

SYNTHESIS, CHARACTERIZATION AND THERMAL DEGRADATION STUDY OF COPOLYMER RESIN-II: RESULTING FROM 2-HYDROXY, 4-METHOXYBENZOPHENONE, 1, 5-DIAMINONAPHTHALENE AND FORMALDEHYDE

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ABSTRACT:

The copolymer HMBPDANF-II has been synthesized by condensation of 2-hydroxy, 4-methoxybenzophenone and 1, 5-diaminonaphthalene with formaldehyde in the presence of hydrochloric acid as a catalyst in the 2: 1: 3 molar proportion of reactants. The structure of copolymer has been characterized by elemental analysis, UV-Visible, FT-IR and ¹H-NMR spectroscopy. The morphology of copolymer has been studied by scanning electron microscopy (SEM). The thermal decomposition behavior of HMBPDANF-II copolymer has been carried out by using TGA in static nitrogen atmosphere at a heating rate of 10 °C/min. Sharp-Wentworth and Freeman-Carroll methods have been applied to calculate the thermal activation energy (E_a), entropy change (ΔS), apparent entropy change (S^{*}), free energy change (ΔF) and frequency factor (Z). The order of reaction (n) has been found to be 0.95.

Key words: - Thermal degradation, copolymer, condensation, thermal stability, Freeman-Carroll method, Sharp-Wentworth method.

INTRODUCTION:

Due to global applications of polymeric materials, polymer science and technology have been developing rapidly and attracted much attention towards the polymer scientists. Polymers have been found to be very useful applications as ion-exchange resins, adhesive, flame resistant fibers, coating materials, semiconductors and catalysts (Jiwatode MM et. al., 2017). Thermal analysis plays a vital role in studying the structure and properties of any material. Thermo gravimetric analysis has been widely used to investigate the

decomposition characteristics of polymeric matter (Liu C et. al., 2003).

Gurnule (Gurnule WB et. al., 2019) have studied the thermal degradation of copolymer resin derived from 2-hydroxy-4-methoxybenzophenone, 1, 5-diaminonaphthalene and formaldehyde. Chaudhary studied thermal microbial reactivity of copolymers and terpolymers of azo-N-4-bromophenyl substituted maleimide chain with acrylates vinyls (Chaudhary et al., 2016). The kinetic study of non- isothermal decomposition of copolymer resin derived from 2, 4-dihydroxypropiofenone, 1,5-

diaminonaphthalene and formaldehyde has been reported. (Gurnule WB et. al., 2019). Studied the thermal properties of copolymer derived from 2, 4-dihydroxypropiophenone and 4-pyridylamine (Rahangdale SS et. al., 2019). Thermal study of polymers derived from acrylamide (Silva ME et. al., 2000). Comparative thermo kinetic study of terpolymeric resins derived from p-hydroxyacetophenone, resorcinol and glycerol has been reported (Kapse et al., 2014). Bisen et. al. synthesized and studied the kinetics of thermal decomposition of copolymer resin-II derived from 4-hydroxy benzaldehyde, phenyl hydrazine and formaldehyde (Bisen VR et. al. 2014).

In the present paper investigation it has been planned to study the synthesis, characterization and thermal degradation study of HMBPDANF-II copolymer resin derived from 2-hydroxy, 4-methoxybenzophenone and 1,5-diaminonaphthalene with formaldehyde which has not been reported so far in literature. The Freeman-Carroll and Sharp-Wentworth methods have been applied for the calculation of activation energy and kinetic parameters such as entropy change (ΔS), apparent entropy change (S^*), free energy change (ΔF), frequency factor (Z) and order of reaction (n).

MATERIAL AND METHODS:

Chemicals

The chemicals used like 2-hydroxy, 4-methoxybenzophenone, 1,5-diaminonaphthalene and formaldehyde were procured from market and were of chemically pure grade. DMF and DMSO were used as solvents of AR grade.

Synthesis of HMBPDAF-II Copolymer

The copolymer HMBPDANF-II was synthesized by condensing 2-hydroxy, 4-methoxybenzophenone and 1, 5-diaminonaphthalene with formaldehyde in a molar ratio 2:1:3 in the presence of 2M, 200 ml HCl as a catalyst at 126 ± 2 °C for about 5 hrs. in an oil bath with occasional shaking to ensure thorough mixing. The separated

brown colour copolymer was washed with hot water and methanol to remove unreacted starting materials and acid monomers. Properly washed resin was dried powdered and then extracted with diethyl ether to remove 2-hydroxy, 4-methoxybenzophenone formaldehyde copolymer which might be present along with MBPDANF-II copolymer. The brown colour resinous product was immediately removed from the flask as soon as the reaction period was over and then purified.

