

Synthesis, Spectral, Morphological, Antimicrobial and Thermal Degradation Kinetics Studies of 2,4-DHATF-I Copolymer Resin

Jyotsna V. Khobragade^{1*}, Rashi Shingade², B. M. Bahirwar³, Mudrika I Ahmed⁴

^{1*}Department of Chemistry, Guru Nanak College of Science, Ballarpur, India

³Department of Physics, Guru Nanak College of Science, Ballarpur, India

⁴Government Polytechnic College, Nagpur

jdr2105@gmail.com, rashishingade2002@gmail.com

bmbahirwar66@gmail.com, mudrika.ahmed2@gmail.com

Abstract: The 2, 4-DHATF-I copolymer was synthesized through a polycondensation process. In this method, a proportionate mixture of 2,4-dihydroxyacetophenone (1.521 g, 0.1 M) and thiosemicarbazide (0.9114 g, 0.1 M) was reacted with formaldehyde (0.2 mol, 7.5 mL) in a molar ratio of 1:1:2 in a round-bottom flask using 2 M acetic acid (CH_3COOH) as a catalyst. The reaction mixture was heated in an oil bath at 126 ± 2 °C for 5 hours. The structure of the synthesized copolymer was elucidated using several physicochemical characterization techniques, including UV-Visible spectroscopy, FTIR spectroscopy, ¹H NMR spectroscopy, and elemental analysis. The number-average molecular weight was determined by non-aqueous medium conductometric titration. The surface morphology and structural features of the synthesized copolymer were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Thermal stability of the copolymer at different temperatures was evaluated using the Sharp-Wentworth and Freeman-Carroll methods. In addition, the antimicrobial activity of the copolymer was investigated against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) microorganisms.

Keywords: Synthesis, terpolymer, structure, polycondensation, thermal analysis, antimicrobial studies, UV-visible spectroscopy, FTIR, ¹H NMR, XRD, SEM.

1. Introduction

In the recent years, we have witnessed a great deal of interest in the synthesis and characterization of copolymers due to their application as catalysts, semiconductors, drugs, biocides, ion-exchanger, luminescent materials and also models for enzymes [1,2]. Copolymers, very special classes of polymers, are known for their versatile uses and are found to be amorphous, crystalline or resinous in nature. Phenolic resins have been the workhorse as matrix resins in composites for structural and thermal operations in aerospace because of their ease of processability, thermal stability, protean characteristics and cost effectiveness. Khobragade and coworkers [3,4] studied the thermal decomposition kinetics and ion exchange of PTF terpolymer made from phthalic acid, thiosemicarbazide. Copolymers occupy an intermediate position between organic and inorganic compounds and it is hoped that the study of copolymers will lead to the production of polymer, which are both thermally stable and useful as fabricating materials. Thakare et al. studied conflation, characterization and thermal declination of 8-hydroxyquinoline-guanidine-formaldehyde terpolymer [5]. Gurnule and coworkers studied thermal degradation of terpolymers derived from 2-hydroxy 4-methoxy-benzophenone, melamine and formaldehyde [6].

Terpolymer resins are derived from 8-hydroxyquinoline 5-sulphonic acid, semicarbazide, and formaldehyde in hydrochloric acid as catalyst and studied their thermal degradation [7,8]. Thermal degradation 2-hydroxy 4-methoxy-benzophenone, 1,5-diaminonaphthalene and formaldehyde has been studied by Dash *et al.* [9] and 2, 2'-dihydroxybiphenyl, ethylenediamine - formaldehyde [10]. Gupta et al synthesized and studied thermal properties of 2-



amino 6-nitrobenzothiazole, melamine, and formaldehyde[11]. The thermal behavior of the synthesized material was examined using TG and DSC techniques [12]. Studying the thermal stability of polymers is essential because many practical applications require materials that can withstand elevated temperatures. Therefore, understanding the influence of heat on polymers is important for determining their stability and degradation characteristics. Most of the conventional kinetic methods assume that the activation energy and reaction model remain constant throughout the degradation process. However, free-model kinetic analysis has demonstrated that the activation energy may vary depending on the extent of conversion or reacted fraction [13].

A survey of the available literature indicates that no copolymer has yet been synthesized from the monomers 2,4-dihydroxyacetophenone, thiosemicarbazide, and formaldehyde. Hence, in the present study, the synthesis, structural characterization, antimicrobial activity, and thermal degradation behavior of the 2,4-DHATF-I copolymer are reported. Elemental analysis was performed to confirm the molecular formula, while various spectral techniques were employed to elucidate the complete structure of the synthesized copolymer. The thermal degradation data were analyzed using the Sharp–Wentworth (SW) and Freeman–Carroll (FC) methods, and kinetic parameters such as activation energy, entropy change (ΔS), enthalpy change (ΔH), frequency factor (Z), apparent entropy (S^*), and reaction order (n) were calculated [18,19].

II. MATERIALS AND METHOD

All the chemicals used in the present disquisition were of logical reagent (A.R.) grade and were attained from markatable sources. These chemicals were of high purity, and whenever required, they were further purified using standard purification techniques. Solvents such as N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethanol, and diethyl ether were also of analytical grade. Before their use in various physicochemical studies, these solvents were purified by established procedures (Merck, India) and used after proper distillation. Double-distilled water was employed throughout the entire experimental work.

