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Synthesis and Non-Isothermal Kinetic Studies of Novel SATF-II Copolymer, Derived from Salicylic acid and Thiosemicarbazide

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ABSTRACT

The Copolymer (SATSF-II) was synthesized by condensation of salicylic acid and thiosemicarbazide with formaldehyde in the presence of 2M HCL as a catalyst at 124 ± 2 ^{0}C for 5 hrs with molar proportion of reactants. Thermogravimetric analysis of copolymer resin in present study has been carried out by non-isothermal thermogravimetric analysis technique in which sample is subjected to condition of continuous increase in temperature at linear rate. Thermal study of the resins was carried out to determine their mode of decomposition and relative thermal stabilities. The copolymer (SATSF-II) was characterized by FT-IR, ^{1}H-NMR Spectroscopy. Thermal activation energy (Ea) calculated with above two mentioned methods are in close agreement. Freeman Carroll and Sharp-Wentworth methods were used to calculate the thermal activation energy (Ea), the order of reaction (n), entropy Change (ΔS), free energy change (ΔF), apperent entropy change (ΔS), and frequency factor (Z). The thermal activation energy determined with the help of these method was in good agreement with each other.

Keywords: Synthesis, condensation, thermogravimetric analysis, activation energy, Kinetic parameter.

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INTRODUCTION

The thermal degradation study of copolymers has become a subject of interest. Study of thermal behaviour of copolymers in air at different temperature provides information about the nature of species produced at various temperatures due to degradation. Copolymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. [1-3].

The study of thermal behaviour of copolymers in air at different temperature provides information about the nature of species produced at various temperatures due to degradation. Copolymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. Terpolymers of salicylic acid, thiourea with trioxane and p-hydroxybenzoic acid, thiourea with trioxane have been reported in the literature [4-7]. Synthesis, characterization and ion exchange properties of 4-hydroxyacetophenone, biuret and formaldehyde terpolymer resin were studied by Gurnule and coworkers [8]. Thermal degradation of m-nitroaniline, m-chloroaniline and m-aminophenol has been studied by Dash et al. [9] and 2-hydroxyacetophenone, oxamide and formaldehyde [10]. S. L. Oswal et al synthesized and studied thermal properties of copoly (maleimidemethylmethacrylate), terpoly (maleimidemethylmethacrylate- acrylicacid) and terpoly (maleimide-methylmethacrylatemethyl-acrylic acid). The thermal behaviour was studied by TG and DSC techniques . Various researchers have been studied the applications of terpolymer resins of substituted phenols and formaldehyde [11].

The present paper deals with the synthesis, characterization, and non-isothermal thermogravimetric analysis of copolymer derived from of Salicylic acid (SA), thiosemicarbazide (T), with formaldehyde (F). However, the literature studies have revealed that no copolymer has been synthesized by using the said monomers. Sample is subjected to thermal degradation data with Sharp-Wentworth (S-W) and Freeman-Carroll (F-C) methods, activation energy and kinetic parameters such as ΔS, Z, S* and n (order of reaction) have been evaluated [12-16].

MATERAILS AND METHODS

The entire chemical used in the synthesis of various new copolymer resins were procured from the market and were analar or Fluka or chemically pure grade. Whenever required they were further purified by standard methods like thin layer chromatography, reprecipitation and crystallization which are generally used for the analytical purification purpose.

Synthesis of SATF-II Copolymer Resin

The new copolymer resin SATF-II was synthesized by condensing salicylic acid (0.2 mol) and thiosemicarbazide (0.1 mol) with formaldehyde (0.3 mol) in a mol ratio of 2:1:3 in the presence of 2 M 200 ml HCl as a catalyst at 126 ^{0}C ± 2 ^{0}C for 5h, in an oil bath with occasional shaking, to ensure thorough mixing. The separated copolymer 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 salicylic acid- thiosemicarbazide formaldehyde copolymer which might be present along with SATF-II copolymer. The yellow color resinous product was immediately removed from the flask as soon as reaction period was over and then purified. The reaction and suggested structure of SATF-II is shown in Fig. 1