The purified copolymer resin was finely ground to pass through 300-mesh size sieve and kept in a vacuum over silica gel. The yield of the copolymer resin was found to be 85%. The reaction and suggested structure of HMBPDANF-II is shown in Figure 1.

The elemental analysis of the copolymer was carried out on Elementar Vario EL III CARLO ERBA 1108 Elemental Analyzers. The electronic absorption spectra in DMSO was recorded on automatic recording double beam spectrophotometer (UV-VIS-NIR Spectrometer) in the range of 200-800 nm. Infrared spectra of copolymer was carried out in Thermo Nicolet Avatar 370, FT-IR spectrometer in KBr pellets in the range of 4000 - 500 cm^{-1} . Proton NMR spectrum was scanned on Bruker 400 Advance-III, FT-NMR spectrometer using DMSO- d_6 as a solvent.

The TGA of the copolymer was carried out using Perkin Elmer diamond TGA/DTA analyzer. All the analytical and spectral studies for the synthesized copolymer were carried out at Sophisticated Analytical Instruments Facility, STIC, Cochin University Cochin, India.

Thermogravimetric Analysis

In non-isothermal or dynamic TGA, the sample is subjected to conditions increase in temperature at linear rate. The thermo gravimetric analysis was performed in with heating rate at 10 °C min^{-1} using 5-6 mg of samples in platinum crucible from temperature 40 °C to 800 °C and thermogram is recorded for HMBPDANF-II. With the help of thermo gravimetric data,

the thermal activation energies (E_a), order of reaction (n), entropy change (ΔS), apparent entropy change (S^*), free energy change (ΔF) and frequency factor (Z) were determined.

Theoretical Considerations

Thermogram was interpreted and analyzed to obtain information about the percentage weight loss at different temperatures which gives information about sample composition, product formed after heating. Kinetic parameters have been determined using Sharp-Wentworth and Freeman-Carroll methods as follows

Sharp- Wentworth Method

Using the equation derived by Sharp and Wentworth (Gurnule WB et. al., 2015),

$$\text{Log } \frac{dC/dT}{1-C} = \text{log } (A/\beta) - \frac{E_a}{2.303R} \cdot \frac{1}{T} \dots\dots(1)$$

where,

dC/dT = rate of fraction of weight with change in temperature

β = linear heating rate dT/dt

The graph of $\text{log } \frac{dC/dT}{1-C}$ versus $\frac{1}{T}$ has been plotted. The graph is a straight line with activation energy (E_a) as slope and 'A' as intercept. The linear relationship confirms that the assumed order ($n=1$) is correct.

Freeman-Carroll Method

The straight line equation derived by Freeman and Carroll (Belsare PV et. al. 2015), which is in the form of

$$\frac{\Delta \text{log}(dW/dt)}{\Delta \text{log}W_r} = n - \frac{E_a}{2.303R} \frac{\Delta(1/T)}{\Delta \text{log}W_r} \dots\dots\dots(2)$$

where,

dW/dt = Rate of change of weight with time.

$W_r = W_c - W$

W_c = Weight loss at completion of reaction.

W = Fraction of weight loss at time t .

E_a = Energy of activation.

n = Order of reaction.

The plot between the terms $\frac{\Delta \text{log}(dW/dt)}{\Delta \text{log}W_r}$ versus $\frac{\Delta(1/T)}{\Delta \text{log}W_r}$ gives a straight line. The slope, $-E_a/2.303R$, gives energy of activation (E_a) and intercept on Y-axis as order of reaction (n). The change in entropy (ΔS), frequency factor (Z), apparent entropy change (S^*) can also be calculated by further calculations.

RESULT & DISCUSSION:

The newly synthesized copolymer was found to be brown in colour. The copolymer is soluble in solvents such as dimethylformamide (DMF), Dimethylsulphoxide (DMSO), Tetrahydrofuran (THF) and con. H_2SO_4 but insoluble in almost all organic and inorganic solvents.

Elemental Analysis

The HMBPDANF-II copolymer was analyzed for the carbon (% C), hydrogen (% H) and nitrogen (% N) content and results obtained are presented in Table 1. Based on the analytical data, the empirical formula of the repeating unit for the HMBPDANF-II copolymer resin is found to be $C_{41}H_{34}N_2O_6$.