2.1. Synthesis of 2,4 Dihydroxy-Acetophenone-Thiosemicarbazide-Formaldehyde(2,4-DHATF-I) Copolymer Resins.

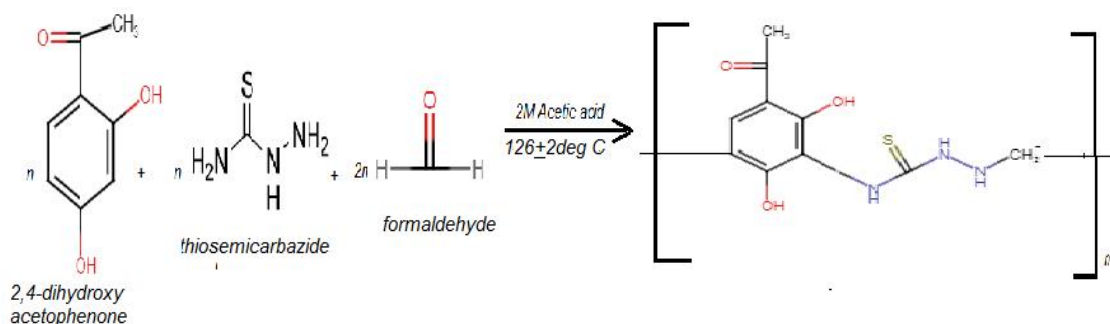


Fig. 1. Synthesis of 2,4-DHATF-I copolymer

The proportionate mixture of 2,4 dihydroxy acetophenone (1.521g, 0.1 M) and Thiosemicarbazide (0.9114g, 0.1 M) was condensed with formaldehyde (0.2mol, 7.5 ml) in a proportion of 1:1:2 in a round bottom flask in presence of 2M acetic acid (CH_3COOH) as a catalyst. This mixture was heated for 5 hrs at $126 \pm 2^\circ\text{C}$ in an oil bath with constant stirring to ensure thorough mixing. The temperature of oil bath was controlled electrically with the help of dimmerstat. Excellent yield of copolymer resin can be obtained by this reaction.

The resinous product so attained was constantly washed with cold distilled water, dried in air and pulverized with the help of mortar and pestle. The powdered sample was washed numerous times with boiling water and ethanol to remove unreacted monomers. The air dried powdered then extracted with diethyl ether and then with petroleum ether to remove 2,4 dihydroxy acetophenone, thiosemicarbazide, Formaldehyde copolymer which might be present along with 2,4-DHATF copolymer resin. It was further purified by dissolving in 8% NaOH solution, filtered and reprecipitated by



gradual drop wise addition of ice cold 1:1 (v/v) concentrated HCl/distill water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated thrice. The performing polymer sample was ltered, washed numerous time with scorching water, dried and air, pulverized and kept in vacuum over silica gel. The yield of the copolymer resin was found to be 85%. The reaction is shown in fig.1.

2.2. Molecular weight determination by non-aqueous conductometric titration

The number-average molecular weight of all newly synthesized 2,4-DHATF copolymer resins was determined using the conductometric titration method in non-aqueous N,N'-dimethylformamide (DMF) as the solvent, with standard 0.05 M potassium hydroxide in absolute ethanol as the titrant. The results obtained from the non-aqueous conductometric titrations are summarized in Table 1.

Careful examination of the titration curves shows the presence of multiple breaks prior to the complete neutralization of all phenolic hydroxyl groups. The first break, which is the smallest among them, is attributed to the neutralization of approximately one phenolic hydroxyl group per polymer chain. Furthermore, most of the subsequent breaks are nearly equal in magnitude or appear as integral multiples of the first break. The conductometric curves exhibit a distinct stepwise increase in conductance until full neutralization of all phenolic hydroxyl groups is achieved [9].

The volume of standard ethanolic potassium hydroxide consumed during titration was converted into milliequivalents per 100 g of copolymer resin and plotted against specific conductance. Using these data, the degree of polymerization of the copolymer resin was calculated with the appropriate formula.

Specific Conductance = Observed Conductance × Cell Constant

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

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

Thus the degree of polymerization (\overline{Dp}) and the number average molecular weight (\overline{Mn}) were evaluated from the conductometric titration curves. It is observed that the molecular weight of copolymers increases with the increase content.

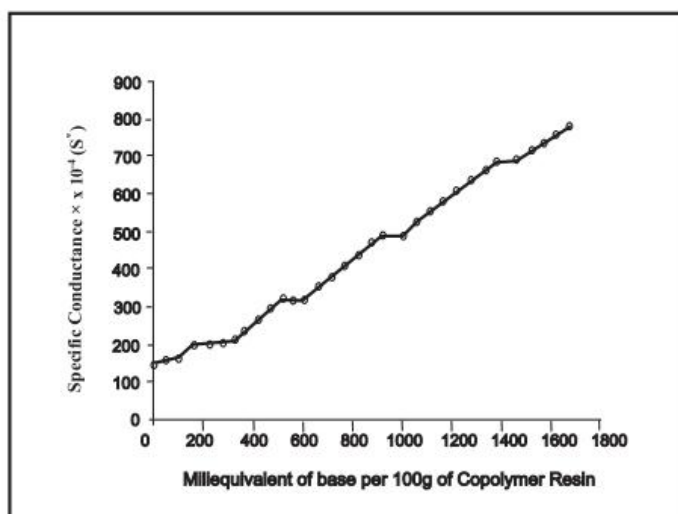


Fig 2. Conductometric Titration Curves of 2,4-DHATF Copolymer Resin



Table 1. Number Average Molecular Weight of 2,4-DHATF-I Copolymer Resins by Conductometric Titration.

Copolymer Resin	First stage of neutralization (meq/100 g of copolymer)	Final stage of neutralization (meq/100 g of copolymer)	Degree of polymerization (\overline{Dp})	Number average molecular weight (\overline{Mn})
2,4-DHATF	170	1185	6.97	1868

III. ANALYTICAL AND PHYSICOCHEMICAL STUDIES

All the analytical and spectral studies for the newly synthesized copolymer were carried out at STIC Analysis centre, Kochi.

3.1. Elemental Analysis Measurements

The elemental analysis was carried out on a Perkin Elmer 2400 Elemental Analyzer instrument of The 2,4-DHATF-I copolymer at Sophisticated Test and Instrumentation Centre , STIC, Kochi, Kerla for C, H and N. The observed results are found to be in good agreement with the calculated values.

Table 2. Elemental Analysis and Empirical Formula of 2,4-DHATF copolymer Resins

Compound	Elemental Analysis (%)				Empirical Formula of Repeating Unit	Formula Mass
	Found (Calc.)					
	C	H	N	S		
2,4-DHATF-I	49.42 (49.2)	5.35 (5.20)	15.74 (15.60)	11.50 (11.94)	$C_{11}H_{14}N_3O_3S$	268

3.2. UV-Visible Spectroscopy

The UV-Visible studies were out carried using Shimadzu UV-1800 Spectrophotometer in the range 200-800 nm at Sophisticated Analysis Instrumentation Facility , SAIF, Kochi, Kerla. UV-visible spectra of the 2,4-DHATF-I copolymer are shown in Fig. 3.

