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Kinetics study of thermal degradation of resin derived from 1-naphthol-4-sulphonic acid, hexamethylene diamine and formaldehyde

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ABSTRACT

The novel terpolymer (1-N-4-SAHDF-Resin-II) has been synthesized by polycondensation of 1-Naphthol-4-sulphonic acid and Hexamethylene diamine with Formaldehyde in an acidic medium with molar proportion of reactants (2:1:3). To reveal the structure of the resin, the resin was characterized by elemental analysis and a spectral method, i.e. composition of terpolymer has been determined on the basis of its elemental analysis. The terpolymer resin has been characterized by FT-IR, NMR (^{1}H & ^{13}C) spectra and by SEM. For thermal decomposition studies, 1-N-4-SAHDF-Resin-II terpolymer has been studied by Thermo Gravimetric Analysis (TGA) at heating rate 10°C min-1 under nitrogen atmosphere. Detailed thermal degradation studies of the 1-N-4-SAHDF-Resin-II terpolymer has been carried out to ascertain its thermal stability. Thermal degradation plot has been discussed in order to determine their mode of decomposition, order of reaction(n), thermal activation energy(Ea), frequency factor(Z), free energy change(ΔF), entropy change(ΔS). Freeman – Carroll and Sharp- Wentworth methods have been applied for the calculation of kinetic parameters while the data from the Freeman – Carroll method has been used to determine various thermodynamic parameters. Thermal activation energy (Ea) values determined by these two methods were in good agreement with each other.

Keywords: Polycondensation, Resins, Semiconductor, Synthesis ,Thermogravimetric analysis

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INTRODUCTION

The synthesized terpolymer resins, showing versatile applications and properties, attracted the attention of scientist and introduce the recent innovations in the polymer chemistry. These terpolymers can be used as high energy material [1], ion-exchanger [2], semiconductors[3], antioxidants, fire proofing agent, optical storage data, binders, molding materials *etc*. Literature survey reveals the chelating ion-exchange properties of 2,4-dinitrophenylhydrazone of 2-hydroxyacetophenone-formaldehyde resin [4] and oximes of 2-hydroxyacetophenone-substituted benzoic acid-formaldehyde resin [5] for different metal ions. Thermogravimetric analysis of urea formaldehyde polycondensate (UFPS) has been reported by Zeman and Tokarova [6]. Terpolymer resins having good thermal stability have enhanced the scope for development of some polymeric materials. The study of the thermal degradation of terpolymer resins have recently become a subject of interest. Zhao Hong *et al*. studied the thermal decomposition behaviour of phosphorous containing copolystar[7]. In an earlier communication [8], [9], [10], [11] from this department numbers of studies on such terpolymers have been reported. However no work seems to have been carried out on thermo analytical and kinetic studies of the terpolymer resins from 1-Naphthol-4-sulphonic acid and Hexamethylene diamine with formaldehyde. The present paper explores the thermal analysis giving their relative thermal stabilities by applying the Sharp-Wentworth and Freeman-Carroll methods. Energy of activation (Ea), Kinetic parameter *viz*. Z, DS, DF, S*, and order of reaction (*n*) were determined by applying Freeman-Carroll Method.

EXPERIMENTAL SECTION

2.1 Materials

The chemicals used in the synthesis of new terpolymer 1-N-4-SAHDF-Resin-II were procured from the market and were Sigma-Aldrich or chemically pure grade. Whenever required they were further purified by standard procedure.

2.2 Synthesis of 1-N-4-SAHDF-Resin-II terpolymer

The new terpolymer 1-N-4-SAHDF-Resin-II was synthesized by condensing 1-Naphthol-4-sulphonic acid (0.2 mol) and Hexamethylene diamine (0.1 mol) with 37% formaldehyde (0.3 mol) in a mol ratio of 2:1:3 in the presence of 200 ml 2M HCl as a catalyst at 140°C ± 20°C for 6h in an oil bath with occasional shaking to ensure thorough mixing. The separated terpolymer was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove 1-Naphthol-4-sulphonic acid formaldehyde copolymer which might be present along with 1-N-4-SAHDF-Resin-II terpolymer. The reddish brown coloured powdery product was immediately removed from the flask as soon as reaction period was over and then purified. The reaction and suggested structure of 1-N-4-SAHDF-Resin-II in shown in Fig. 1.

