

Synthesis and Study of Thermal Degradation Process of 2,4-Dihydroxyacetophenone-Guanidine-Formaldehyde Copolymer

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Abstract: The resin DAPGF-III, in a molar ratio of 3: 1: 5 was made by heating in the presence of 2M hydrochloric acid for 5h by polycondensation of Guanidine hydrochloride and 2,4-Dihydroxyacetophenone in the presence of formaldehyde. The preliminary structure of the copolymer was evaluated by spectral methods such as elemental analysis, ¹H-NMR, FTIR and UV-Visible techniques. The molecular weight of the copolymer was determined by non-aqueous conductivity titration performed by using alcoholic KOH. TGA analysis of the synthesized copolymer is carried out by non-isothermal thermogravimetric analysis, where the sample is exposed to continuous temperature rise at a heating rate of 20°C / min in an air atmosphere and is used to study the rate, decomposition and thermal stability analysis of newly synthesized copolymer at which it was executed. Thermal parameters such as apparent entropy (ΔS), frequency factor (A), change in free energy (ΔG), and rate of reaction were determined according to the methods of Freeman Carroll (FC) and Sharp Wentworth (SW). The activation energy measured by the FC method was confirmed by the SW method.

Keywords: Polycondensation, Spectral methods, TGA, Thermokinetic parameters, Guanidine, Synthesis

I. INTRODUCTION

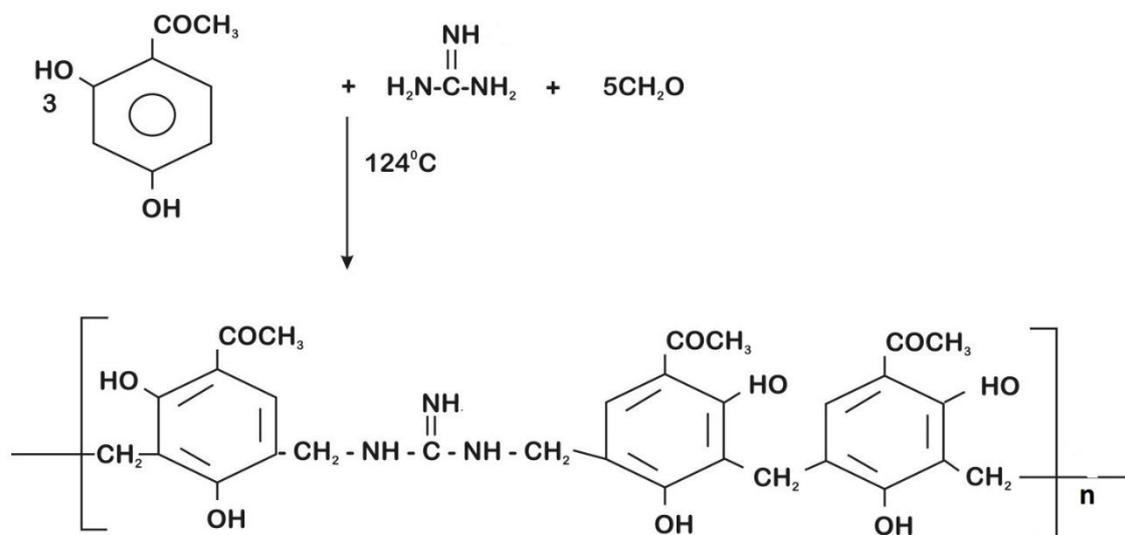
In current years, the usage of polymers in all regions of lifestyles has extended significantly. Although numerous scientists have urgently recommended the synthesis of environmentally pleasant polymers with a few organic activities, consisting of antibacterial agents. The examination of thermal decomposition of terpolymer resins has currently grow to be a subject of interest. Polymer component enhance the producing procedure and product quality. A non-stop coating section may be shaped without adversely affecting the coating, enhancing thermal balance [1]. The thermally solid terpolymer resin has advanced the improvement of polymer materials. These terpolymers, that are acetophenone changed with formaldehyde / furfuraldehyde, show off first rate thermal and antibacterial activity [2]. Gurnule et al. synthesized copolymer become constituted of 4-hydroxyacetophenone, biuret, and formaldehyde, and pyrolysis become investigated for thermal balance [3]. Katkamwar et al. A terpolymer resin (8HQDF) synthesized via way of means of condensation of 8-hydroxyquinoline, dithiooxamide, and formaldehyde in an acidic medium [4]. Kushwaha et al. p-nitrophenol resorcinol with antibacterial activity-A resin synthesized from formaldehyde [5]. Singru et al, investigated thermal and kinetic research of resins derived from 8-hydroxyquinoline-five sulfonic acid-oxamide-formaldehyde [6]. Jadhao et al. investigated the thermal decomposition of terpolymer resins crafted from 2,2-dihydroxybiphenyl, urea and formaldehyde [7]. Due to the excessive thermal balance of the copolymer, specific issues had been made to research the synthesis of the copolymer. Thermogravimetric evaluation offers records on cloth degradation and thermal balance, as a consequence many analysts mixed copolymers to enhance thermal balance [8] [9] [10]. Kinetic parameters consisting of activation power (E_a) and thermodynamic parameters consisting of entropy change (ΔS), unfurnished power change (ΔF), obvious entropy (S^*), and frequency factor (Z) are It may be decided via way of means of analysing the thermal evaluation information. [11-13], Sharp Wentworth [14], Freeman Carroll [15], Phadnis Deshpande technique [16]. Pratik et al. Investigating the thermal decomposition of copolymers of salicylic acid, guanidine, and formaldehyde [17],