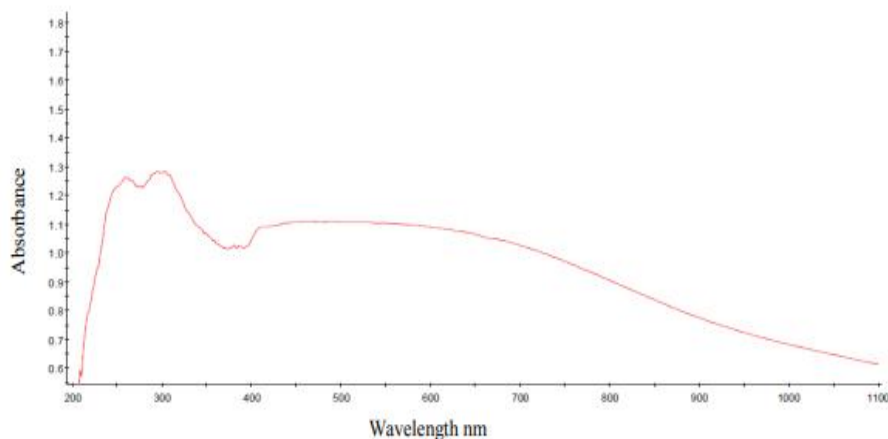


Fig.3. UV-Visible Spectra of 2,4-DHATF-I Copolymer Resins



The observed positions of the immersion bands with different intensities indicate the further violet band 240 nm is due to ($\pi \rightarrow \pi^*$) allowed transition which readily attains coplanarity and shoulder coupling (loss of fine structure) and also due to chromophore groups like $>C=C$, $>C=S$, $>C=O$ groups are in conjugation with an aromatic nucleus and the less intense band at 370 nm may be due to ($n \rightarrow \pi^*$) forbidden transition in $>C=O$ and $-OH$ groups. The presence of aromatic nuclei and $n \rightarrow \pi^*$ transition indicates the presence $-OH$ group. The bathochromic shift from the basic value viz. 240 nm and 370 nm may be due to combined effect of conjugation (due to chromophore) and phenolic hydroxyl groups. The hyperchromic effect is due to the presence of $-OH$ group, which act as auxochrome [10].

3.3. Infra-Red Spectra

The Infrared spectrum was recorded in the region of $500-4000\text{ cm}^{-1}$ on Shimadzu IR Affinity Spectrophotometer at Department of Chemistry, Kamla Nehru Mahavidyalaya, Nagpur. FTIR spectra of 2,4-DHATF copolymer is presented in Fig. 4.

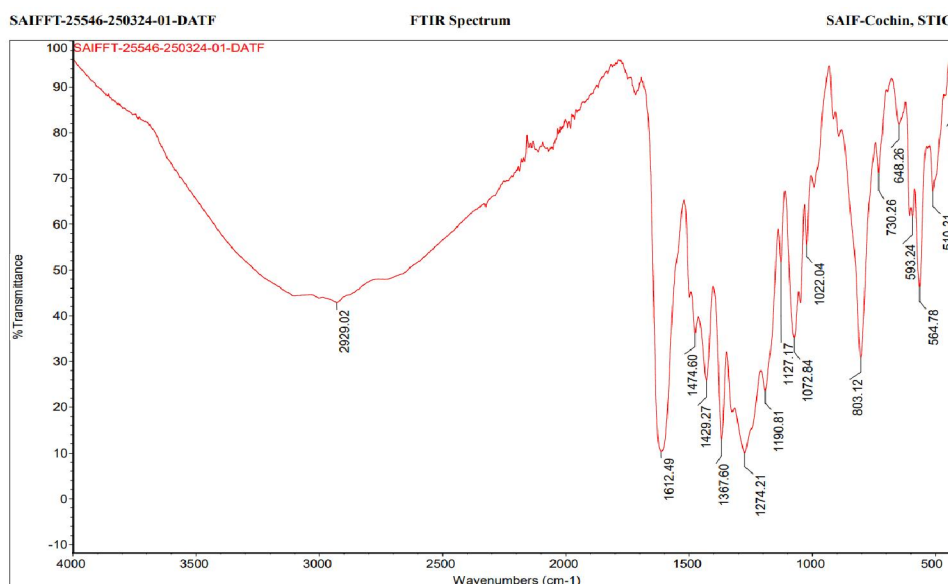


Fig. 4. FTIR Spectra of 2,4-DHATF-I copolymer

The copolymer spectrum showed a broad absorption band appeared in the region 3100 cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxyl ($-OH$) groups exhibiting intramolecular hydrogen bonding [11-12]. The presence of sharp and strong band at 2929.02 cm^{-1} indicates the presence of $-NH$ bridge. This band seems to be merged with very broad band of phenolic hydroxyl group.

A band appeared at 2700.25 cm^{-1} is assigned to aromatic ring ($-CH$) stretching modes. The 1, 2, 3, 4 substitution of aromatic ring is confirmed from the sharp, medium/weak bands appearing at 730, 1022.04, 1127, 1190.81 cm^{-1} , respectively. A weak band appeared at 2547 cm^{-1} is attributed to $-CH_2$ group present in the copolymer. The band appeared in the region of 1367.60 cm^{-1} to 1274.21 cm^{-1} is attributed to $-CH_2$ -bending (twisting and wagging) mode of vibrations. Stretching mode and a strong band at 1612.49 cm^{-1} is attributed to $C=O$ stretching of benzene ring and 1476.60 cm^{-1} the band may be assigned due to the stretching vibration of $C=S$.

3.4. Nuclear Magnetic Resonance

The NMR (H^1) spectra for 2,4-DHATF-I copolymer was recorded to substantiate the linkages of the proposed structure. H^1 -NMR studied using Bruker Avance-II FT-NMR Spectrometer in $DMSO-d_6$ solvent at SAIF Analysis, Kochi, Kerla.