The terpolymer was purified by dissolving in 10% aqueous sodium hydroxide solution, filtered and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v) concentrated hydrochloric acid / distilled water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated twice. The terpolymer sample 1-N-4-SAHDF-Resin-II thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desiccators over silica gel. The yield of the terpolymer resin was found to be 75%.

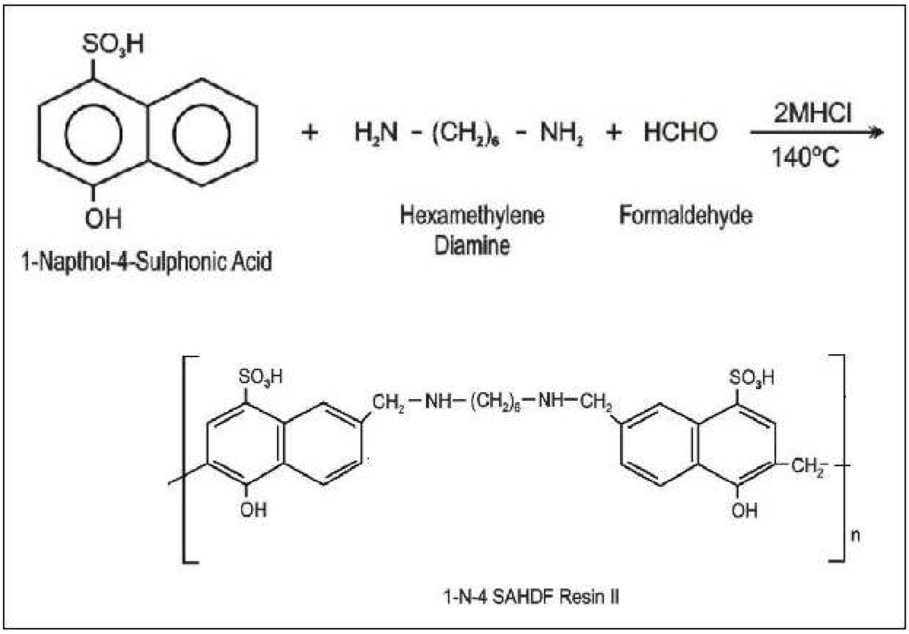

Figure1: Reaction and suggested structure of representative 1-N-4-SAHDF-Resin-II terpolymer

2.3 Characterization:

1-N-4-SAHDF-Resin-II terpolymer resin was subjected to microanalysis for C, H, S and N at STIC, Cochin. The number average molecular weight (Mn) was determined by conductometric titration in non aqueous medium such as dimethylsulphoxide (DMSO) using ethanolic KOH as a titrant. From the graph of specific conductance against milliequivalents of base, first and last break were noted from which degree of polymerization (DP) and the number average molecular weight (Mn) has been calculated for terpolymer resin under investigation. An infra-red spectrum of 1-N-4-SAHDF-Resin-II was recorded on Perkin-Elmer-R-XR Spectrophotometer in KBr pallets in the wave number region of 4000-400 cm^{-1} at Sophisticated Analytical Instrumentation Facility (SAIF), Punjab University; Chandigarh. Both ^{1}H & ^{13}C NMR spectrum of newly synthesized terpolymer resin has been scanned on Bruker Avance II 400 MHz NMR spectrometer using DMSO-d6 at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. SEM has been scanned by FEI-Philips XL-30 electron microscope at STIC, Cochin.

2.4 THERMOGRAVIMETRIC ANALYSIS

The non-isothermal thermogravimetric analysis was performed in air atmosphere with heating rate of 10 °C .min-1 from temperature range of 50 0C to 1000 0C using Perkin Elmer Diamond 3 II thermogravimetric analyzer in Nitrogen environment. The thermograms were recorded at VNIT, Nagpur. 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. A plot of percentage mass loss versus temperature i.e. thermogram is shown in the Fig. 6 for a representative 1-N-4-SAHDF-Resin-II. From the TG curves, the thermoanalytical data and the decomposition temperatures were determined for different stages. To obtain the relative thermal stability of the terpolymer, the method described by Sharp-Wentworth and Freeman- Carroll adopted.