The UV-visible spectra of HMBPDANF-II copolymer sample has been carried out in pure DMSO in the region 190-800 nm and shown in Figure 2. The spectra displayed two characteristics broad band at 282 nm and 335 nm. These observed position for absorption bands indicate the presence of a carbonyl ($>C=O$) group having a carbon oxygen double bond which is in conjugation with the aromatic nucleus. The appearance of former band can be account for $\pi \rightarrow \pi^*$ transition while the later band may be due to $n \rightarrow \pi^*$. The shift from basic value (viz. 240 nm and 310 nm respectively) may be due to conjugation effect and presence of phenolic hydroxyl group, which is responsible for hyperchromic effect i.e. ϵ max higher value (Ullah S et. al., 2014).

FT-IR Spectra

Infrared spectra of HMBPDANF-II copolymer resin is presented in Figure 3 and IR spectral data are tabulated in Table 2. A very broad and strong band observed at 3400 cm^{-1} may be due to the stretching vibration of the

phenolic hydroxyl group exhibiting intramolecular hydrogen bonding –NH group. The strong band appeared at 2937 cm^{-1} may be assigned to the stretching vibrations of –NH (imide) group. A sharp and strong band at 1617 cm^{-1} may be assigned to the stretching vibration of $>\text{C}=\text{O}$ group. The strong band obtained at 1106 cm^{-1} region is attributed to the Ph-O-CH₃ ether linkage. The weak band at 1343 cm^{-1} may be due to –CH₂ methylene bridge. The presence of 1, 2, 3, 4, 5- pentasubstituted aromatic ring is recognized from the weak band appearing in the region $925\text{--}860\text{ cm}^{-1}$ (Dontulwar J et. al., 2007 and Michael PEP et. al., 2016).

¹H-NMR Spectra

The ¹H-NMR spectra of HMBPDANF-II copolymer is shown in Figure 4 and spectral data are presented in Table 3. The weak multiplet signal (unsymmetrical pattern) at $\delta\ 6.6$ ppm, which may due to proton of aromatic ring (Ar-H). The weak signal appears at $\delta\ 7.6$ ppm is attributed to phenolic –OH proton in intramolecular hydrogen bonding (Ar-OH). The presence of singlet in the region $\delta\ 3.5$ ppm reveals the presence of Ar-O-CH₃ proton. The methylenic proton of Ar-CH₂-N linkage may be recognized from signal which appears at $\delta\ 2.5$ ppm. The triplet signal in the region $\delta\ 6.9$ ppm may be due to proton of –NH bridge (Masram DT et. al., 2009 and Kohad CG et. al., 2018).

Scanning Electron Microscopy

The morphology of the synthesized HMBPDANF-II copolymer sample was investigated by scanning electron micrograph at different magnification which is presented in Figure 5. The morphology of copolymer resin shows spherules and fringed model. The spherules are complex polycrystalline formation smooth surface. This indicates the copolymer resin are crystalline in nature. It also shows a fringes model of the amorphous-crystalline structure. The extent of crystalline character depends on the acidic nature of monomer.

Thermogravimetry Analysis of the Copolymer

The thermal degradation curve for HMBPDANF-II copolymer is shown in Figure 6, depicts three steps in decomposition reaction, after loss of water molecule in the temperature range $40\text{ }^{\circ}\text{C}\text{--}700\text{ }^{\circ}\text{C}$. The initially decomposition takes place between $40\text{ }^{\circ}\text{C}\text{--}80\text{ }^{\circ}\text{C}$ corresponds to 2.82 % loss which may be attributed to loss of water molecule against calculated 2.69 % present per repeat unit of the copolymer. The first stage decomposition from $80\text{ }^{\circ}\text{C}\text{--}510\text{ }^{\circ}\text{C}$ which may due to loss of phenolic-OH, –CO-C₆H₅ and –O-CH₃ groups (observed 48.23 % and calculated 48.50 %) attached to aromatic benzene ring. The second step of decomposition from $510\text{ }^{\circ}\text{C}\text{--}560\text{ }^{\circ}\text{C}$ corresponding to 74.98 %, loss of aromatic ring along with two methylene group against calculated 74.55 %. The third step starts from $560\text{ }^{\circ}\text{C}\text{--}620\text{ }^{\circ}\text{C}$ corresponding to removal of naphthalene moiety (99.60% observed and 100% calculated). The half decomposition temperature for copolymer resin is found to be $515\text{ }^{\circ}\text{C}$.