Velmurugan and co-employees [18] investigated the thermal conduct of terpolymers and their composites. The thermodynamic parameters of the copolymer of salicylic acid and a combination of thiosemicarbazide and formaldehyde had been decided via way of means of Nandekar et al. [19]. The thermokinetic parameters of the resin received from cresol and hexamine and formaldehyde had been mentioned via way of means of Hiwase et al. [20]. The present communication deals with the synthesis, characterization and thermal degradation study of DAPGF-III copolymer. The Sharp-Wentworth and Freeman-Carroll methods have been used for the evaluation of activation energy and kinetic parameters such as entropy change, free energy change, apparent entropy change (S^*), frequency factor (Z) and order of reaction (n).

II. SYNTHESIS OF DAPGF-III COPOLYMER

2,4-Dihydroxyacetophenone (4.5645gms, 0.3mole) and Guanidine hydrochloride (0.9553gms, 0.1mole) with formaldehyde (18.75ml, 0.5mole) was taken as a monomer in a clean round bottom flask and refluxed water condenser using 2M HCl (200ml) in 3:1:5 ratio. The homogeneous mixture was refluxed in an oil bath at $122^{\circ}\text{C} \pm 2^{\circ}\text{C}$ with constant stirring for 5Hrs. The reaction mixture was equilibrated overnight. A cream-colored precipitate was thus obtained which was separated by filtration method and washed with cold water to remove unreacted monomer, then it was air-dried and powdered. The dried copolymer was further purified by dissolving in 8%NaOH and regenerated in 1:1 (v/v) HCl/H₂O. The process was repeated several times to get the pure copolymer. The resulting copolymer was washed with boiling water, air-dried, powdered, and kept in a vacuum desiccator with silica gel. Scheme 1 shows a schematic representation of the synthesis of DAPGF-III copolymer.

3) DAPGF (3:1:5)



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

III. CHARACTERIZATIONS

3.1 Elemental Analysis

The elemental analysis of DAPGF-III has been carried out from STIC Cochin by using Vario EL III (Elementar, Germany) to find out the percentage of elements, such as carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) present in the copolymers.

3.2 Molecular Weight Determination by Non-Aqueous Medium

The non-aqueous conductometric titration method is used to determine the number average molecular weight of the DAPGF-III copolymer in DMSO medium by using 50mg of DAPGF-III copolymer sample and ethanolic KOH as the titrant, then a graph of the specific conductance against the milli equivalents of KOH needs to neutralize 100gm of the

copolymer was plotted and it shows that numbers of breaks in the plot and from it, the first and last break in the plot were determined. The number average molecular weight has to be determined by the following equation which the based on the average degree of polymerization[21].