RESULT AND DISCUSSION

Newly synthesized, purified 1-N-4-SAHDF-Resin-II was found to be amorphous and reddish brown in colour. The terpolymers are soluble in solvents such as DMF, DMSO, THF and aq. NaOH while insoluble in almost all other organic solvents. The resin synthesize did not show sharp melting point but undergo decomposition above 240°C .These resins were analyzed for carbon, hydrogen, nitrogen and sulphur content. The Mn of the terpolymer resin was determined by non-aqueous conductometric titration in DMSO against KOH in 50% (v/v) DMSO-Alcohol mixture using 100mg of resin sample. A plot of specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100 g of terpolymer was made. Inspection of such a plot revealed that there are many breaks in plot. From this plot the first break and the last break were noted. The calculation of (Mn) by this method is based on the following considerations. (1) The first break corresponds to neutralization of the more acidic phenolic hydroxy group of all the repeating units and (2) the break in the plot beyond which a continuous increase in conductance is observed represents the stage at which phenolic hydroxyl group of all repeating units are neutralized. On the basis of the average, degree of polymerization (DP) is given by the following relation.

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

(Mn) = (DP) X Repeat unit weight

On the basis of degree of polymerization (DP), the average number molecular weight (Mn) is calculated by multiplying the (DP) by the formula weight of repeating unit [12]. The details of Elemental analysis, molecular weight determination are incorporated in Table 1.

Table 1: Elemental analysis and molecular weight determination of 1-N-4-SAHDF-Resin-II

Empirical formula of repeat unit	Carbon%	Hydrogen %	Nitrogen%	Sulphur%	Empirical weight of repeat unit, g	Average degree of polymerization (DP)	Average molecular weight (Mn)
$C_{29}H_{30}O_8N_2S_2$	58 (Cal)	5.33(Cal)	4.66(Cal)	10.66 (Cal)	600	18.00	10800
	57.76 (F)	5.42(F)	4.13(F)	11. 02 (F)			

3.1. Infrared spectra

Infrared spectrum of the 1-N-4-SAHDF-Resin-II has been shown in Fig. 2. Very broad band appeared in the region 3229 cm^{-1} may be assigned to the stretching vibration of phenolic -OH groups exhibiting intermolecular hydrogen bonding between -OH and -NH-. The band obtained at 1371 cm^{-1} suggests the presence of methylene (-CH_2-) bridges. A sharp and strong peak at 1607 cm^{-1} may be ascribed to aromatic skeletal ring. The 1,2,3,5 tetra substitution of aromatic ring can be recognized from sharp and medium absorption bands appeared at 912, 1098, 1149 cm^{-1} respectively. The presence of C-H stretching of aromatic ring may be assigned as a sharp and strong band at 3011cm^{-1} which seems to be merged with very broad band of phenolic hydroxyl group [13], [14]. A sharp and strong peak at 1379 cm^{-1} may be ascribed to -CH_2- symmetrical deformation. A sharp peak at 2917 cm^{-1} may be ascribed to >CH2, -NH-, -CH_3 stretching. A broad and sharp peak at 1481 cm^{-1} may be ascribed to -NH bending of secondary amide. A sharp peak at 1286cm^{-1}may be ascribed to -CH_2 bending (wagging & twisting). The band obtained at 1231cm^{-1} suggests the presence of -CH_2- plane bending.