Thermoanalytical Data

A plot of percentage mass loss versus temperature is presented in the Figure 6 for a representative HMBPDANF-II copolymer to obtain the relative thermal stability, the method described by Freeman-Carroll and Sharp- Wentworth were adopted. The thermal stability of copolymer, based on the initial decomposition temperature, has also been used here to define their relative thermal stability, neglecting the degree of decomposition (Gurnule WB et. al., 2017). By applying above methods and using thermal decomposition data, the activation energy (E_a) is calculated which are not perfectly in agreement with each other but the average activation energy (E_a) calculated by Freeman- Carroll and Sharp-Wentworth methods is nearly same. The activation energy calculated by these methods is presented in Table 4.

A representative thermal activation energy plot of Sharp-Wentworth (Figure 7) and Freeman- Carroll (Figure 8, 9) methods for the copolymer have been shown. The parameters such as entropy change (ΔS),

free energy change (ΔF), frequency factor (Z), and apparent entropy change (S^*) calculated on the basis of activation energy (E_a) using equation (3), (4), (6) and (7). These values are given in the Table 5.

(i) Entropy change

$$\text{Intercept} = \log \frac{KR}{h\Phi E_a} + \frac{\Delta S}{2.303R} \dots\dots\dots(3)$$

where,

$K = 1.3806 \times 10^{-16}$ erg/deg/mole,
 $R = 1.987$ cal/deg/mole, $h = 6.625 \times 10^{-27}$ erg sec, $\Phi = 0.166$, $\Delta S =$ change in entropy,
 $E_a =$ Activation energy from graph.

(ii) Free energy change

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

where,

$\Delta H =$ Activation energy ,
 $T =$ Temperature in Kelvin
 $\Delta S =$ Entropy change from equation (3)

(iii) Frequency factor

$$\frac{B_{2/3}}{\frac{\log Z E_a}{R\Phi}} = \dots\dots\dots(5)$$

$$B_{2/3} = \log (3) + \log [1 - 3\sqrt{1 - \alpha}] - \log p(x) \dots\dots\dots(6)$$

where,

$Z =$ Frequency factor,
 $B =$ Calculated from (6),
 $\log p(x) =$ Calculated from Doyle table corresponding to activation energy.

(iv) Apparent entropy change

$$S^* = 2.303R \log \frac{Z h}{RT^*} \dots\dots\dots(7)$$

Where,

$T^* =$ Temperature at which half of the compound decomposed from its total loss
 Fairly good straight line plots are obtained using the two methods. This is expected since the decomposition of copolymer is known not to obey first order kinetics perfectly. Due to abnormally low value of frequency factor, it may be concluded that the decomposition reaction of HMBPDANF-II copolymer can be classed as a slow reaction. There is no other obvious reason (Nandekar KA et. al., 2012 and Bawankar SV et. al., 2015).

CONCLUSION

Copolymer HMBPDANF-II was synthesized by condensation polymerization technique from 2-hydroxy, 4-methoxybenzophenone and 1,5-diaminonaphthalene with formaldehyde in the presence of acid catalyst. The proposed structure of the copolymer has been determined from the physico-chemical analysis, elemental analysis, UV-Visible, FT-IR and $^1\text{H-NMR}$ spectral studies. Activation energy calculated by both Sharp-Wentworth and Freeman-Carroll methods are in good agreement with each other. The negative values for entropy indicate that the activated polymer has more ordered structure than the reactants. Low value of frequency factor may be concluded that the decomposition reaction of copolymer can be classified as slow reaction. Thermogravimetric study concluded that HMBPDANF-II copolymer resin is stable even at high elevation temperature.

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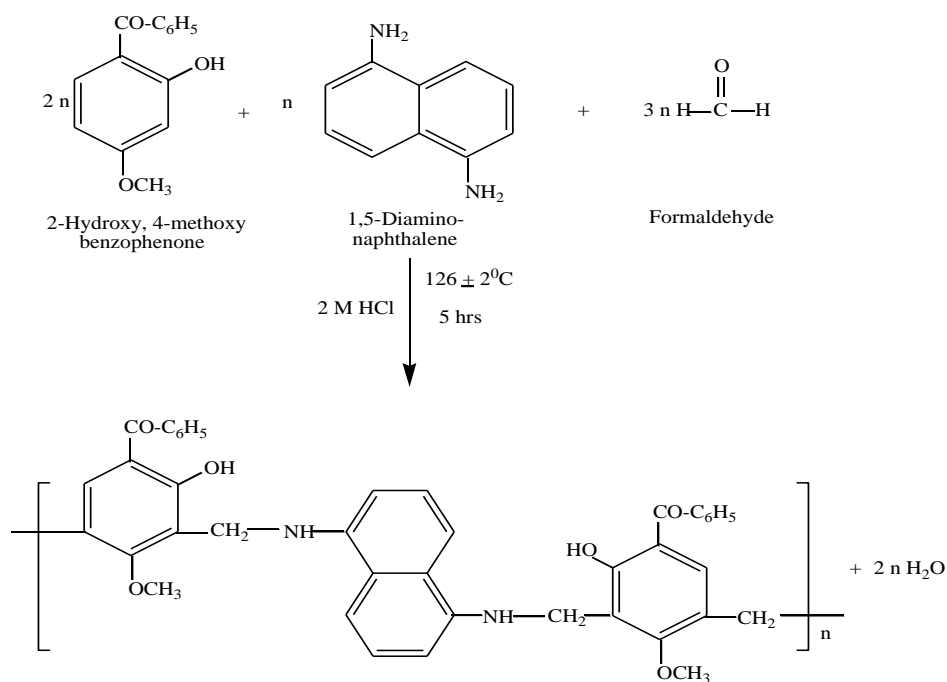