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

$$M_n = DP \times \text{Repeat unit weight.}$$

3.3 UV-Visible Spectroscopy

The UV-Visible spectra of the copolymer were carried out at room temperature in DMSO on a double beam spectrophotometer fitted with an automatic pen chart recorder in the range of 200nm – 800nm.

3.4 FT-IR Spectroscopy

Infrared spectra of copolymer have been scanned indanol mull on Perkin-Elmer-Spectrum RXI, FT-IR Spectrophotometer in KBr pellets in the range of 4000-500 cm⁻¹.

3.5 H-NMR Spectroscopy

The proton NMR spectrum of the copolymer was carried out using DMSO-d₆ as a solvent on Bruker Advance -II400 MHz NMR spectrophotometer.

3.6 SEM Analysis

The surface morphology of the DAPGF-III copolymer was examined at different magnifications by using Jeol 6390 LV

3.7 Thermogravimetric Analysis

The non-isothermal thermogravimetric analysis of DAPGF-III copolymer was performed in an air atmosphere with a heating rate of 20^oC.min⁻¹ from a temperature range of 40 to 600^oC. The TGA has been scanned by using a Perkin Elmer diamond TGA/DTA analyzer. All the spectral and detailed analytical studies for the newly synthesized copolymer were carried out at Sophisticated Analytical Instruments Facility (SAIF), STIC, Cochin University, Cochin, India.

IV. RESULTS AND DISCUSSION

4.1 Solubility Test

The newly blended DAPGF-III copolymer was found to be soluble in solvents such as DMF, DMSO and THF while insoluble in almost all inorganic and organic solvents. The yield of the copolymer was found to be 82 %.

4.2 Elemental Analysis

The results of the elemental analysis which are used to analyze the percentage of carbon, nitrogen and hydrogen in the sample are shown in Table: 1. The composition of the copolymer obtained based on elemental analysis data was found to be in good correlation with the calculated values which shows that, empirical formula and empirical weight of a repeated unit of DAPGF-III copolymer were found to be and 359 respectively.

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

Copolymer	Empirical formula of repeated unit	Empirical formula weight	%C (found/cal.)	%H (found/cal.)	%N (found/cal.)
DAPGF-III	C ₃₀ H ₃₂ N ₃ O ₈	249	63.2% (64%)	4.9% (5.6%)	6.54% (7.4%)

Molecular weight by non-aqueous conductometric titration

The number average molecular weight (Mn) of this copolymer has been determined by the nonaqueous conductometric titration method in DMSO medium using standard potassium hydroxide (0.05M) in absolute ethanol as a titrant. A plot of specific conductance was plotted against milliequivalents of ethanolic KOH required for the neutralization of 100g of each copolymer. A plot revealed the number of breaks within the plot. The first break at 93 milliequivalents of base and the last break at 1133 milliequivalents of the base were noted and which has been depicted in Figure 1. The number average molecular weight (Mn) of copolymer could be obtained by multiplying the average degree of polymerization (DP) by the formula weight of the repeating unit. The number average molecular weight determination by non-aqueous conductometric titration method is a simple and effective method that has been proved by earlier workers [22-23]. Conductometric titration curve results are presented in Table 2.

Table 2: Molecular weight determination of DPPGF-III copolymer

Polymer	1 st phase of neutralization	Final phase of neutralization (Meq/100g sample)	Degree of polymerization (\overline{Dp})	Empirical weight (gm)	Number average molecular weight (\overline{Mn})
DAPGF-III	93	1133	12	562	6847