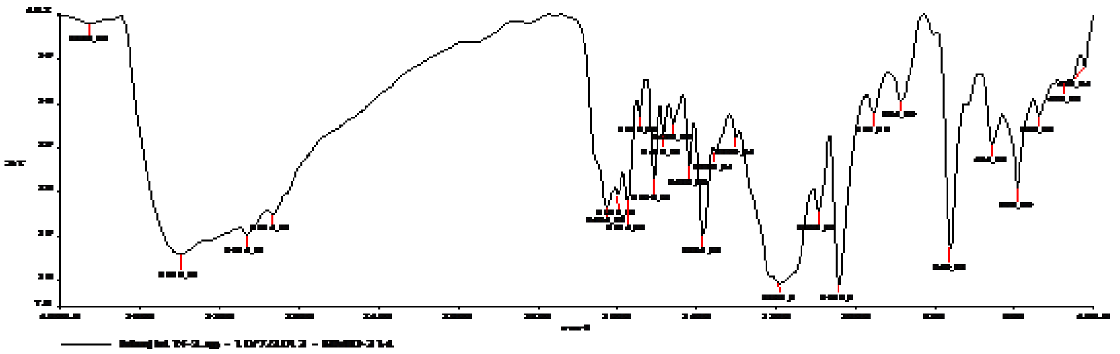

Figure 2: Infrared spectra of 1-N-4-SAHDF-Resin-II

3.2. H^1 Nuclear magnetic resonance spectra

The H^1 NMR spectrum of 1-N-4-SAHDF-Resin-II terpolymer was scanned in DMSO-d^6 and has been shown in Fig.3. The chemical shift (δ) in ppm has been assigned on the basis of data available in literature [15]. The 1-N-4-SAHDF-Resin-II terpolymer resin shows an multiplate signals at δ 2.56 ppm which may be attributed to methyl proton of Ar-CH_3group. The singlet obtained in the region of δ 3.46 ppm may be due to the methylene proton of Ar-CH_2-N moiety. The signal in the region of δ 6.2 ppm is attributed to protons of bridge –NH. The weak multiplate signal (unsymmetrical pattern) in the region of δ 6.62 ppm may be due to terminal methylene group. The signals in the range at δ 10.21 ppm may be due to phenolic hydroxyl protons. The much downfield chemical shift for phenolic –OH indicates clearly the intramolecular hydrogen bonding of -OH group [16], [17]. The multiplates at δ 1.29 ppm and 1.55ppm may due to -CH_2-CH_2- moiety of amine. The signal at δ 7.52 ppm may due to aromatic proton (Ar-H). The singlet obtained at 9.41ppm may be assigned to sulphonic group.

