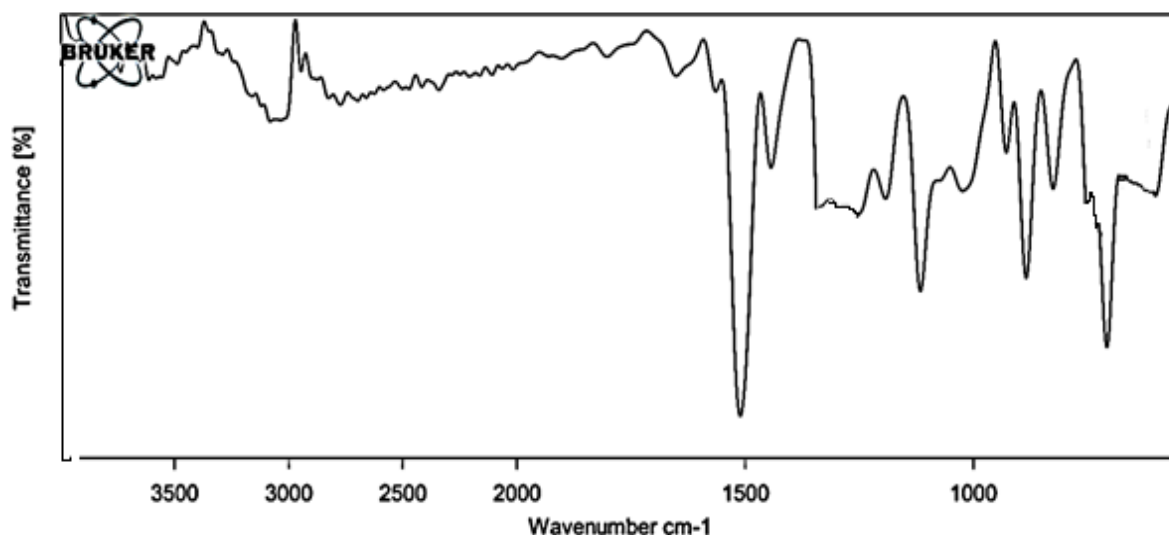


Figure 3: FTIR spectra of BDF-III copolymer

NMR spectra of BDF-III copolymer were scanned in $\text{DMSO}-d_6$ solvent, as shown in Figure 4. The signals in the proton NMR spectra of the BDF-III copolymer were investigated using literature [28][29]. The $-\text{NH}$ proton of the benzothiazole ring is responsible for the singlet signal at 8.32 ppm . The thioimide's $-\text{NH}$ proton is responsible for the

singlet signal at 4.62 ppm . The 2.55 ppm signal is caused by the methylene protons in the copolymer. All of the protons in the aromatic ring are responsible for the faint multiple signals that showed in the range of $7.20-8.16\text{ ppm}$. The singlet signal at 3.43 ppm is caused by the proton of the $\text{N}-\text{CH}_2-\text{N}$ bridge.

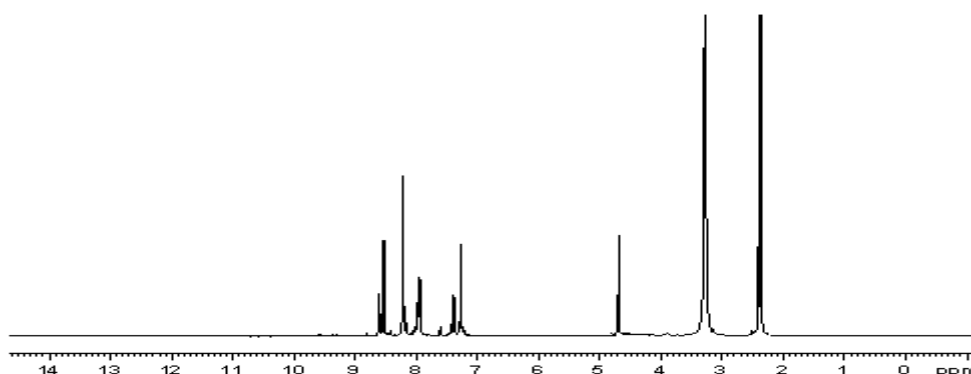


Figure 4: ^1H -NMR spectra of BDF-III copolymer

For determining material surface qualities, surface analysis has shown to be a useful method. Figure 5 shows a scanning electron micrograph of the newly produced BDF-III copolymer at various magnifications. Spherules and fringed models can be detected in the

copolymer morphology. Spherules have a smooth surface due to their complex polycrystalline structure. This demonstrates the crystalline nature of the BDF-III copolymer. The amorphous-crystalline structure is sometimes depicted using a fringes model. A

model of amorphous-crystalline structure fringes is also included. The acidic nature of the monomer determines the degree of crystalline property. The copolymer appears more

amorphous when it has a closed packed surface with deep pits and reactive active sites buried in the matrix. A few holes and cracks observed could have been caused by air voids[30][31].