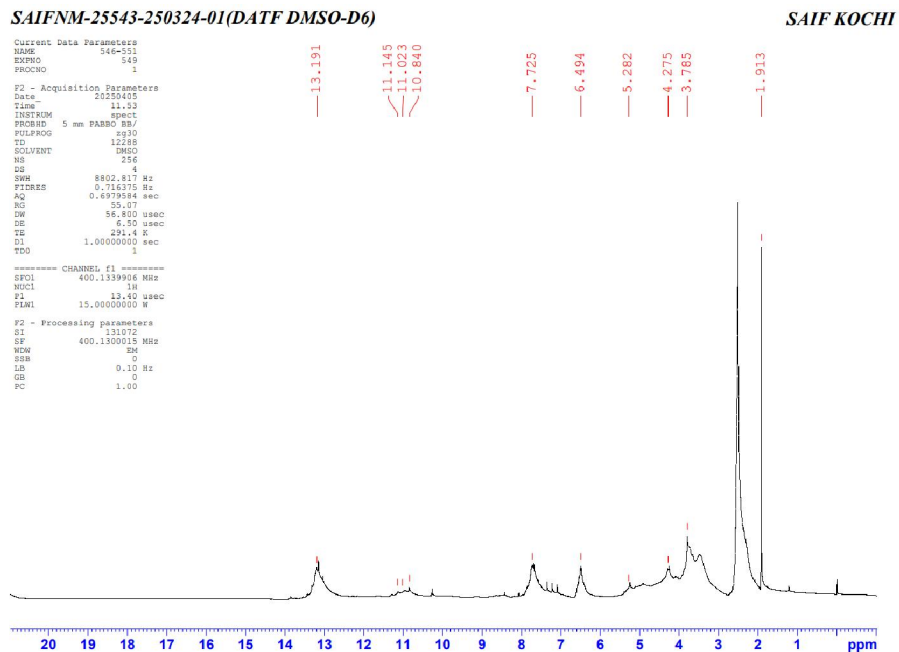


Fig. 5. ^1H -NMR Spectra of 2,4-DHATF-I Copolymer Resin

In the spectrum of copolymer, the resonance signal appeared in the range at 9.04 (δ) ppm may be due to phenolic hydroxyl protons. The much downfield chemical shift for phenolic -OH indicates easily the intramolecular hydrogen bonding of -OH group. The signals in the region 7.44 (δ) ppm are attributed to protons of -NH group present in the ligand structure and the signals appeared in the range of 4.67 ppm are assigned to methylene protons of Ar-CH₂-N half. The weak multiplet signals (unsymmetrical pattern) in the region of 8.97 (δ) ppm may be attributed to aromatic proton (Ar-H)[13]. The signals appeared in the region of 8.23 ppm is assigned to aromatic protons and the signal appeared in the region of 3.86 ppm is attributed to methylene bridges. The signal appeared for -NH bridge is 6.56 in the spectrum[14-17].

3.5. Morphological Analysis

3.5.1. Scanning Electron Microscopy

Understanding the surface aspects of the materials has greatly benefited from surface analysis. Scanning electron micrographs taken at various magnifications to examine the morphology of the reported 2,4-DHATF-I resin sample are presented in Fig. 6. It provides information on surface topography and structural flaws. The polymer resin's morphology exhibits spherulites and fringed models. The spherules have a nice and smooth surface and are a complicated polycrystalline structure. This demonstrates that the 2,4-DHATF-I copolymer resin sample is crystalline. Additionally, a realistic model of the crystalline amorphous structure may be seen in the resin polymer's morphology. The acidity of the monomer affects how crystalline the substance is. However, the image depicts a nature that is scattered and bordered with small pits that stand in for the transition between crystalline and amorphous. More amorphous figures with a closed-packed surface and deep holes may be seen in the resin. Thus, the 2,4-DHATF-I copolymer resin is amorphous in nature than, which results in increased metal ion exchange capacity. SEM micrographs of the resin's morphology thus illustrate the transition between crystalline and amorphous nature[18-19].