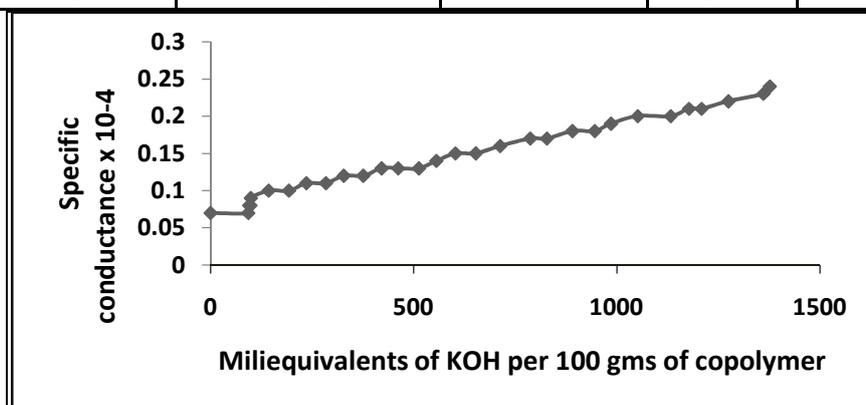


Figure 1: Conductometric titration curve of DAPGF-III copolymer

4.3 UV-Visible Spectroscopy

The UV-visible spectrum of the DAPGF-III copolymer is depicted in Figure 2 which is recorded in DMSO in the 200-800nm range. The newly synthesized DAPGF-III copolymer exhibits two characteristic bands at 270 nm and 340 nm. The absorption band shown by copolymer have two different intensities, these observed positions of two absorption bands indicate the presence of chromophore group like >C=O, C=C which are in conjugation with the aromatic nucleus i.e., acetophenone and -NH respectively. The absorption band at 270nm due to $\pi \rightarrow \pi^*$ allowed transition is more intense and the band at 340 nm are because of $n \rightarrow \pi^*$ transition which is less intense. Hence, the presence of aromatic nucleus is confirmed by $\pi \rightarrow \pi^*$ transition and -NH groups by $n \rightarrow \pi^*$ transition[24]

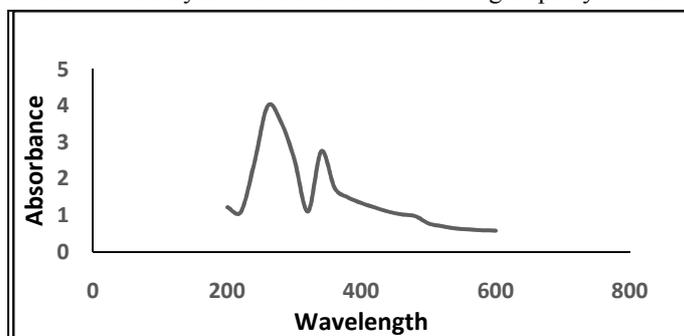


Figure 2: UV-visible spectra of DAPGF-III copolymer

4.4 H-NMR Spectroscopy

The ¹H-NMR spectrum of DAPGF-III copolymer was scanned in DMSO-d₆ solvent which is shown in Figure 3. The signals observed in the ¹H-NMR spectra of DAPGF-III copolymer were interpreted based on the literature. The signal that appeared at 2.47 ppm is attributed to methylene protons of the copolymer. The weak multiple signals that appeared in the region of 6.26 to 6.54 ppm are due to all the protons of the aromatic ring.