Figure 1. Reaction and suggested structure of HMBPDANF-II copolymer resin

Table 1. Elemental analysis and empirical formula of copolymer resin

Copolymer resin	% of C Observed (cal.)	% of H Observed (cal.)	% of N Observed (cal.)	% of O Observed (cal.)	Empirical Formula of repeated unit	Empirical Formula weight
HMBDAF-II	74.85	5.44	5.01	14.23	$\text{C}_{41}\text{H}_{34}\text{N}_2\text{O}_6$	650
	75.69	5.23	4.30	14.76		

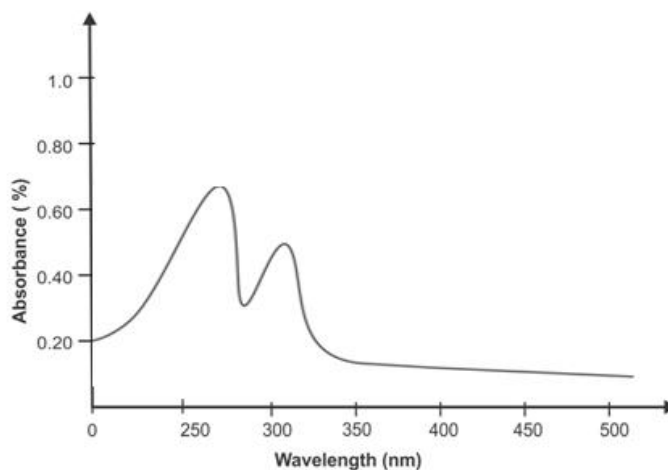


Figure 2. UV-visible spectra of HMBPDANF-II copolymer resin

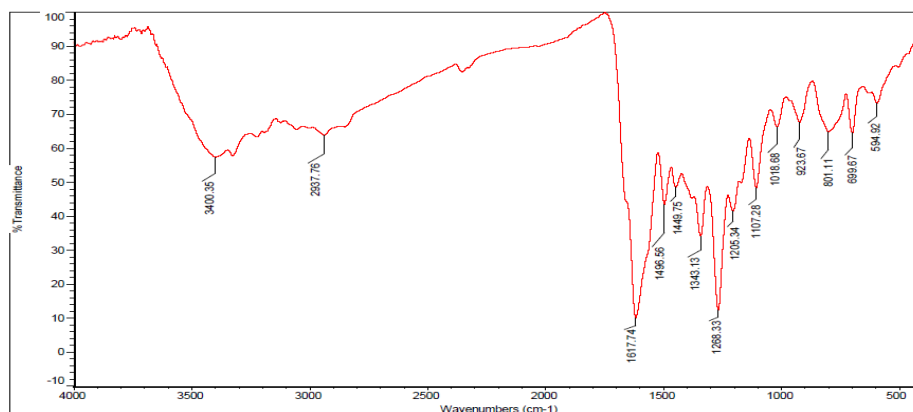


Figure 3. FT-IR spectra of HMBPDANF-II copolymer resin

Table 2: FT-IR data of HMBPDANF-II copolymer resin

Observed band frequencies (cm ⁻¹)	Assignment	Expected band frequencies (cm ⁻¹)
3400(b,st)	-OH phenolic, intramolecular hydrogen bonding	3750 - 3200
2937 (w)	-CH ₂ , -NH, -CH ₃ stretching	3500 - 2800
1449 (m)	Aromatic ring	1445 - 1485
1343(st)	-CH ₂ - bridge	1380 - 1340
1106(st,sh)	Ph-O-CH ₃ , ether linkage	1300 - 1050
1617(sh, st)	>C=O	1670 - 1610
923(m)	1,2,3,4,5-substitution in benzene ring	925 - 860