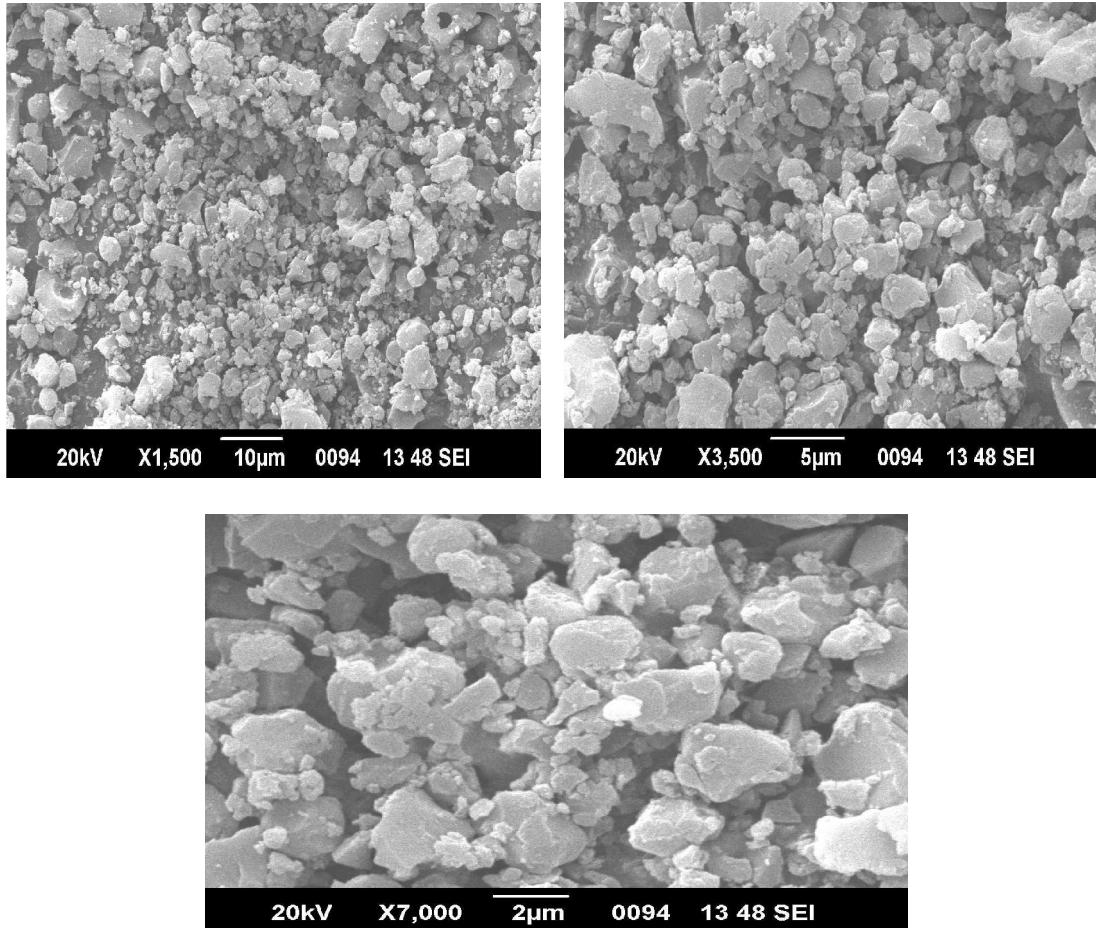


Fig. 6. SEM Micrographs of 2,4-DHATF-I Copolymer

3.5.2. X-ray diffraction

X-ray diffraction pattern observed for SATF-I showed transition between amorphous and crystalline nature of polymer. If high intensity with narrow band graph it characterize crystalline state and broadness shows amorphous. Fig.7 XRD graph shows both feature high intensity with narrow band and small broadness[20-21].



X-Ray Diffractogram- SAIF Kochi
DATF (Coupled TwoTheta/Theta)

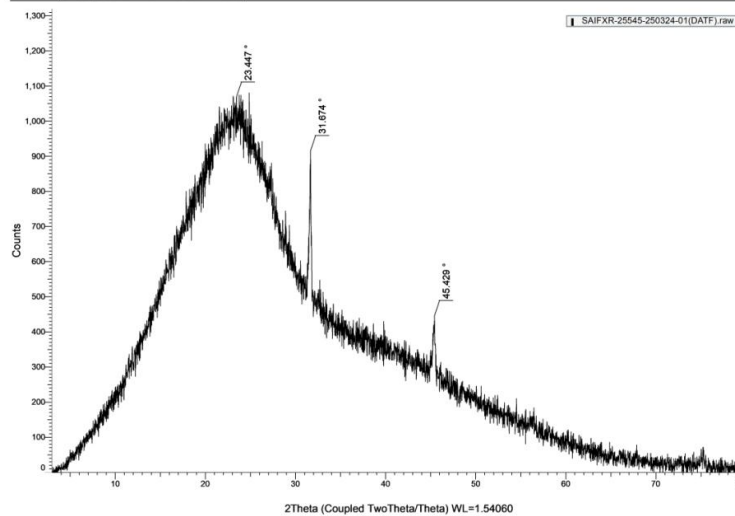


Fig. 7. XRD graph of 2,4-DHATF-I copolymer Resin.

Since the polymer under examination is a copolymer, it is particularly challenging to pinpoint its precise structure. The most likely structures for copolymer resin have been presented based on the nature and reactivity, location of the monomer, elemental analysis, electronic, FT-IR, 1H NMR, spectra, SEM, XRD and molecular weight.

IV. THERMAL ANALYSIS

Theoretical considerations

The degradation mechanism of the studied materials was further analyzed from TG data using the **Sharp–Wentworth** and **Freeman–Carroll** kinetic methods.

Freeman–Carroll Method:

The Freeman–Carroll differential equation relates the change in the logarithm of the rate of weight loss with the change in the logarithm of the remaining weight fraction. From the plot of $\Delta \log(dw/dt)/\Delta \log W_r$ versus $\Delta(1/T)/\Delta \log W_r$, the activation energy (E_a) was calculated from the slope ($-E/2.303R$), while the intercept on the Y-axis provided the order of reaction (n). Using the obtained activation energy values, thermodynamic parameters such as entropy change (ΔS), free energy change (ΔF), frequency factor (Z), and apparent entropy (S^*) were also evaluated.

Sharp–Wentworth Method:

The Sharp–Wentworth method was applied using the relationship $\log[(dc/dt)/(1-c)]$ versus $1/T$. A straight-line plot was obtained, where the slope corresponds to the activation energy (E_a) and the intercept gives the pre-exponential factor (A). A linear relationship between $\ln(dc/dt)$ and $1/T$ indicates that the reaction follows first-order kinetics ($n = 1$). Although the activation energy values calculated by the two methods are not exactly identical, their average values are nearly the same. The calculated activation energies and other thermodynamic parameters are summarized in Table 2, and the representative plots obtained from the Sharp–Wentworth and Freeman–Carroll methods are shown in the respective figures[22-23].

Kinetics of Thermal Degradation

Formulas for Calculating Kinetic Parameters

(i) Entropy Change (ΔS)

The intercept can be expressed as:

$$\text{Intercept} = \log(KR/h \phi E) + \Delta S/2.303R$$

where:



- $K = 1.380 \times 10^{-16}$ erg/deg/mole-
- $R = 1.987$ cal/deg/mole (or 8.314 J/K/mol)
- $h = 6.625 \times 10^{-27}$ erg sec
- $U = 0.166$
- ΔS = change in entropy
- E = activation energy derived from the graph.

(ii) Free Energy Change (ΔF)

The free energy change can be calculated using the formula:

$$\Delta F = \Delta H - T\Delta S$$

where:

- ΔH = enthalpy change (activation energy)
- T = temperature in Kelvin

(iii) Frequency Factor (Z)

The frequency factor can be derived from:

$$B_{2/3} = \log Z E_a / R \Phi$$

$$B_{2/3} = \log 3 + \log [1 - 3\sqrt{(1-\alpha)}] - \log p(x)$$

where:

- Z = frequency factor
- $\log p(x)$ = calculated using Doyle's table related to activation energy
- α = degree of transformation, defined as $a = w/Wc$.

(iv) Apparent Entropy (S^*)

The apparent entropy can be calculated as:

$$S^* = 2.303 R \log (Zh/RT)$$

where:

- Z = Frequency factor
- T^* = half decomposition temperature.