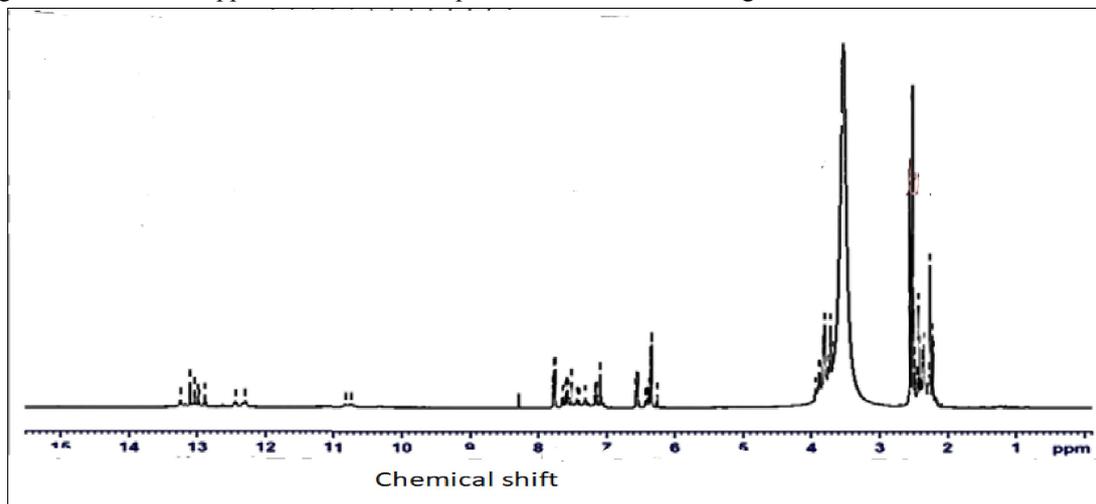


Figure 3: ¹H-NMR spectra of DAPGF-III copolymer

4.5 FT-IR Spectroscopy

The FT-IR spectra of the DAPGF copolymer are presented in figure 4 and spectral data are specified. A broad and strong band has appeared in the region 3295cm⁻¹ which may be due to the stretching vibration of the phenolic hydroxyl group. The strong band at 1626 cm⁻¹ may be assigned due to the stretching vibration of the Ar-CO- group. A sharp band appearing at 1478 cm⁻¹ describes the presence of >C=C< (aromatic) group. The sharp and strong band observed at 1372.4cm⁻¹ suggests the presence of -CH₂- methylene bridge in the copolymer chain. Weak bands appearing in the region 905-860 cm⁻¹ may be due to the presence of 1,2,3,4 and 5-pentasubstituted aromatic rings[25-26].

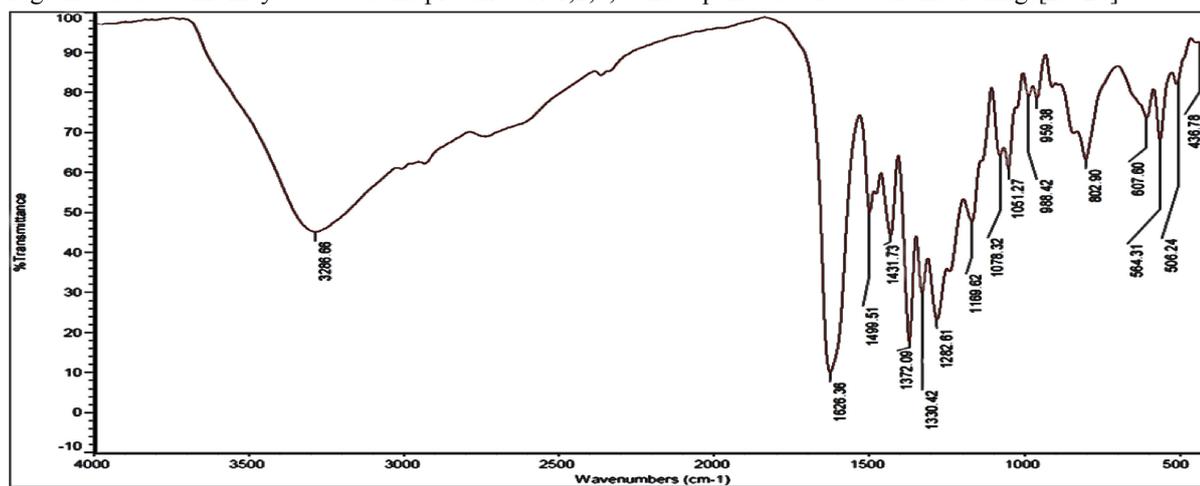


Figure 4: FTIR Spectra of DAPGF-III copolymer

4.6 Scanning Electron Microscopy

The SEM micrograph of the DAPGF-III copolymer obtained in x3500 and x5000 magnification is used to understand the surface morphology of the copolymer which is shown in Figure 4. The DAPGF-III copolymer shows the irregular granular particles-like appearance and it exhibits a closed packed arrangement with deep pits and more active sites.

