THERMAL DEGRADATION STUDIES OF COPOLYMER DERIVED FROM 2-HYDROXY, 4-METHOXYBENZOPHENONE, 1,5-DIAMINONAPHTHALENE AND FORMALDEHYDE

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ABSTRACT

Copolymer 2-H, 4-MBP-1,5-DANF-I has been synthesized by the condensation of 2-hydroxy, 4-methoxybenzophenone, 1,5-diaminonaphthalene and formaldehyde in 1:1:2 molar proportions. The structure of copolymer has been characterized by elemental analysis and various physico-chemical techniques i.e. UV-visible absorption spectra, Infrared spectra and proton nuclear magnetic resonance spectra. The morphology of copolymer was studied by scanning electron microscopy (SEM). The thermal decomposition behavior of 2-H, 4-MBP-1,5-DAF-I copolymer has been studied by using TGA in static nitrogen atmosphere at a heating rate of 10 ^{0}C/min. The activation energy (Ea) and thermal stability calculated by using the Sharp-Wentworth and Freeman-Carroll methods. Thermodynamic parameters such as entropy change (ΔS), apparent entropy change (S*), free energy change (ΔF) and frequency factor (Z) have also been evaluated on the basis of TGA curves and by using data of Freeman-Carroll method. The order of reaction (n) was found out to be 0.98.

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

INTRODUCTION

The synthesized copolymer showing numerous applications and properties attracting much attention of scientist [1, 2]. Copolymers resin has been become subjects of interest and are found to be amorphous, crystalline or resinous in nature [3,4]. Phenolic resin have a large number of practical applications in the electronic controls, insulating materials, protective adhesive, aerospace industries etc. because of their high thermal stability, heat and chemical resistance and electrical insulation properties [5-7]. A considerable attention has been paid in the past two decades to the synthesis of copolymer resin due to their exciting features such as high thermal stability. The properties may be profoundly affected by the presence of particular sequence of co-monomers as well as of quite small proportion of additives and have been expensively studied, employing the method of thermo gravimetric analysis by several authors [8, 9]. Terpolymers of 4-hydroxybenzoic acid, thiourea with formaldehyde and 8-hydroxyquinoline, formaldehyde with pyrogallol have been reported in the literature [10, 11]. Jadhao et al. studied the thermal degradation of terpolymer resins derived from 2, 2-dihydroxy biphenyl, urea and formaldehyde [12].

Michael and coworker studied the synthesis, characterization and thermal degradation of 8-hydroxyquinoline, guanidine with formaldehyde terpolymer [13]. Thermal degradation of salicylic acid, ethylenediamine and formaldehyde has been studied by Masram et al. [14]. Belsare et al. studied the thermal degradation of terpolymer derived from 2-aminophenol, hexamethyenediamine with formaldehyde [15]. Hung et al. synthesized and studied the kinetics of thermal degradation of thermotropic (p-oxybenzoate-co-ethylene terephthalate) [16]. M. Karunakaran and C. Mangesh, synthesized copolymer by condensation of o-cresol and biuret with formaldehyde and TGA analysis was employed to study the thermal stability and kinetic data like activation energy of the copolymer resins [17].

However the literature studies have revealed that no copolymer has been synthesized using monomer of 2-hydroxy, 4-methoxybenzophenone, 1, 5-diaminonaphthalene and formaldehyde. The present paper deals with the synthesis, structural, characterization and thermal degradation studies of 2-H, 4-MBP-1, 5-DANF-I copolymer. Methods for the estimation of kinetic parameters from thermo gravemetric studies are generally based on the assumption that the Arrhenius equation is valid with thermal and diffusion barriers are negligible. 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).

EXPERIMENTAL

Materials

The important chemicals (starting materials) like 2-hydroxyl, 4-methoxybenzophenone (Sigma Aldrich, India), 1,5-diaminonaphthalene (Himedia, India) and formaldehyde (S. D. Fine Chemicals, India) were procured from market and were of chemically pure grade. All the used solvents like N, N-dimethyl formamide, dimethyl sulphoxide, tetrahydrofuran, acetone and diethyl ether were purchased from Merck, India.

Synthesis of 2-H, 4-MBP-1, 5-DAF-I copolymer

The new copolymer 2-H, 4-MBP-1, 5-DANF-I was synthesized by condensing 2-hydroxy, 4-methoxybenzophenone

(2.2824 g, 0.1mol) and 1, 5-diaminonaphthalene (1.5820 g, 0.1mol) with formaldehyde (7.5 ml, 0.2 mol) in a molar

ratio 1:1:2 in the presence of 2M, 200 ml HCl as a catalyst at 126 ± 2 ^{0}C for about 5 hrs. in an oil bath with occasional shaking to ensure thorough mixing. The separated brown color 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 along with 2-H, 4-MBP-1, 5-DANF-I copolymer.