Antimicrobial Screening

In recent years, polymers have been widely utilized as biocidal agents. The incorporation of biologically active organic groups into the polymer backbone can impart such biological activities. Antimicrobial polymers show great potential in improving the performance of existing antimicrobial agents while reducing the environmental issues associated with conventional agents. This is achieved by lowering residual toxicity, enhancing efficiency and selectivity, and extending the effective lifetime of antimicrobial agents. Biological activities of the terpolymer were screened for their antimicrobial activity.

The antibacterial activity of 2,4-DHATF-I was performed by Kirby-Baur well diffusion method (Bauer *et al.*, 1966). 24 hours freshly grown (0.5 McFarland turbidity Standard) cultures of Strain-EC11 *Escherichia coli* (Gram negative) and Strain-SA09 *Staphylococcus aureus* (Gram positive) in nutrient both medium were inoculated by lawn culture technique on sterile solidified Muller Hinton Agar (Himedia-M173) plates with the help of sterile cotton swabs [24-25].

The stock solutions of concentration 1 mg/ml were prepared in DMSO solvents. Three wells were bored on the MHA media plates with the help of sterile cork borer (8mm). Each well loaded with solution following concentration 25 μ l (25 μ g), 50 μ l (50 μ g), 100 μ l (100 μ g) respectively. Then allowed to diffuse at room temperature for 2-3 hours. The plates were incubated in the upright position at 37 °C for 24 hours. Then the zone of inhibition were observed.



V. RESULTS AND DISCUSSION

Thermogravimetric Analysis of the 2,4-DHATF-I Copolymer on the basis of TGA graph

Table 3. Thermogravimetric Analysis of 2,4-DHATF-I Copolymer.

Copolymer Resins	Temperature range °C	Stage of Decomposition	Species Degradation	% weight loss	
				Found	Calculated
2,4-DHATF-I	40-170 °C		Loss of H ₂ O	4.18	5.26
	170-320°C	First	Loss of both -OH	34.25	33.91
	320-540 °c	Second	Removal of aromatic Nucleus	53.55	52.44
	540-700 °c	Third	Removal of Semicarbazide moiety	76.86	77.52

Thermianalytical Data

These methods were used to determine the kinetic parameters like activation energy (E_a) and order (n) of the decomposition reaction. By using Freeman-Carroll method different thermodynamic parameters [26] have been calculated such as, entropy change, free energy change, frequency factor and apparent entropy change etc.

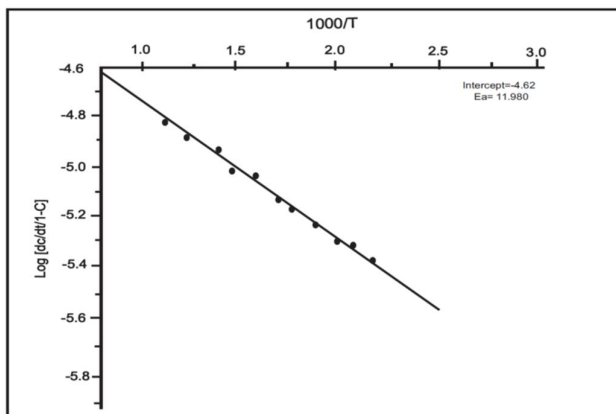


Fig. 8: Sharp-Wentworth Plot of 2,4-DHATF-I



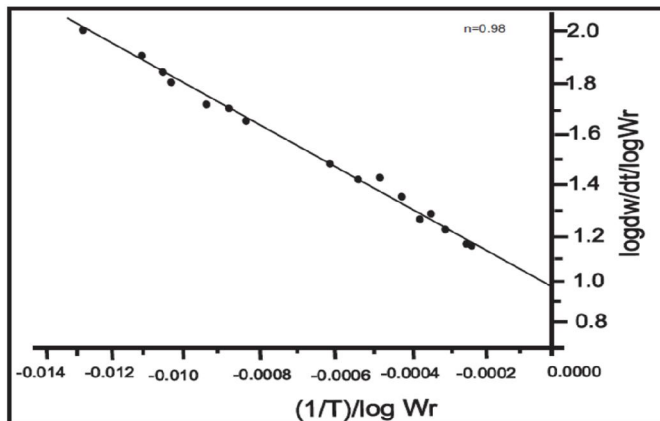


Fig. 9: Freeman-Carroll Plot of 2,4-DHATF-I

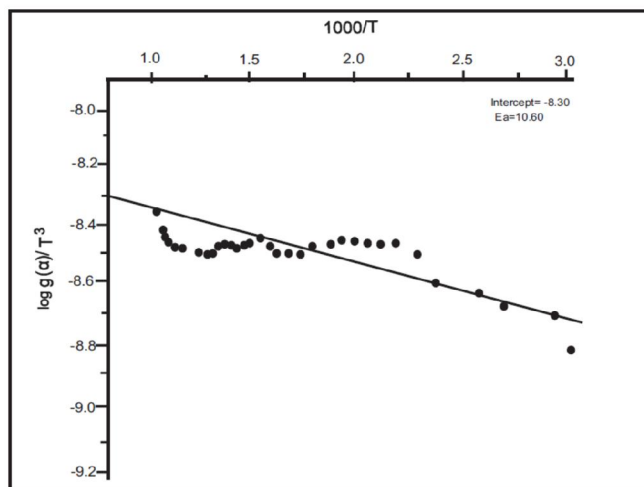


Fig. 10: Freeman-Carroll Plot of 2,4-DHATF-I

Table 4. Results of Thermogravimetric Analysis of 2,4-DHATF-I Terpolymer

Copolymer	Half Decomposition Temp. (T)	Activation Energy Ea (KJ)/mol	
		SW	FC
2,4-DHATF-I	653	5.98	5.84

SW–Sharp–Wentworth; FC–Freeman–Carroll

Table 5. Kinetic and Thermodynamic Parameters of 2,4-DHATF-I Copolymer

Copolymer	Entropy change ΔS (J)	Free energy ΔF (KJ)	Frequency Z (S ⁻¹)	Apparent entropy (S*)	Order reaction
2,4-DHATF-I	-142.26	65.56	673.10	-32.08	0.85



Using the activation energy obtained from the Freeman–Carroll method, various thermodynamic parameters can be determined. The order of reaction (n), activation energy (Ea), and thermodynamic parameters such as frequency factor (Z), entropy change (ΔS), free energy change (ΔF), and apparent entropy (S^*) are listed in Table 5. The calculated Ea values are consistent with one another. The sequence of activation energy for 2,4-DHATF-I corresponds well with the order of its thermal stability [27]. The thermodynamic parameter values are similar, suggesting that the compounds undergo decomposition through a common mechanism [28]. The unusually low value of the frequency factor (Z) suggests that the decomposition of the 2,4-DHATF-I terpolymer proceeds slowly, and no other reasonable explanation can be proposed [29]. The reaction order (n) for the terpolymer is found to be approximately 0.90.