b= broad, st= strong, sh= sharp, w= weak, m=medium

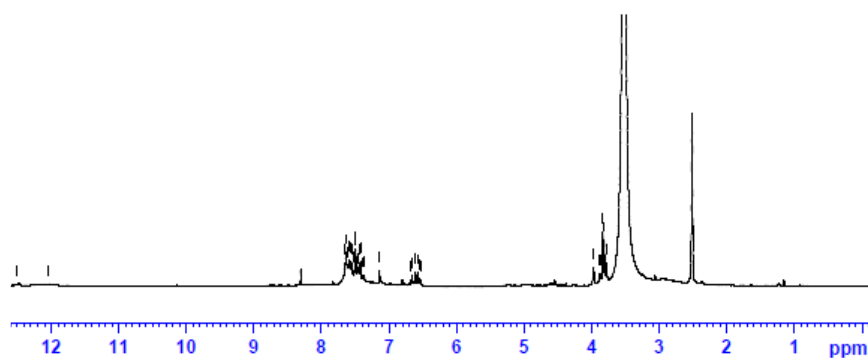


Figure 4. ¹H-NMR spectra of HMBPDANF-II copolymer resin

Table 3. ¹H-NMR data of HMBPDANF-II copolymer resin

Observed chemical shift δ (ppm)	Nature of proton assigned	Expected chemical shift δ (ppm)
7.6(s)	Proton of phenolic -OH involving intramolecular hydrogen bonding	8.0 - 12.0
6.6.(m)	Aromatic proton (Ar-H)	6.2 - 8.5
6.9(t)	Proton of -NH- bridge	5.0 - 8.0
3.5(s)	Proton of Ar-O-CH ₃	3.3 - 4.0
2.5(d)	Methylene proton of Ar-CH ₂ -N	2.0 - 3.5

s= singlet, d= doublet, t=triplet, q= quartet, m=multiplet

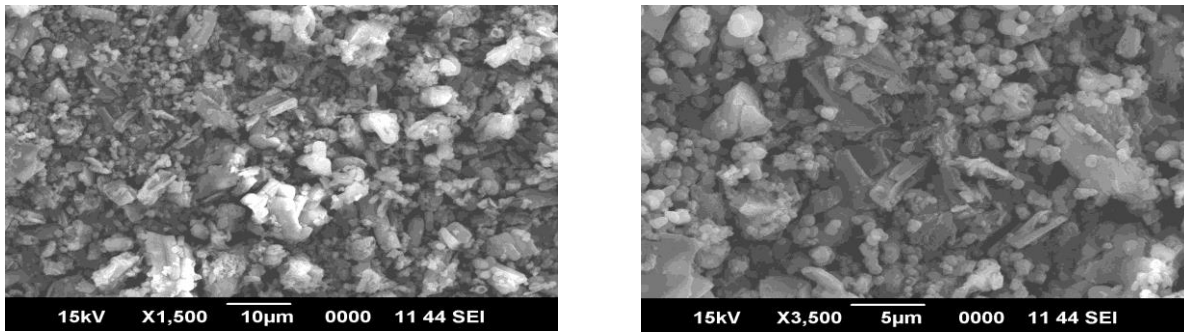


Figure 5. SEM micrograph of HMBPDANF-II copolymer resin

The copolymer exhibits a more amorphous character with closed packed surface having deep pits and the reactivity of active sites buried in the copolymer matrix. The presence of few holes and cracks are noted which may due to air voids (Yeole MM et. al., 2015).