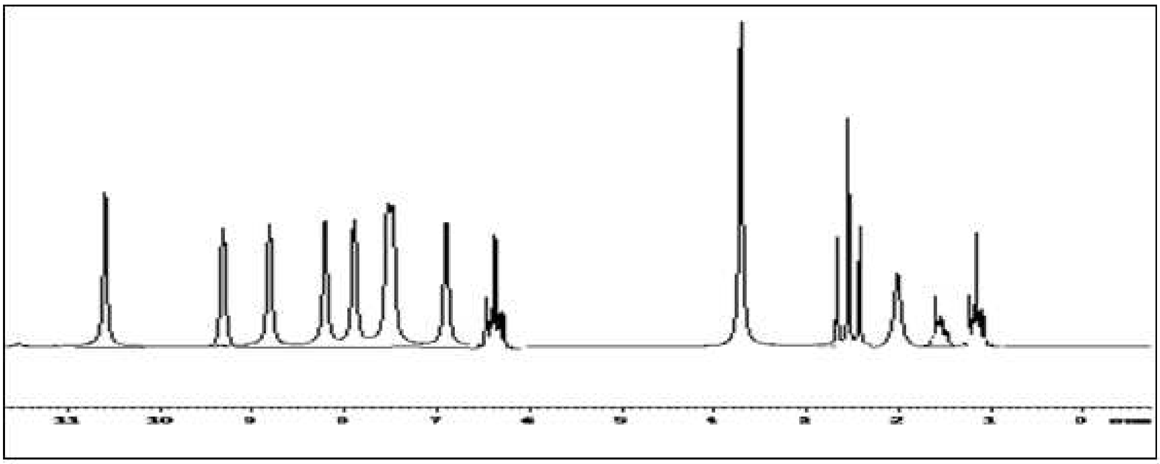

Figure 3: H^1 Nuclear Magnetic Resonance Spectra of 1-N-4-SAHDF-Resin-II

3.3. ^{13}C Nuclear magnetic resonance spectra

^{13}C NMR spectrum of 1-N-4-SAHDF-Resin-II has been recorded as shown in Fig. 4. ^{13}C NMR spectra display signals arising from all the carbon atoms and hence provide direct information about the carbon skeleton of the terpolymer. The ^{13}C NMR spectrum of 1-N-4-SAHDF-Resin-II shows the corresponding peaks at 155.56, 107.8, 126.1, 133.89, 130.2, 126.6, 127.4, 126.32, 122.45, 126.21 ppm with respect to C_1 to C_{10} of the aromatic naphthalene ring. The shifting of signals is due to the substitution in naphthalene ring. More electronegative group is bonded to Carbon atom, deshielding shifts increases[15]. Thus, the peak of C_1 at 155.56 ppm may be because of deshielding effect by –OH grp. The signal at 42.1 ppm may be assigned to -C-NH- grp. Of hexamethylene diamine moiety. Two peaks more are obtained for hexamethylene diamine, out of which peak at 26.5 ppm may be because of methylene -CH_2- grp. The ^{13}C NMR spectrum after analysis minutely confirmed that the monomers are arranged in a straight manner, giving the linear structure for terpolymer, which we have proposed is obviously correct given in Fig. 1.

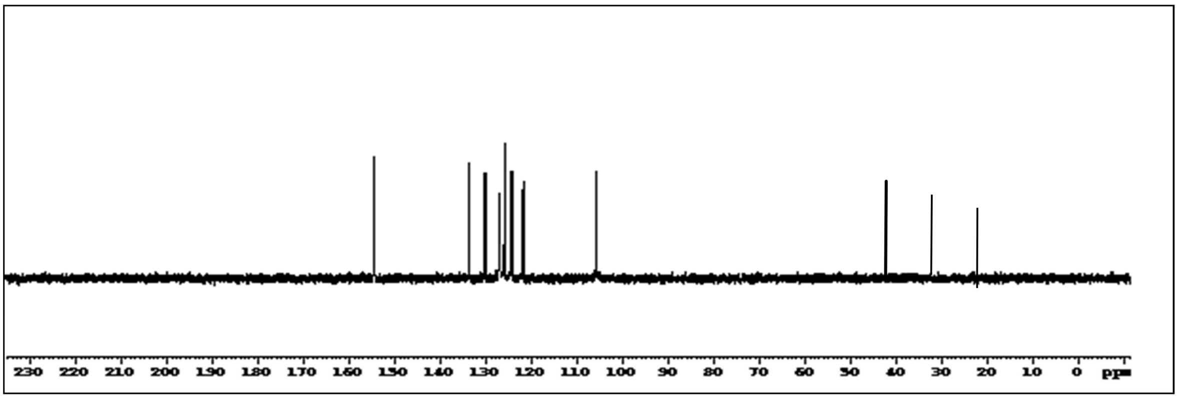

Figure 4:^{13}C Nuclear Magnetic Resonance Spectra of 1-N-4-SAHDF-Resin-II

3.4. Scanning electron microscopy (SEM)

Scanning electron micrographs of the 1-N-4-SAHDF-Resin-II has been recorded as shown in Fig. 5. The SEM micrographs of 1-N-4-SAHDF-Resin-II sample exhibits spherulites with deep corrugation. The spherulites are typical crystalline formation and they grow in high viscous and concentrated solution. In the present case, the spherulites are complex polycrystalline. The crystals are smaller in surface area with less closely packed structure. The spherulites morphology of resin exhibit crystalline structure with deep corrugation which is clearly visible in SEM photographs of resin. These evidences indicate that more or less the resin shows amorphous character with less close packed surface having deep pits. The resin thus possesses amorphous nature and showing higher exchange capacity for metal ions [18]. Thus SEM study shows that the 1-N-4-SAHDF-Resin-II has crystalline and some amorphous characters. Thus it has the transition structure between crystalline and amorphous.

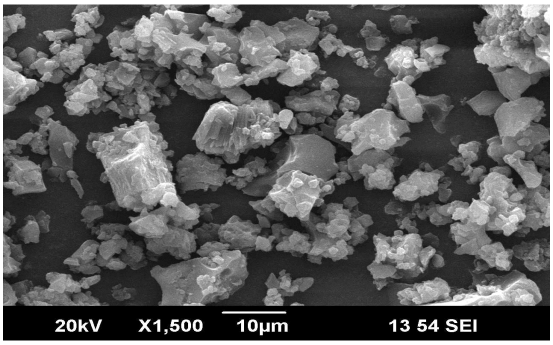

Fig. 5: SEM micrographs of 1-N-4-SAHDF-Resin-II

The polymer under study is a terpolymer hence it is very difficult to assign its exact structure. However on the basis of the nature and relative position of the monomers, results of elemental analysis, IR, ^1H NMR, ^{13}CNMR studies [19], [20] and taking into consideration the linear structure of other phenol-formaldehyde resin and the linear branched nature of urea-formaldehyde polymers, the most probable structure has been proposed for 1-N-4-SAHDF-Resin-II (Figure 1).