Antimicrobial Screening

2,4-DHATF-I copolymer was screened for antibacterial activity by disc diffusion technique. The test solutions of the copolymer was prepared in sterile dimethyl formamide (DMF) solvent for the study. The test results copolymer resin are not active against the selected organisms. During the course of time, the test solution diffuses and the growth of the inoculated microorganisms such as *S. aureus*, *E. coli*, was found to be affected (Fig.11). The activity developed on the plate was measured by measuring the diameter of the inhibited zone in millimetres. The standard antibiotic gentamycin was used as the for anti-bacterial screening and the standard antibiotic amphoteric in was used as the for anti-fungal activity[30].

The bacterial activity was assayed against *Escherichia coli* (ETEC), *Staphylococcus aureus*. The standard antibiotic disc (Gentamycine disc 5 μ g/disc) shows the growth of *E. coli* by 15 mm at 50 μ l and 17 mm at 100 μ l. The 2,4-DHATF-I copolymer showed a moderate activity against this bacterial growth. *E. coli* is an aerobic, gram-negative, rod shaped bacterium. Infection of *E. coli* and can leads to bloody diarrhea and kidney failure. *Staphylococcus aureus*, a gram-positive and spherical bacterium leads to life threatening diseases like pneumonia, osteomyelitis, endocarditis, and toxic shock syndrome. The 2,4-DHATF-I copolymer showed not activity against the growth of *S. aureus* species.

Table 6: Antimicrobial activities of 2,4-DHATF-I copolymer resin

Organism	25 μ l	50 μ l	100 μ l
<i>E. coli</i> (ETEC)	0	15	17
<i>S. aureus</i>	0	0	0

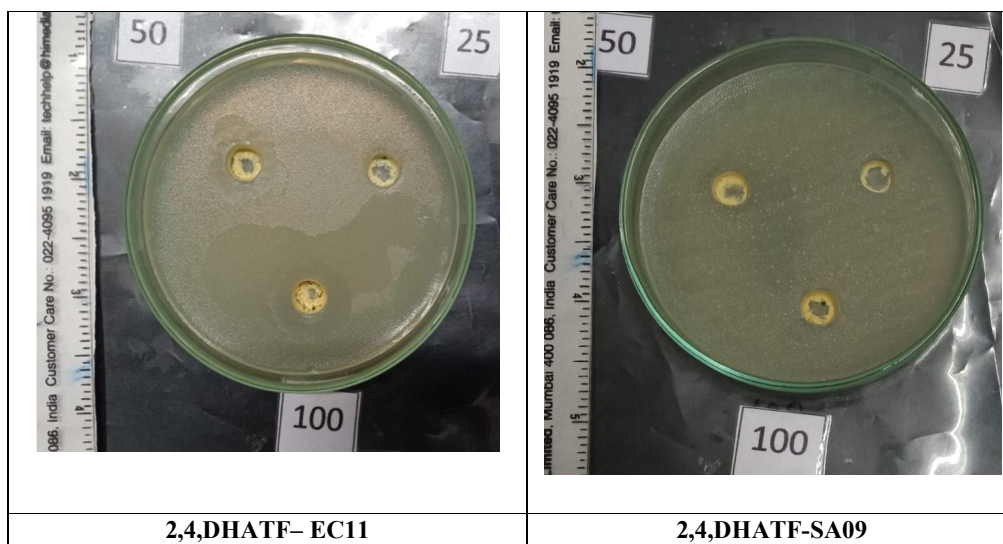


Fig. 11: Antimicrobial Screening of 2,4-DHATF-I Copolymer.



VI. CONCLUSION

1. The **2,4-DHATF-I copolymer** was synthesized through a condensation polymerization reaction involving **2,4-dihydroxyacetophenone** and **thiosemicarbazide** with **formaldehyde**, using **acetic acid as a catalyst**.
2. Thermogravimetric (TG) analysis shows that the **activation energy** calculated by the **Freeman–Carroll** and **Sharp–Wentworth** methods is almost identical. The thermodynamic parameters obtained from the Freeman–Carroll method are also comparable, suggesting that the degradation follows a common reaction mechanism.
3. The relatively low value of the **frequency factor (Z)** indicates that the thermal decomposition of the **2,4-dihydroxyacetophenone–thiosemicarbazide–formaldehyde copolymer** proceeds as a **slow reaction**.

ACKNOWLEDGEMENT

The author expresses sincere gratitude to the **Department of Chemistry, Guru Nanak College of Science, Ballarpur**, for providing the necessary laboratory facilities. The author is also thankful to **STIC, Kochi** for carrying out the spectral analysis and TGA studies. Special thanks are extended to the **Econext Unit of Sai Biosystem Pvt. Ltd., Nagpur**, for conducting the antimicrobial screening.