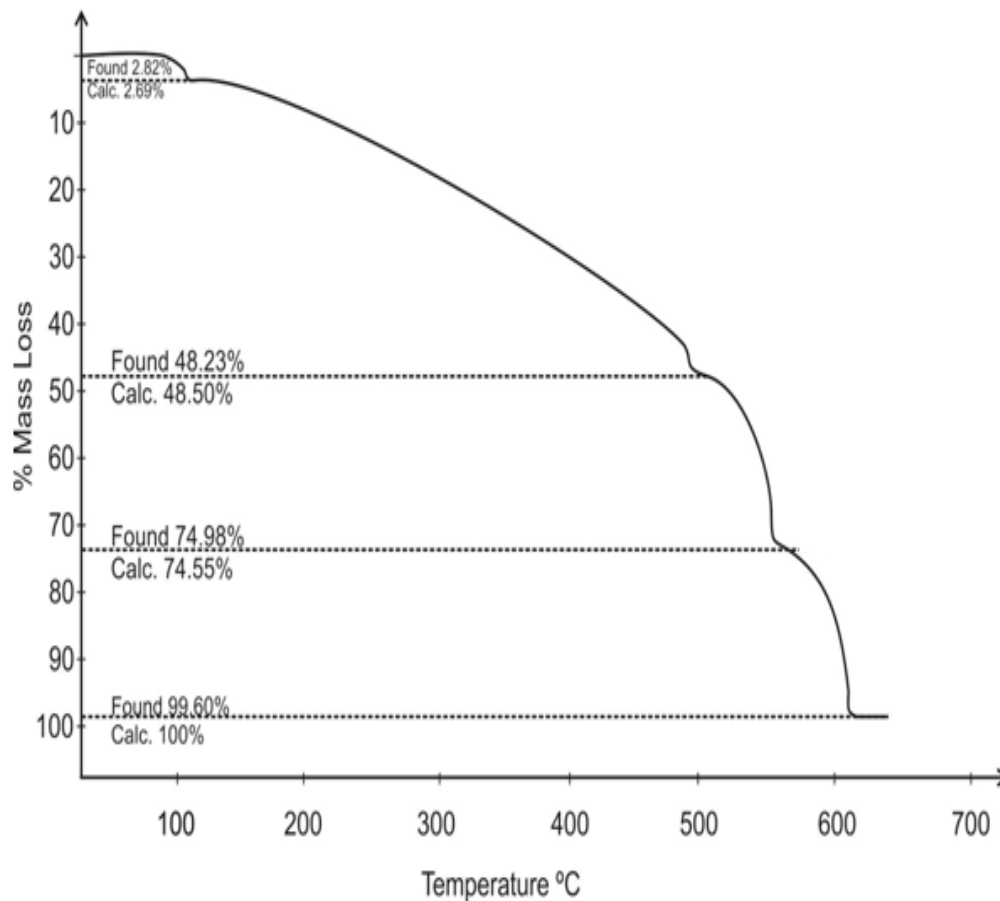


Figure 6. Decomposition pattern of HMBPDANF-II copolymer resin

Table 4. Thermal degradation behavior of HMBPDANF-II copolymer resin and activation energy at different stages

Copolymer resin	Stages	Temperature range (°C)	Group degraded	% Weight loss		Activation Energy KJ/mol	
				Observed	Calculated	FC	SW
HMBPD-ANF-II	First	40 – 80	One water molecule entrped	2.82	2.69	9.91	9.98
	Second	80 – 510	Degradation of COC ₆ H ₅ , -OCH ₃ with-OH group	48.23	48.50	38.48	39.21
	Third	510 – 560	Loss of aromatic ring along with -CH ₂ group	74.98	74.55	56.12	54.46
	Fourth	560 – 620	Loss of Naphthalene moiety	99.60	100	16.27	15.12

Table 5. Results of thermo gravimetric analysis of HMBPDANF-II copolymer resin

Copolymer resin	Half decomposition temperature (T*),°C	Entropy change (ΔS), (J)	Free energy change (ΔF),(KJ)	Frequency factor(Z) (sec ⁻¹)	Apparent entropy (S*), (J)	Order of reaction (n)
HMBPD-ANF-II	515	-232.56	212.24	463.1	-657.03	0.95