3.5 Thermal Degradation studies of 1-N-4-SAHDF-Resin-II

In order to explore the thermal degradation study of 1-N-4-SAHDF-Resin-II, the thermogram has been studied minutely. Decomposition pattern of 1-N-4-SAHDF-Resin-II is shown in Fig. 6. The data of thermogravimetric analysis revealed that the sample loss 4.54% found and 4.71% calculated weight loss when temperature was raised from 40 - 200ºC. This initial weight loss may be due to the loss of water of crystallization associated with terpolymer resin [21], [22]. After loss of water molecule thermograph of 1-N-4-SAHDF-Resin-II has depicted three stages decomposition. The first decomposition step represents degradation of phenolic hydroxyl group and sulphonic group substituted to naphthalene ring, in the temperature range of 210-340ºC, corresponded the weight loss of 32.36% found and 30.36% calculated. The weight loss by increasing temperature may be due to activating the macromolecules which may develop the cross linking in the molecules. Cross linking developed the strain in the macromolecule with result of weight loss to acquire the stability. The second stage of decomposition of 1-N-4-SAHDF-Resin-I has been started by increasing temperature from 340 – 660ºC, when observed a rapid mass loss corresponding to 62.59% found and 62.82% calculated weight loss, which may be due to the loss of naphthalene ring due to unzipping of cross linking, high strain, unstability and depolymerization occurred in the resin. In the third stage, the temperature has been increased from 660-930ºC which might increasing the strain in the molecule, cross linking increased, unstability increased, leading to weight loss of about 99.62% found and 100% calculated and the rigid prepolymeric part after the third stage is left as the char residue which is negligible in 1-N-4-SAHDF-Resin-II decomposition .

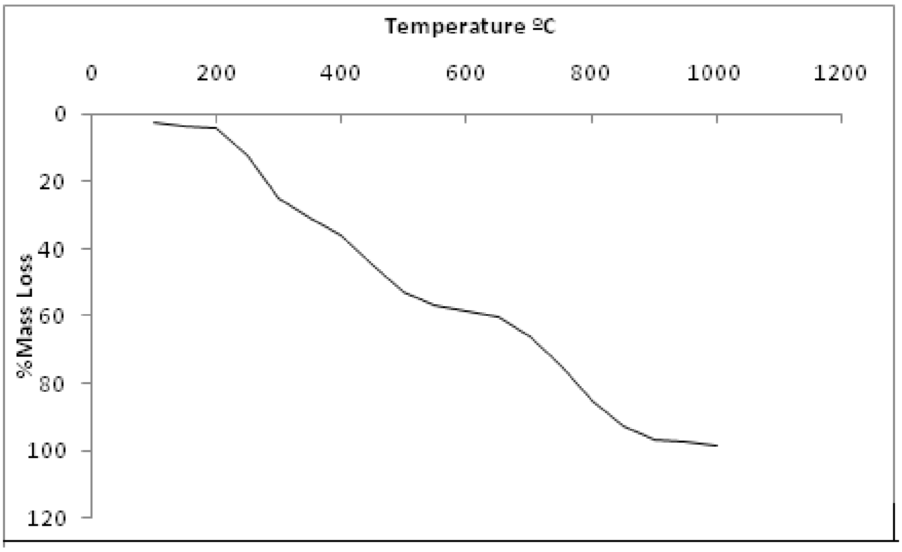

Figure 6 : Thermo gram of 1-N-4-SAHDF-II

With the help of thermo gravimetric data the thermal activation energies (Ea) and order of reaction (n) calculated. Also other thermodynamic parameters such as entropy change (ΔS), apparent entropy change (S*) and frequency factor (Z) are determined and reported in the Table 2. To provide further evidence regarding the degradation system of analyzed compounds, we derived the TG curves by applying an analytical method proposed by Sharp- Wentworth and Freeman-Carroll. The 'average Ea' calculated by Freeman-Carroll (22.87 KJ/mole) and 'average Ea' by Sharp-Wentworth (23.12KJ/mole) are nearly same.