From the SEM photograph, it is quite clear that the copolymer is porous and the surface morphology of the DAPGF-III copolymer depicted a fringed model of the semicrystalline structure. The fringes in the micrograph show that copolymer exhibit transition state between amorphous and crystalline state. During the polymerization crystalline structure of the monomer is converted into the amorphous phase of the copolymer. There are some holes and cracks are seen which may be because of air voids[27].

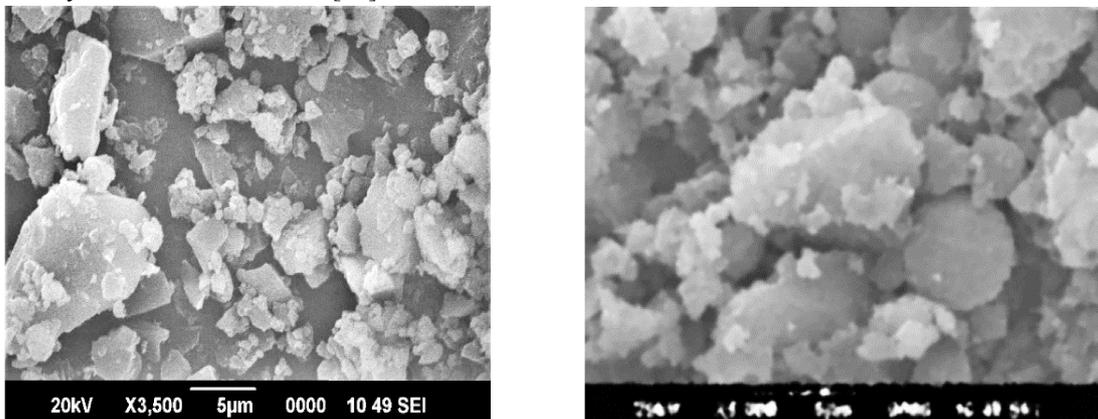


Figure 4: SEM images of DAPGF-III copolymer

4.7 Thermogravimetric Analysis

The thermogram of DAPGF-III copolymer Figure 5, portrays three stages in decay response (120-320⁰C, 320-540⁰C, and 540-700⁰C), after the loss of water molecule in the temperature range 40-800⁰C. The first disintegration happens between 40-180⁰C compares to 3.12% calculated which might be credited to loss of water molecule against determined 3.66% present per repeat unit of the polymer. The principal stage decay from 180-340⁰C may be because of loss of . The second step of disintegration begins from 320-540⁰C comparing to 78.98% loss of the disposal of basic molecules like -NH and -CH₂ group present in the copolymer against determined 79.31%. The third step begins from 540-800⁰C affirming the degradation of the melamine from the copolymer (98.79% noticed and 100% determined). The half decomposition temperature for copolymer is discovered to be 310⁰C[28-30].