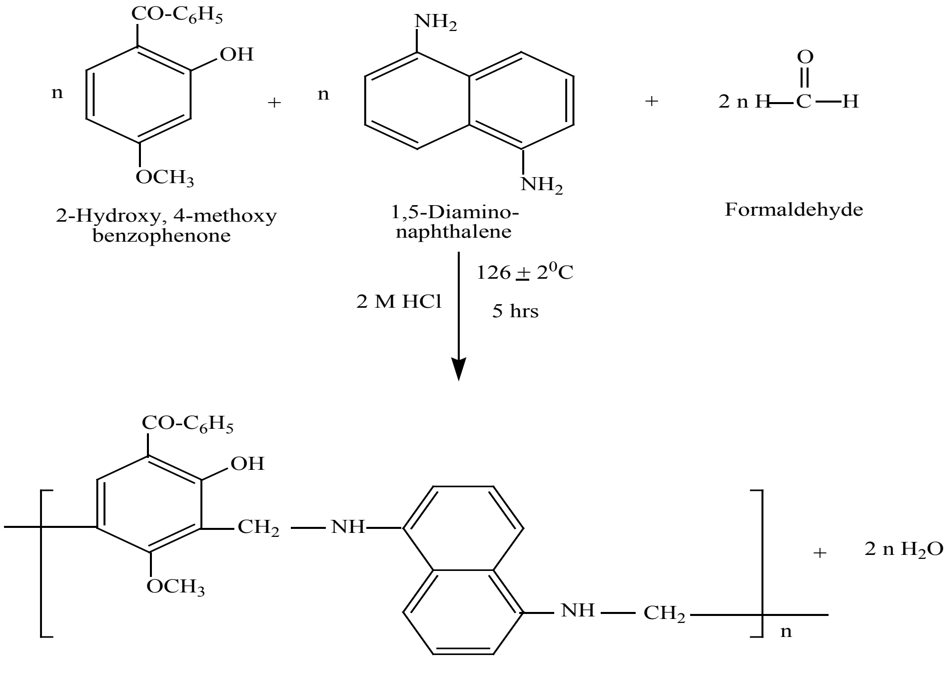

Figure 1. Synthesis of 2-H, 4-MBP-1,5-DANF-I copolymer resin

It was further purified by dissolving in 8% NaOH and then filtered. The copolymer was then reprecipitated by drop wise addition of 1:1 (v/v) con. HCl/water with constant and rapid stirring to avoid lumping formation. The process of reprecipitation was repeated twice. The copolymer sample thus obtained was filtered, washed several times with hot water, dried in a vacuum at room temperature. 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 82% .The reaction and suggested structure of 2-H, 4-MBP-1, 5-DANF-I has been depicted in figure 1.

Analytical and physico-chemical studies

The elemental analysis was carried out on Elemental Vario EL III Carlo Erba1108 elemental analyzer instrument. The electronic absorption spectra (UV-visible) of the copolymer in DMSO was recorded on double beam spectrophotometer fitted with automatic pen chart recorder on thermo sensitive paper in the range of 200-800 nm. Infrared spectra of copolymer was carried out in najol mull on Perkin-Elmer-Spectrum RX-I, FT-IR spectrophotometer in KBr pellets in the range of 4000-500 cm^{-1}. Proton NMR spectrum was recorded on Bruker Advance –II 400 MHz NMR spectrophotometer using DMSO-d_6 as a solvent.

The surface analysis was performed using scanning electron microscope at different magnifications. SEM has been scanned by a JEOL JSM-6380, an analytical scanning electronic microscope. The TGA of the copolymer has been carried out using Perkin Elmer diamond TGA/DTA analyzer. All the analytical and spectral studies for the newly synthesized copolymer were carried out at sophisticated analytical instruments facility SAIF, Cochin University, Cochin, India.

Thermal studies

Thermal analysis method is associated with a change in weight with respect to temperature. Heating is performed under strictly controlled conditions and can reveal changes in structure and other important properties of the material being studied. 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 air atmosphere with heating rate at 10 $^0C\ min^{-1}$ using 5-6 mg of samples in platinum crucible from temperature of 40 ^0C to 800 ^0C and thermogram is recorded for 2-H, 4-MBP-1, 5-DANF-I. With the help of thermogravimetric data the thermal activation energies (Eà) and order of reaction (n) calculated. Also the other thermodynamic parameters such as 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 [18],

$$\log\frac{dC/dT}{1-C}=\log(A/\beta)-\frac{Ea}{2.303R}\cdot\frac{1}{T} \quad \text{………………}(1)$$

where,

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

β = linear heating rate dT/dt.