REFERENCES

1. J. Khobragade., M. Ahamed, and W. B. Gurnule, "Synthesis and characterization of copolymer resin derived from phthalic acid and melamine," *Rasayan J. Chem.*, vol. 7, 413-419, (2014).
2. W. B. Gurnule, and D. B. Patle, "Metal ion binding properties of a copolymer resin: synthesis, characterization, and its applications," *Polymer Bulletin*, Vol. 66, 803-820, (2011).
3. Thengane, R., Khobragade, J.V. and Gurnule, W.B., ion exchange properties of copolymer resin derived from phthalic acid, thiosemicarbazide and formaldehyde (2023).
4. Shedmake, D., Khobragade, J.V. and Gurnule, W.B., synthesis, characterization and antimicrobial activity of copolymer metal complexes and their thermal studies (2023).
5. M.B. Thakre, W.B. Gurnule, *Mater. Today Proc.* 15, 525–532, (2019).
6. Khobragade Jyotsana, Synthesis and characterization of copolymer resin derived from phthalic acid and semicarbazide with formaldehyde, *Int. Res. J. of Science & Engineering*, 2020; Special Issue A7: 89-95 ,ISSN: 2322-0015.
7. Jyotsana Khobragade, M. Ahamed M. Ahamed, and W. B. Gurnule. "Removal of cations using ion-binding copolymer involving 8-hydroxyquinoline 5-sulphonic acid and semicarbazide with formaldehyde by batch equilibrium technique."364-374 ((2014).
8. W. B.Gurnule, J.Khobragade, and M.Ahamed,"Thermal degradation studies of high performance copolymer resin derived from 8-hydroxyquinoline 5 sulphonic acid, semicarbazide and formaldehyde," *Der PharmaChem*, Vol. 6, 334-342, 2014.
9. W. B. Gurnule, N. C. Das, S. Vajpai, and Y. U. Rathod,"Synthesis, characterization and thermal degradation study of copolymer resin," *Material Today: Proceeding*, Vol. 29, 1071-1076, (2020).
10. S. P. Chakole, K. A.Nandekar, and W B Gurnule."Photoluminescent studies of 2, 2'-dihydroxybiphenyl, ethylenediamine - formaldehyde copolymer," In *Journal of Physics: Conference Series*, Vol. 1913, No. 012062, (2021).
11. P. M. Gupta, Y. U. Rathod, V. U. Pandit, R. H. Gupta, and W. B. Gurnule,"Non-isothermal decomposition study of copolymer derived from 2-amino 6-nitrobenzothiazole, melamine, and formaldehyde," *Material Today: Proceedings*, Vol. 53, 101-106, 2022.
12. W.B. Gurnule, J. Khobragade and M. Ahamed, "Synthesis, Spectral, Morphology and Thermal Degradation Kinetics Studies of Copolymer." *Chem. Sci. Rev. Lett*, 3(12), pp.1329-1340 (2015).
13. Vogel. A. I., *Textbook of Practical Organic Chemistry*, Longman Scientific and Technical, UK, 1989.



14. El-Sonbati A. Z. and Hefni M. A., Polym Deg Stab 43 (1994) 33.
15. Jacobs P. W. M. and Tompkins F. C., Chemistry of the Solid State, Garner W. E., Publication, London, (1955) 188.
16. Coats A. W. and Redfern J. P., J Poly Sci 3 (1965) 917.
17. H. J. Patel, M. G. Patel, A. K. Patel, K. H. Patel, R. M. Patel., *eXPRESS Polymer Letters* **2**, (10), 727–734 (2008)
18. Rahangdale, S.S., Kamdi, D.D., Khobragade J. and Gurnule W. B., 2020. Separation of Toxic Metals Ions from Waste Water Using Pyrogallol-Biuret-Formaldehyde Copolymer Resin. *IJBAT*, 3, pp.274-283.
19. Khobragade, J.V., Borikar, D.M. and Gurnule, W.B., Sorption Investigation on the Removal of Metal Ions from Aqueous Solutions using Copolymer Resin.
20. D. Shedmake, J. V. Khobragade and W. B. Gurnule, “Synthesis, Characterization and Physicochemical Studies of Terpolymer Resin SATF-I Derived from Sulphanilic Acid, Thiourea and Formaldehyde.”, Futuristic Trends in Chemical, Material Sciences and NanoTechnology, e-ISBN: 978-93-5747-640-9 IIP series, Vol. 3, Book 18, Chapter 33, (2023).
21. D. Shedmake, J. V. Khobragade and W. B. Gurnule, “Chelation Ion-Exchange Studies of Acrylamide and Furfural Copolymer Resin.”, Journal of Survey in Fisheries Science, 10(3) 269-276(2023).
22. Gurnule, W.B. and Das, N., 2019. Kinetic study of non-isothermal decomposition of copolymer resin derived from 2, 4-dihydroxypropionophenone, 1, 5-diaminonaphthalene and formaldehyde. *Materials Today: Proceedings*, 15, pp.611-619.
23. Khobragade, J. and Gurnule, W.B., 2017. Removal of Toxic Metal Ions Using Ion-Binding Copolymer Resin by Batch Equilibrium Technique. *Int J Res Biosci Agric Technol*, 7, pp.519-26.
24. Rahangdale, S.S. and Gurnule, W.B., 2011. Antimicrobial activity and thermal properties of copolymer resin derived from 2, 2'-dihydroxybiphenyl, dithioamide and formaldehyde.
25. Gurnule, W.B., Khobragade, J. and Ahamed, M., 2015. Synthesis, Spectral, Morphology and Thermal Degradation Kinetics Studies of Copolymer. *Chem. Sci. Rev. Lett*, 3(12), pp.1329-1340.
26. Rahangdale, S.S., Das, N.C., Vajpai, K.S. and Gurnule, W.B., 2020. Synthesis, Characterization And Thermal Degradation Study Of Copolymer Resin-li: Resulting From 2-Hydroxy, 4-Methoxybenzophenone, 1, 5-Diaminonaphthalene And Formaldehyde. *IJBAT*, 8(1), pp.194-204.
27. Jyotsna V. Khobragade, 2020, synthesis and characterization of copolymer resin derived from phthalic acid and thiosemicarbazide, Parishodh journal, Vol.IX(III), ISSN NO:2347-6648, pp.3274-3282.
28. J.M. Criado, d. Dollimore * and G.R. Heal, a critical study of the suitability of the Freeman and Carroll method for the kinetic analysis of reactions of thermal decomposition of solids, Elsevier, *Thermochimica Acta*. 54 (1972) 159-165.
29. Burkanudeen, A.R., Ahamed, M.A.R., Azarudeen, R.S., Begum, M.S. and Gurnule, W.B., 2016. Thermal degradation kinetics and antimicrobial studies of terpolymer resins. *Arabian Journal of Chemistry*, 9, pp.S296-S305
30. J. V. Khobragade, W. B. Gurnule and S. V. Hunge, “Synthesis and characterization of 2-Hydroxy, 4-Methoxy, Benzophenone - Melamine - Formaldehyde (2-H,4-M, Bphn-M-F) Copolymer Resins.”, *JETIR*, Volume 8, Issue 3, (March 2021)