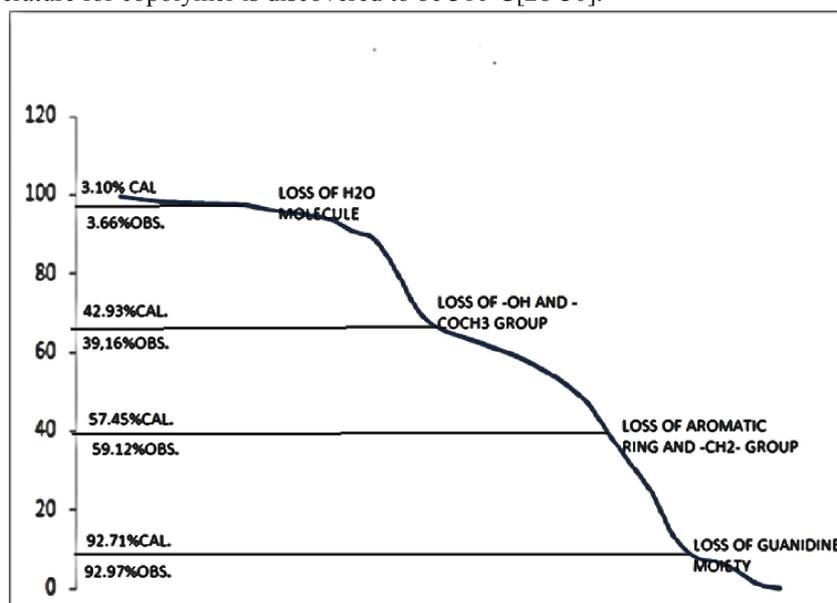


Figure 5: Decomposition pattern of DAPGF-III copolymer



Copolymer	Activation energy Ea (kJ/mol)		Entropy Change S(J)	Free Energy Change ΔF (kJ)	Frequency factor Z (S ⁻¹)	Apparent Entropy Change (S*)	Order of reaction (n)	Half decomposition temperature °C
	*SW	*FC						
DAPGF-III	15.08	14.87	-193.327	60.526	675.6	-50.926	0.744	460°C

Table 3: Kinetic Parameters of DAPGF-III copolymer

*SW: Sharp-Wentworth and *FC: Freeman-Carroll

With the assistance of thermogravimetric information the kinetic parameters like activation energies (Ea) and order of reaction (n) and thermodynamic parameters such as entropy change (ΔS), apparent entropy change (S*), and frequency factor (Z) are resolved and detailed in Table 3 which was determined by examining the strategies depict by Sharp-Wentworth and Freeman-Carroll.

Sharp-Wentworth Method

By using the Sharp and Wentworth equation,

$$\log[(dc/dt)/(1-c)] = \log(A/\beta) - [E_a/2.303R] \cdot 1/T \dots \dots \dots (1)$$

Where, dc/dt=rate of change of fraction of weight with change in temperature

β=linear heating rate dT/dt.

By plotting the graph between (logdc/dt)/(1-c) vs 1/T obtained the straight line which gives activation energy (Ea) calculated from its slope (Figure 6)

Where, β is the conversion at time t,

R is the gas constant (8.314 J mol⁻¹ K⁻¹),

T is the absolute temperature.

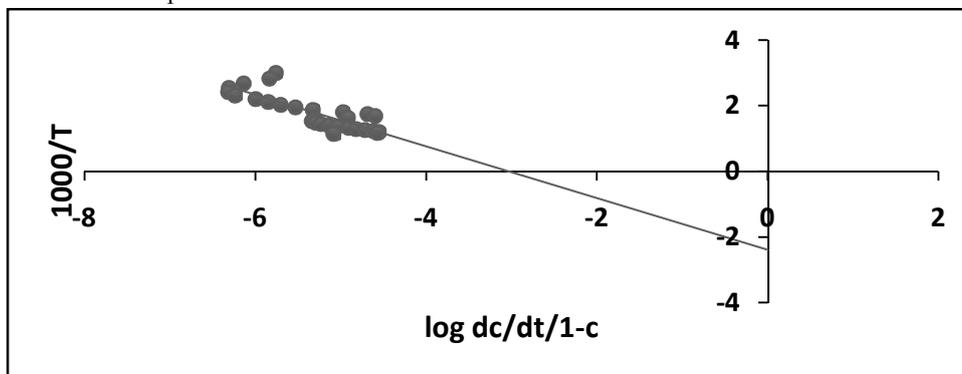


Figure 6: Sharp-Wentworth plot of DAPGF-III copolymer

Freeman-Carroll method:

The equation derived by Freeman and Carroll is:

$$[\Delta \log(dw/dt)] / \Delta \log W_r = (-E_a/2.303R) \cdot \Delta(1/T) / \Delta \log W_r + n \tag{2}$$

Where, dw/dt=rate of change of mass with time.

W_r=W_c-W

W_c=weight loss after the reaction.

W=fraction of weight loss at time t.

E_a=energy of activation

n=order of reaction.

The plot between the [Δ log (dw/dt)] / Δ log W_r vs Δ (1/T) / Δ log W_r gives a straight line and from the value of the slope, we obtained energy of activation (Ea) and intercept on Y-axis as the order of reaction (n) (Figure 7). The change in entropy(S), frequency factor (Z), apparent entropy(S*) also can be calculated by further calculations [23][24].