The graph of $\log\frac{dC/dT}{1-C}$ versus $\frac{1}{T}$ has been plotted. The graph is a straight line with activation energy (Ea) 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 [19], which is in the form of

$$\frac{\Delta\log(dW/dt)}{\Delta\log Wr}=n-\frac{Ea}{2.303R}\frac{\Delta(1/T)}{\Delta\log Wr} \quad \text{………………}(2)$$

where,

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

Wr = Wc-W

Wc = weight loss at completation of reaction.

W = fraction of weight loss at time t.

E_a = energy of activation.

n = order of reaction.

The plot between the terms $\frac{\Delta\log(dW/dt)}{\Delta\log Wr}$ versus $\frac{\Delta(1/T)}{\Delta\log Wr}$ gives a straight line. The slope, -Ea/2.303R, gives energy of activation (Ea) 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.

RESULTS AND DISCUSSION

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

Elemental analysis

The 2-H, 4-MBP-1,5-DANF-I copolymer was analyzed for the carbon, hydrogen and nitrogen content. The composition of copolymer obtained on the basis of elemental analysis data was found to be in good correlation which is presented in table1.

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
2-H,4-MBP-1,5-DAF-I	75.03 76.09	5.11 5.36	6.42 6.82	12.04 11.70	$C_{26}H_{22}N_2O_3$	410

Molecular weight by non-aqueous conductometric titration

Number average molecular weight $\overline{Mn}$ of the copolymer has been determined by conductometric titration method in non-aqueous medium and using standard potassium hydroxide (0.05N) in absolute ethanol as a titrant.

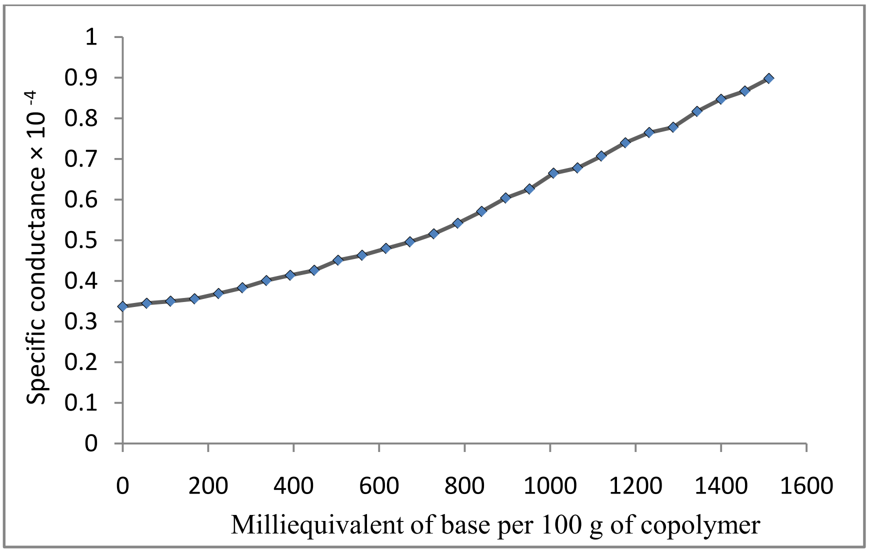

Figure 2. Conductometric titration curve of 2-H, 4-MBP-1, 5-DANF-I copolymer resin

The specific conductance was plotted against milliequivalents of ethanolic KOH required for neutralization of 100g of each copolymer. Inspection of such a plot revealed the number of breaks in the plot. The first break at 392 milliequivalents of base and the last break at 1288 milliquivalents of base were noted and which has been depicted in figure 2. The calculation of $\overline{Mn}$ by this method is based on the following considerations; (1) The first break corresponds to neutralization by more acidic phenolic hydroxyl group of all the repeating units; (2) The break in the plot beyond which a continuous increase is observed represents the stage at which phenolic hydroxyl group of all the repeating units are neutralized [20]. On the basis of the average degree of polymerization ($\overline{DP}$), the number average molecular weight has been determined by the following relations

$$(\overline{DP}) = \frac{\text{Total milliequivalents of base for complet neutralization}}{\text{Milliequivalents of base required for smaller intervals}}$$

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

The results are incorporated in the table 2.

Table 2. Determination of number average molecular weight of 2-H, 4-MBP-1, 5-DANF-I copolymer resin

Copolymer resin	First stage of neutralization (Meq./100 g sample)	Final stage of neutralization (Meq./100 g sample)	Degree of polymerization ($\overline{DP}$)	Empirical formula weight (n)	Number average molecular weight $\overline{\text{Mn}}$
2-H,4-MBP-1,5-DAF-I	392	1288	3.28	410	1344

UV-visible spectra

The uv-visible spectra (figure 3) of 2-H, 4MBP-1, 5-DANF-I copolymer sample has been recorded in pure DMSO in the region 190-800 nm. The spectra displayed two characteristics broad band at 280 nm and 330 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 (more intense) can be account for n→π* electronic transition. The shift from basic value (viz. 240 nm and 310 nm respectively) may be due to conjugation effect and presence of phenolic hydroxyl group (auxochrome) is responsible for hyperchromic effect i.e. ∈ max higher value.