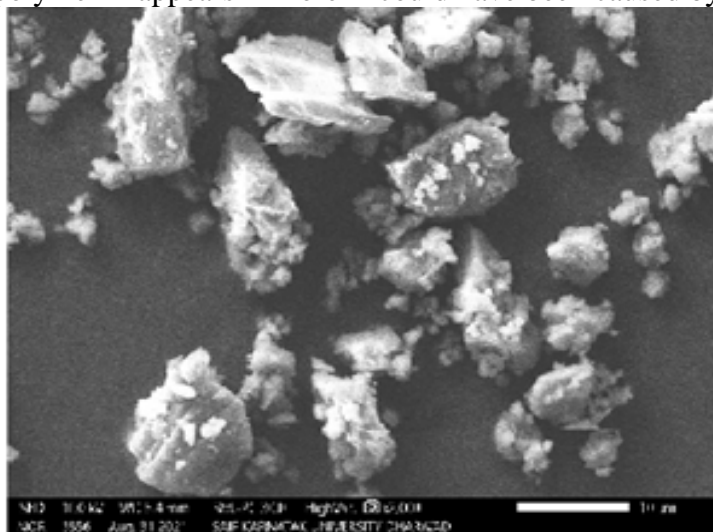


Figure 5: SEM micrograph of BDF-III copolymer

3.3 Photoluminescence study of BDF-III copolymer

The photoluminescence spectra of BDF-III copolymer were recorded using a Shimadzu MODEL RF-501(PC) S CE (LVD) LS55 spectrophotometer at Kamla Nehru College in Nagpur. The luminescence of organic compounds is mostly dependent on localized π -electron systems within individual molecules. The copolymer emits light as a result of the conjugated side chains and the conjugated polymer chains π - π^* transition. The emission and excitation spectra of BDF-III copolymer are shown in Figures 6 and 7. The emission is in the blue region, with λ_{\max}

wavelength 458nm. The copolymer shows the excitation spectra at 380 nm and 415 nm. As illustrated in Figure 6 and 7, when the copolymer is excited, it generates intense blue light with a wavelength of 458 nm, which is suitable for OLED. As a result, the PL spectra of these copolymers show that the material produced is of enough quality to be utilized in semiconductor device research. The results show that the newly synthesized copolymer can be employed as a supporting material for photoluminescent liquid crystal displays (PLLCD) and solid state lighting applications [32].

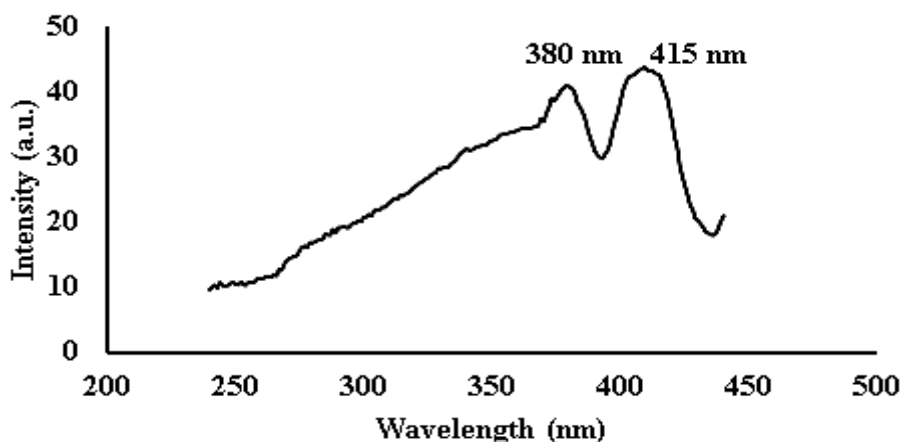


Figure 6: PL Spectra (Excitation) for BDF-III copolymer

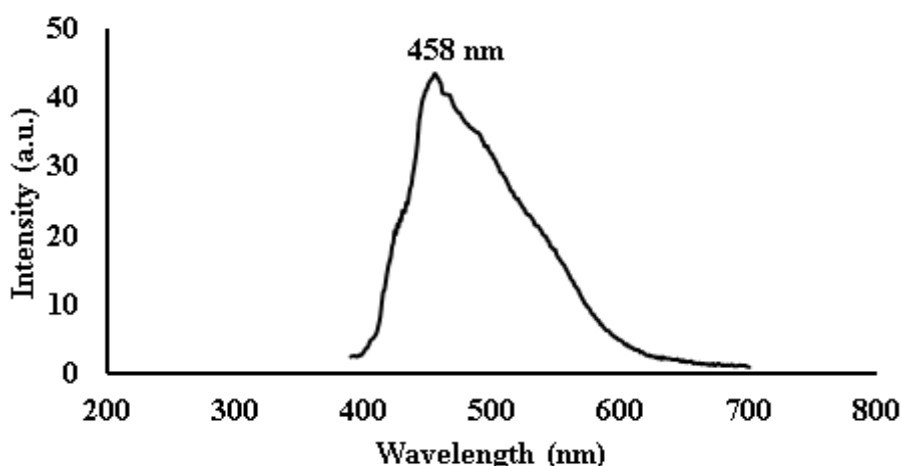


Figure 7: PL Spectra (Emission) for BDF-III copolymer

4. Conclusion

BDF-III is a new copolymer made by condensation of 2-amino 6-nitrobenzothiazole and dithiooxamide with formaldehyde monomer in 3:1:5 molar ratios in the presence of an acidic catalyst. The proposed structure of the copolymer was determined by elements analysis, UV-Visible, FT-IR, ¹H-NMR spectral analysis, and physicochemical analysis. The copolymer's semicrystalline structure was confirmed using scanning electron microscopy. The photoluminescence investigation of the BDF-III copolymer reveals that it has various properties that could be useful in the testing of semiconductor devices and light emitting materials.

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