FC=Freeman-Carroll, SW= Sharp-Wentworth

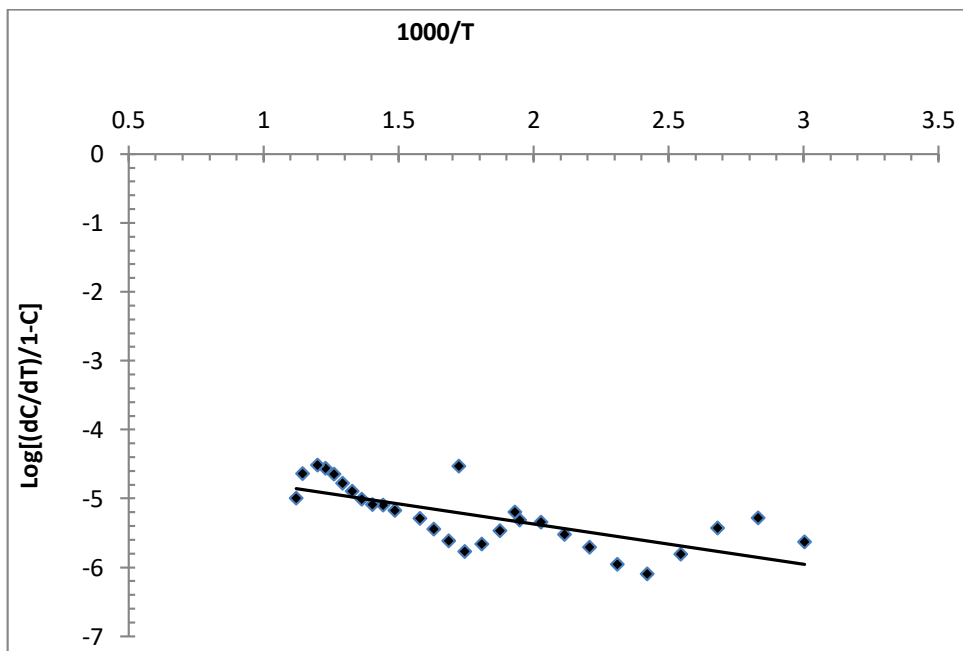


Figure 7. Sharp-Wentworth plot of HMBPDANF-II copolymer resin

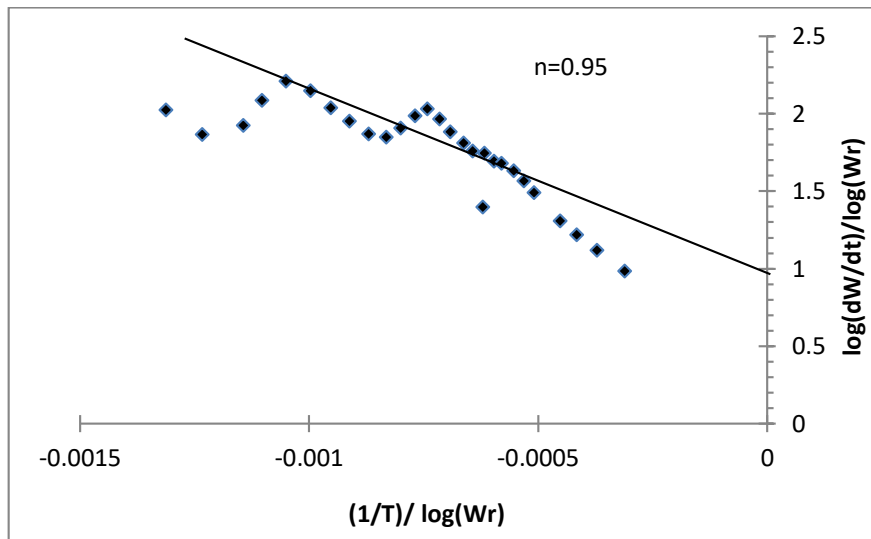


Figure 8. Freeman-Carroll plot of HMBPDANF-II copolymer resin for activation Energy and order of reaction

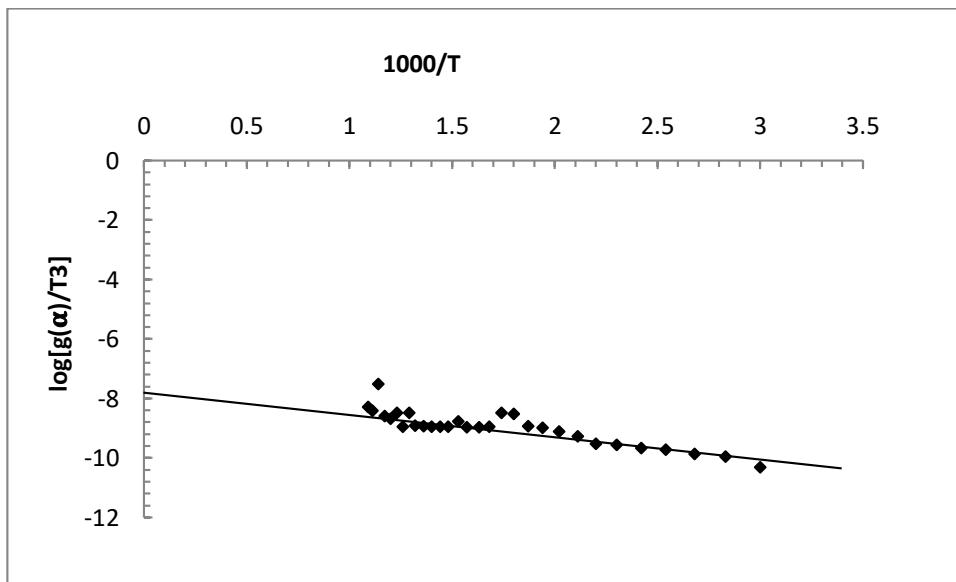


Figure 9. Freeman-Carroll plot of HMBPDANF-II copolymer resin