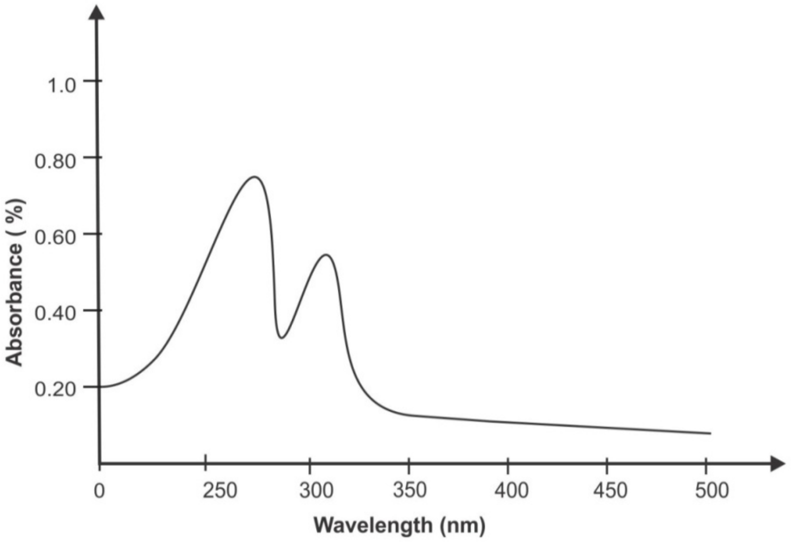

Figure 3. UV-visible spectra of 2-H, 4-MBP-1, 5-DANF-I copolymer resin

FT-IR Spectra

Infrared spectra of 2-H, 4-MBP-1, 5-DANF-I copolymer resin is shown in figure 4 and IR spectral data are tabulated in table 3. The assignment of vibration frequency is based on the data available in the literature. A very broad and strong band appeared at 3325 cm^{-1} may be due to the stretching vibration of the phenolic hydroxyl group exhibiting intramolecular hydrogen bonding –NH group. The strong band observed at 2936 cm^{-1} may be assigned to the stretching vibrations of –NH (imide). A sharp and strong band at 1619 cm^{-1} may be assigned to the stretching vibration of >C=O group. The strong band obtained at 1107 cm^{-1} region is attributed to the Ph-O-CH_3 ether linkage. The weak band at 1344 cm^{-1} may be due to –CH_2 methylene bridge. The presence of 1, 2, 3, 4, 5-pentasubtituted aromatic ring is recognized from the weak band appearing in the region 905-860 cm^{-1} [21].