Sharp -Wentworth method:

Using the equation derived by Sharp and Wentworth,

$$\log [(dc/dT)/ (1-c)] = \log (A/\beta) – [Ea/2.303R]. 1/T \qquad (1)$$

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 (log dc/dt)/ (1-c) vs 1/T, we obtained the straight line which give energy of activation (Ea) from its slope. Where β is the conversion at time t, R is the gas constant (8.314 Jmol-1K-1) and T is the absolute temperature. The plot in fig. 7 gives the activation energy (Ea) and Doyel's graph gives the value of -log p(x).

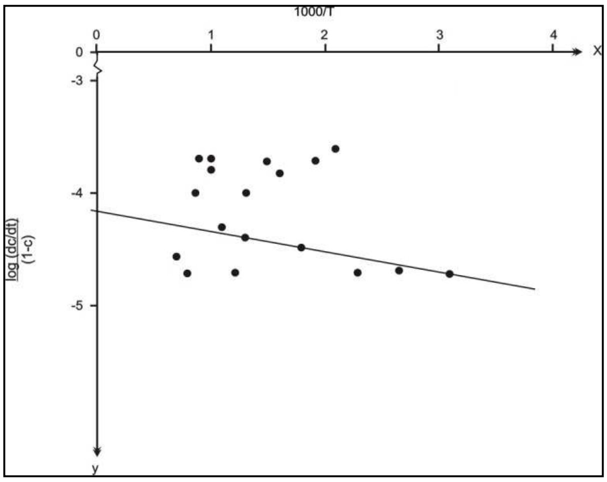

Fig. 7: Sharp-Wentworth Plot

Freeman-Carroll method:

The straight-line equation derived by Freeman and Carroll, which is in the form of n

[Δlog (dw / dt)] / Δ log Wr = (-E / 2.303R) - Δ (1/ T) / Δ log Wr + n (2)

Where,

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

Wr = Wc-W

Wc = weight loss at completion of reaction.

W = fraction of weight loss at time t.

Ea = energy of activation.

n = order of reaction.

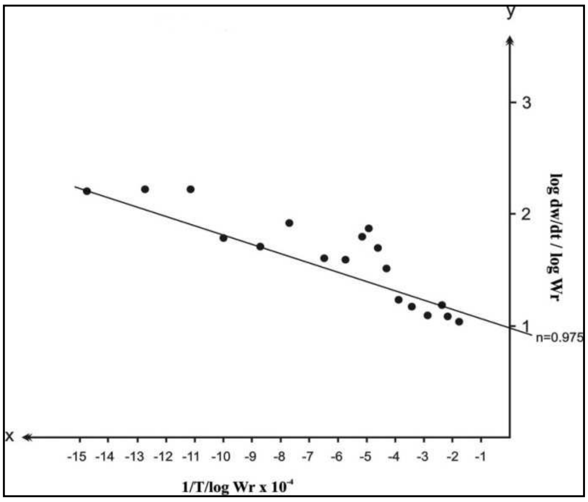

Fig. 8(a): Thermal Activation Energy Plots (Freeman-Carroll Plot)

The plot between the terms [Δ log (dw/dt)] / Δ log Wr Vs Δ (1/T) / Δ log Wr gives a straight line which give energy of activation (Ea) from its slope , shown in figure 8(b) and intercept on Y-axis as order of reaction (n) shown in

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figure 8(a). The change in entropy (S), frequency factor (z), apparent entropy (S*) can also be calculated by further calculations.

From the abnormally low values of frequency factor, it may be concluded that the decomposition reaction of 1-N-4-SAHDF-II 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 terpolymer is known not to obey first order kinetics perfectly [23].

CONCLUSION

1. A terpolymer 1-N-4-SAHDF-II, based on the condenssation reaction of 1Naphthol-4-sulphonic acid-Hexamethylene diamine-formaldehyde in the presence of acid catalyst, was synthesized.

2. As the degradation of the terpolymer under investigation started at high temperature which indicates that the terpolymer 1-N-4-SAHDF-II is thermally stable at elevated temperature.

3. Low value of frequency factor may be concluded that the decomposition reaction of 1-Naphthol-4-sulphonic acid-Hexamethylene diamine-formaldehyde terpolymer can be classified as 'slow reaction'.

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