Change of Entropy:

$$\text{Intercept} = [\log KR/h\phi E] + S / 2.303 R \quad (3)$$

Where, $K = 1.3806 \times 10^{-16}$ erg/deg/mole,

$R = 1.987$ Cal/deg/mole

$h = 6.625 \times 10^{-27}$ erg sec,

$\phi = 0.166$

$S =$ Change in entropy,

$E =$ Activation energy from graph.

Free Energy Change

$$\Delta F = \Delta H - T\Delta S \quad (4)$$

Where, $\Delta H =$ Enthalpy Change = activation energy

$T =$ Temperature in K

$S =$ Entropy change from (i) used.

Frequency Factor

$$B_n = \log ZEa / \phi R \quad (5)$$

$$B_1 = \log [\ln 1 / 1 - \alpha] - \log P(x) \quad (6)$$

Where, $Z =$ frequency factor,

$B =$ calculated from equation (6)

$\log P(x) =$ calculated from Doyle's table corresponding to the activation energy.

Apparent Entropy Change:

$$S^* = 2.303 \log Zh / KT^* \quad (7)$$

$Z =$ from relation (5)

$T^* =$ temperature at which half of the compound is decayed from its total loss.

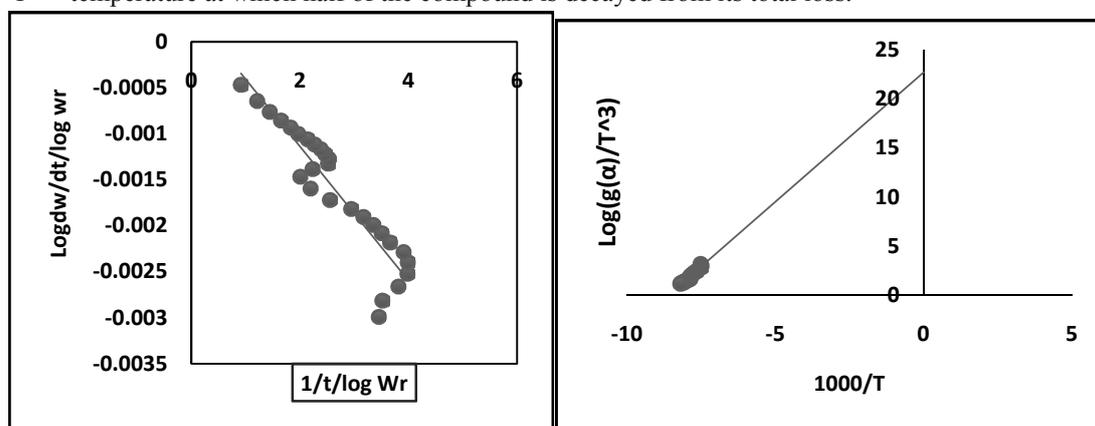


Figure 7: Freeman –Carroll plot of DAPGF-III copolymer

The E_a values calculated by SW and FC methods are in good agreement with each other which are presented in Table 3. Based on the initial deterioration temperature, the thermal stabilities of the copolymer have additionally been utilized here to characterize thermal stability, ignoring the degree of disintegration. The decomposition reaction of DAPGF-III copolymer takes place in a slow phase because of the abnormally low value of frequency factor (Z). This fact is further supported by the negative value of the entropy change. Straight-line plots are obtained using the two methods shown in Figure 7 and from the plot, the order of reaction (n) of DAPGF-III copolymer was found to be 0.744. From the above data, it is quite clear that the decomposition reaction approximately follows first-order kinetics[31].

V. CONCLUSION

The DAPGF-III copolymer was synthesized by polycondensation polymerization with good yield. The proposed structure of copolymer resin has been elucidated by elemental analysis, FTIR, ¹H-NMR, and UV-visible spectral studies. The surface morphology confirmed the semicrystalline nature of copolymer. The non-isothermal thermogravimetric analysis shows that the synthesized copolymers were thermally stable and from the values of activation energy calculated by using SW and FC methods, are in close agreement with each other. Degradation of the copolymer is slow reaction is explained based on the low value of frequency factor and from the value of the order of reaction, copolymers approximately follow first-order kinetics.

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