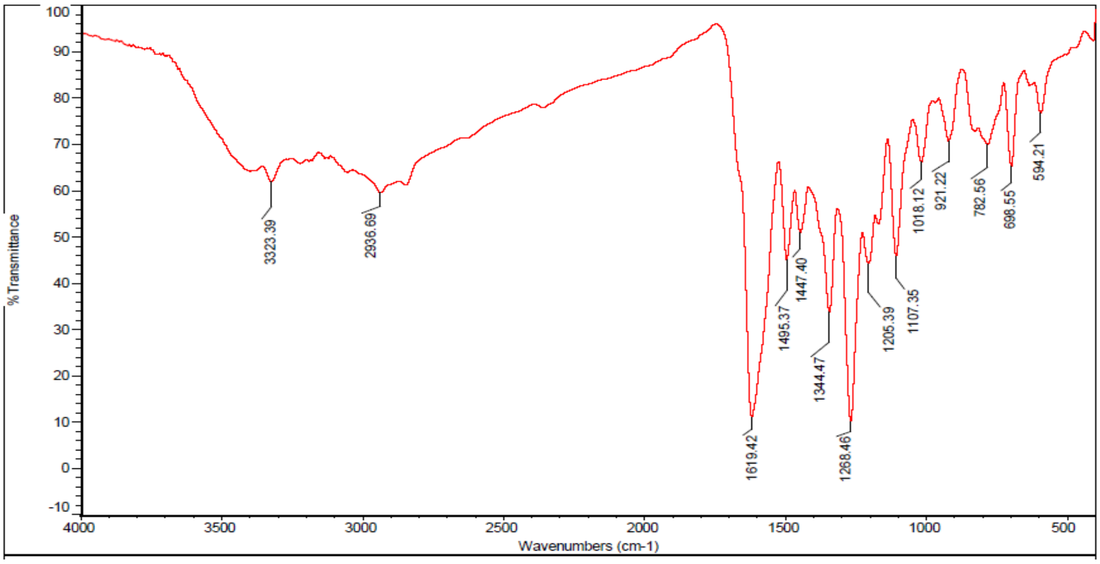

Figure 4. FT-IR spectra of 2-H, 4-MBP-1,5-DANF-I copolymer resin

Table 3: FT-IR data of 2-H, 4-MBP-1, 5-DANF-I copolymer resin

Observed band frequencies (cm^{-1})	Assignment	Expected band frequencies (cm^{-1})
3325(b,st)	-OH phenolic, intramolecular hydrogen bonding	3750 - 3200
2936 (w)	$-CH_2$,-NH, $-CH_3$stretching	3500 - 2800
1447 (m)	Aromatic ring	1445 - 1485
1344(st)	$-CH_2$- bridge	1380 - 1350
1107(st,sh)	Ph-O-CH_3, ether linkage	1300 - 1050
1619(sh, st)	>C=O	1670 - 1630
1018(m)	1,2,3,4,5-substitution in benzene ring	905-860

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

^{1}H-NMR Spectra

The ^{1}H-NMR Spectra of 2-H, 4-MBP-1,5-DANF-1 copolymer is presented in figure 5 and spectral data are given in tablel 4. The weak multiplet signal (unsymmetrical pattern) in the region at δ 7.6 ppm, which may due to proton of aromatic ring (Ar-H).

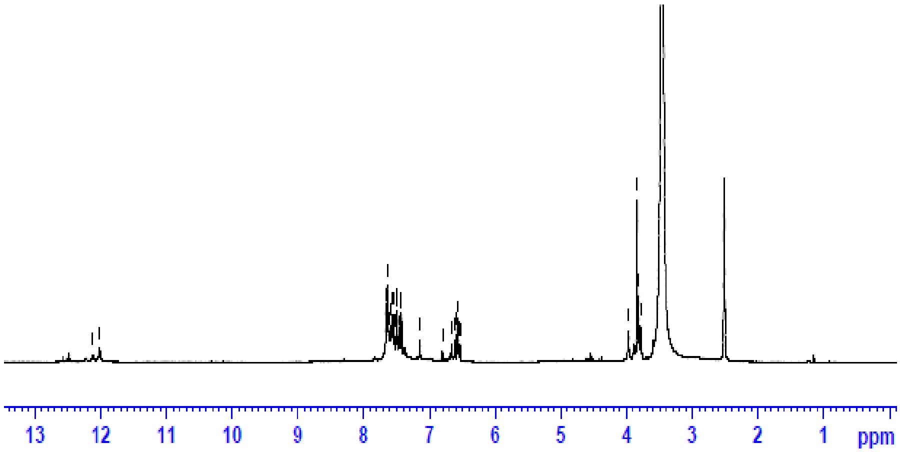

Figure 5. ^{1}H-NMR spectra of 2-H, 4-MBP-1,5-DANF-I copolymer resin

The weak signal in the region δ 7.7 ppm is attributed to phenolic –OH proton in intramolecular hydrogen bonding (Ar-OH). The presence of singlet at δ 3.4 ppm reveals the presence of Ar-O-CH_3 proton. The methylenic proton of Ar-CH_2-N linkage may be recognized from signal which appears in the region of δ 3.8 ppm. The triplet signal in the region δ 6.7 ppm may be due to proton of –NH bridge [22].

Table 4.^{1}H-NMR data of 2-H, 4-MBP-1,5-DANF-I copolymer resin

Observed chemical shift δ (ppm)	Nature of proton assigned	Expected chemical shift δ (ppm)
7.7(s)	Proton of phenolic –OH involving intramolecular hydrogen bonding	8.0 - 12.0
7.6.(m)	Aromatic proton (Ar-H)	6.2 - 8.5
6.7(t)	Proton of –NH- bridge	5.0 - 8.0
3.4(s)	Proton of Ar-O-CH_3	3.3 - 4.0
3.8(d)	Methylene proton of Ar-CH_2-N	2.0 - 3.5

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

Scanning Electron Microscopy

Surface analysis has found great use in understanding the surface features of the materials. The morphology of the newly synthesized copolymer sample was investigated by scanning electron micrograph at different magnification which is shown in figure 6. The morphology of copolymer resin shows spherules and fringed model. The spherules are complex polycrystalline formation smooth surface. This indicates the 2-H, 4-MBP-1, 5-DAF-I 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. 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 [23].

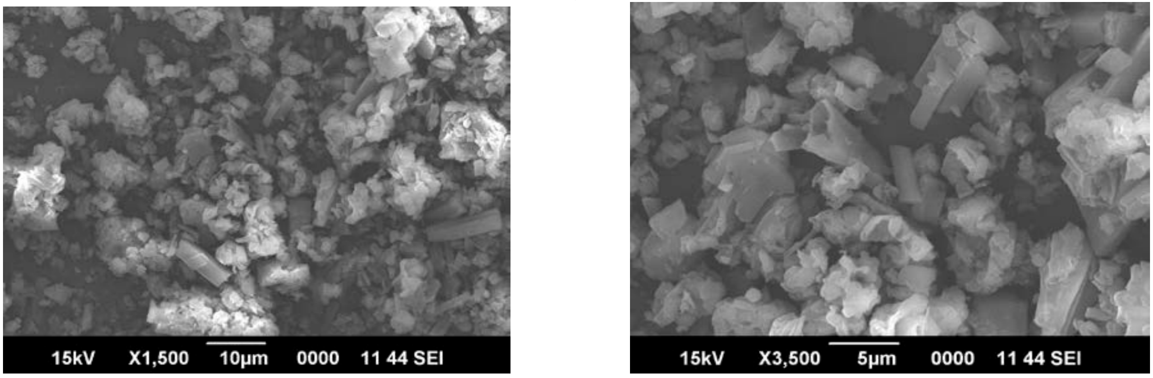

Figure 6. SEM micrograph of 2-H, 4-MBP-1, 5-DANF-I copolymer resin

Thermogravimetry analysis of the copolymer

The thermal degradation curve for copolymer 2-H,4-MBP-1,5-DANF-1 is shown in figure 7, depicts three steps in decomposition reaction, after loss of water molecule in the temperature range 40 ^{0}C-700 ^{0}C. The initially decomposition take place between 40 ^{0}C-190 ^{0}C corresponds to 4.08% loss which may be attributed to loss of water molecule against calculated 4.20% present per repeat unit of the polymer. The first stage decomposition from 190 ^{0}C – 480 ^{0}C which may due to loss of phenolic -OH, -CO-C_6H_5 and -O-CH_3 groups (observed 39.97% and calculated 39.95%) attached to aromatic benzene ring. The second step of decomposition starts from 480^{0}C-510 ^{0}C corresponding to 63.812% loss of aromatic ring along with two methylene group against calculated 63.08%. The third step starts from 510 ^{0}C – 640 ^{0}C corresponding to removal of naphthalene moiety (98.23% observed and 99.53% calculated). The half decomposition temperature for copolymer resin is found to be 510 ^{0}C.

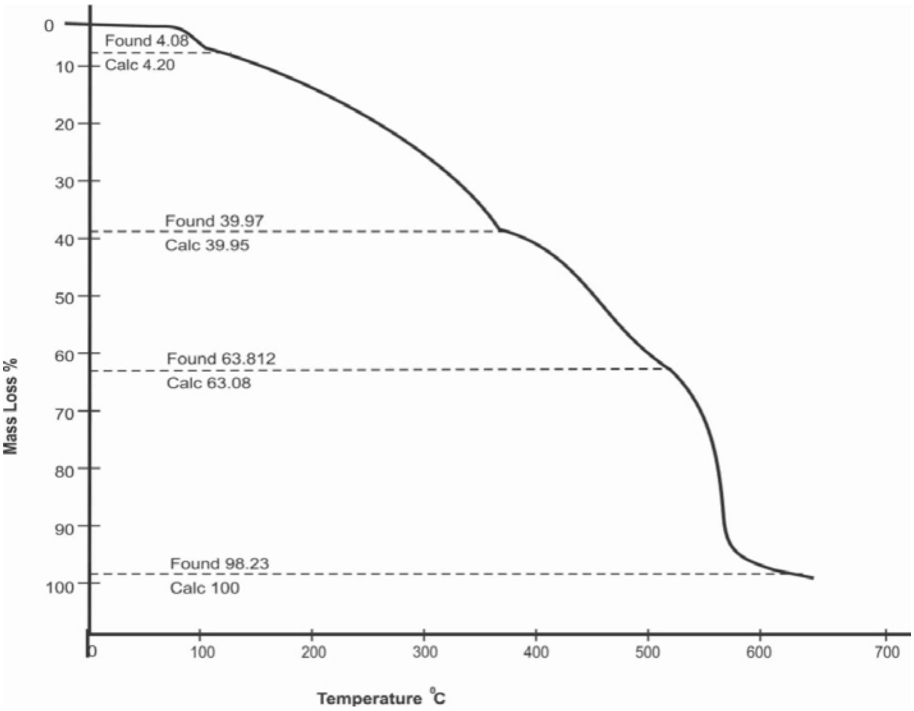

Figure7. Decomposition pattern of 2-H, 4-MBP-1,5-DANF-I copolymer resin

Table 5. Thermal degradation behavior of 2-H, 4-MBP-1, 5-DANF-I copolymer resin and activation energy at different stages

Copolymer resin	Stages	Temp range ^{0}C	Group degraded	% Weight loss		Activation energy ,KJ/mol	
				Observed	Calc .	FC	SW
	First	40-190	H_2O molecule entrapped	4.08	4.20	22.73	22.62
2-H,4-MBP -1,5-DANF-I	Second	190-480	Degradation of $-COC_6H_5$, $-OCH_3$ with–OH group	39.97	39.95	21.99	21.52
	Third	480-510	Loss of aromatic ring along with $-CH_2$ group	63.81	63.08	42.12	42.61
	Fourth	510-640	Loss of naph-thalene moiety	98.23	99.53	28.72	29.48

Thermoanalytical data

A plot of percentage mass loss versus temperature is shown in the figure 6 for a representative 2-H,4-MBP-1,5-DANF-1 to obtain the relative thermal stability of the copolymer, the method described by Sharp-Wentworth and Freeman-Carroll was adopted. The thermal stability of copolymer, based on the initial decomposition temperature, has also been use here to define their relative thermal stability, neglecting the degree of decomposition. By using thermal decomposition data and then applying above methods the activation energy (Ea) is calculated which are not perfectly in agreement with each other but the average (Ea) calculated by Freeman- Carroll and Sharp-Wentworth methods is nearly same. The activation energy calculated by these methods is depicted in Table 5. A representative thermal activation energy plot of Sharp-Wentworth (figure 8) and Freeman- Carroll (figure 9, 10) methods for the copolymer have been shown. Thermodynamic parameters such as entropy change (ΔS), free energy change (Δ F), frequency factor (Z), and apparent entropy change(S*) calculated on the basis of thermal activation energy (Ea) using equation (3), (4), (6) and (7). These values are given in the table 6.

(i) Entropy change

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

where,

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

$R = 1.987$ cal/deg/mole,$h = 6.625 \times 10^{-27}$ erg sec, $\Phi = 0.166$, ΔS = change in entropy,

Ea= activation energy from graph.

(ii) Free energy change

$$\Delta F=\Delta HT\Delta S\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

where,

ΔH = activation energy ,

T = temperature in Kelvin

ΔS = entropy change from equation (3)

(iii) Frequency factor

$$B_{2/3}=\frac{\log ZEa}{R\Phi}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

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

where,

Z= Frequency factor,

B= Calculated from (6),

log p(x)= Calculated from Doyle table corresponding to activation energy.

(iv)Apparent entropy change

$$S^*=2.303R\log\frac{Zh}{RT*}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

Where,

T^* = Temperature at which half of the compound decomposed from its total loss

Due to abnormally low value of frequency factor, it may be concluded that the decomposition reaction of 2-H,4-MBP-1,5DANF-I copolymer can be classed as a slow reaction. There is no other obvious reason. 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 [24].

Table 6. Result of thermo gravimetric analysis of 2-H, 4-MBP-1, 5-DANF-I copolymer resin

Copolymer resin	Half decomposition temperature (T*),^{0}C	Entropy change (ΔS), (J)	Free energy change (ΔF),(KJ)	Frequency factor(Z) (sec^{-1})	Apparent entropy (S*),(J)	Order of reaction (n)
2-H, 4-MBP-1, 5-DANF-I	510	-82.03	64.26	112.0	-124.17	0.98

FC=Freeman-Carroll, SW= Sharp-Wentworth

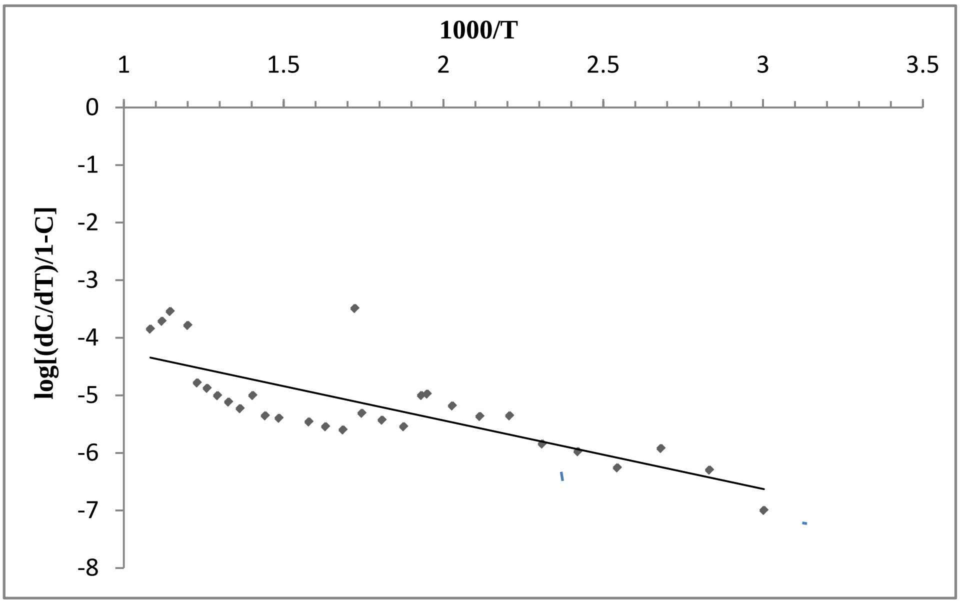

Figure 8. Sharp-Wentworth plot of 2-H, 4-MBP-1,5-DANF-I copolymer resin

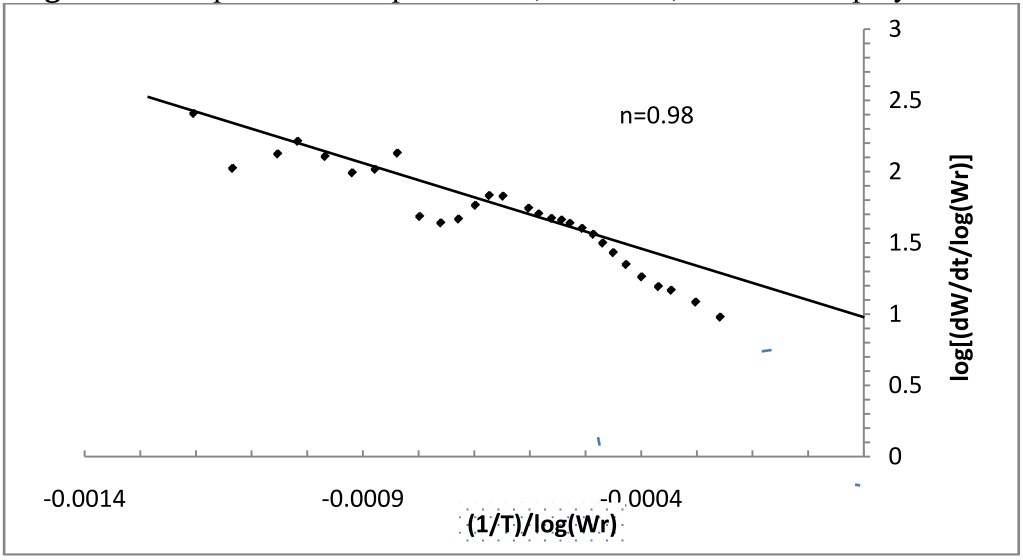

Figure 9. Freeman-Carroll plot of 2-H, 4-MBP-1,5-DANF-I copolymer resin for activation energy order of reaction

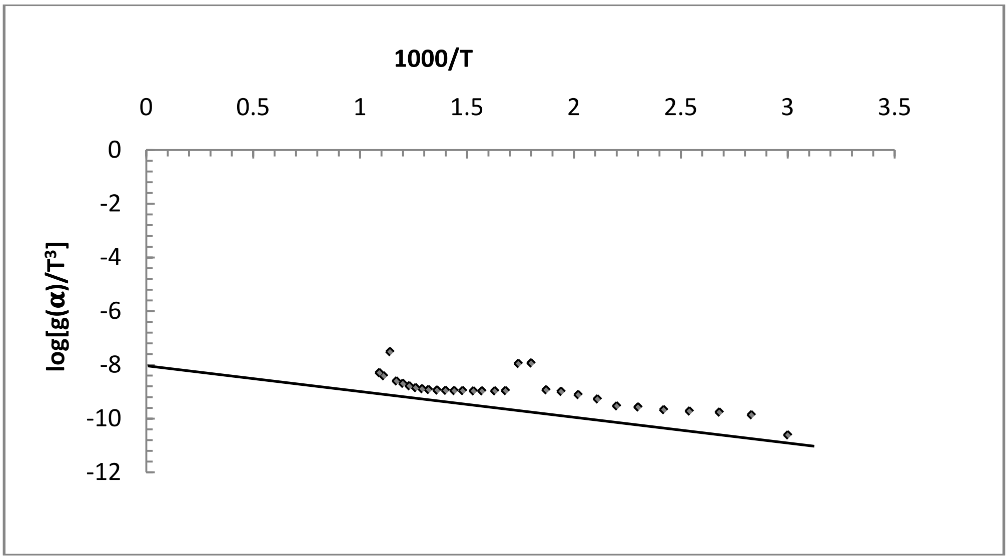

Figure 10. Freeman-Carroll plot of 2-H, 4-MBP-1,5-DANF-I copolymer resin

CONCLUSION

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

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