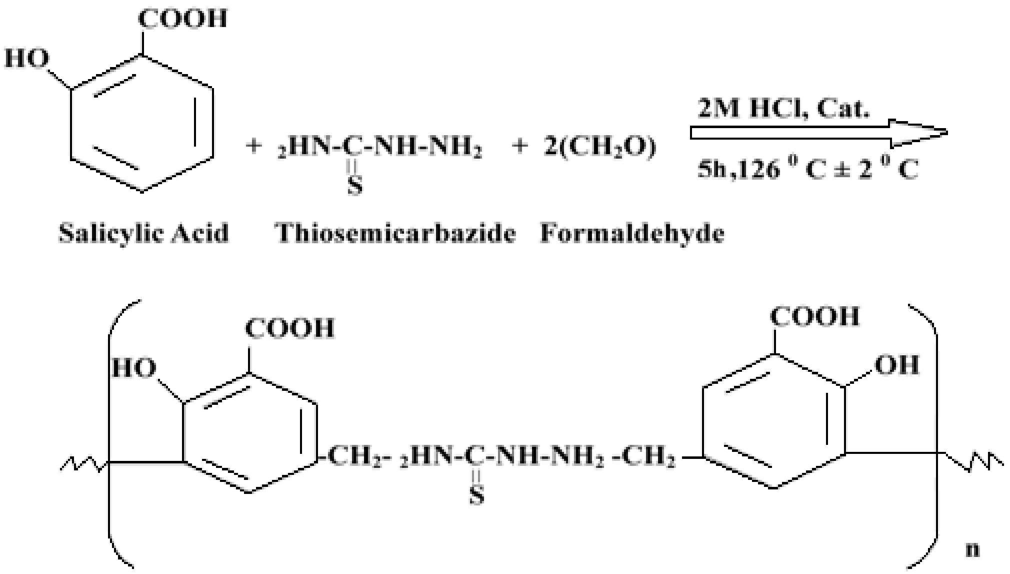

Fig.1: Synthesis of SATF-II Copolymer Resin.

The copolymer 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 copolymer sample p-HBSF thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desicator over silica gel.

Thermogravimetric Analysis:

The non-isothermal thermogravimetric analysis was performed in air atmosphere with heating rate of 10 ^{0}C. min^{-1} from temperature range of 50 ^{0}C to 600 ^{0}C using Perkin Elmer Diamond TGA analyzer in argon environment. The thermograms were recorded at Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Vallabh Vidyanagar, Gujrat . 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 is shown in the

Fig. 4 for a representative SATF-II copolymer. From the TG curves, the thermoanalytical data and the decomposition temperatures were determined for different stages. To obtain the relative thermal stability of the copolymer, the method described by Sharp-Wentworth and Freeman-Carroll adopted.

RESULTS AND DISCUSSION

The newly synthesized purified SATF-II copolymer resin was found to be yellow in color. The copolymer is soluble in solvents such as DMF, DMSO and THF while insoluble in almost all other organic solvents. The melting point of SATF-II copolymer resin is 190 ^{0}C and the yield of the copolymer resin was found to be 89 %.

FT-IR Spectra: A broad band appeared in the region 2800-3200cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxy (-OH) groups exhibiting intermolecular hydrogen bonding. The sharp band displayed at 1600-1680 cm^{-1} may be due to the stretching vibrations of carbonyl group (C=O) and 1600-1400 cm^{-1} may be due to (C=S) moiety. The presence of -NH in thiosemicarbazide moiety may be assigned due to sharp band at 2800-3000 cm^{-1} . A strong sharp peak at 1625-1500 cm^{-1} may be ascribed to aromatic skeletal ring. The bands obtained at 1400 – 1200 cm^{-1} suggest the presence of methylene bridges in the polymer chain. The weak band appearing at 720 - 760 cm^{-1} is assigned to C – OH bond. 1,2,4,6 tetrasubstitution of aromatic ring is recognized from the bands appearing at 902, 1084, 1201, and 1290 cm^{-1} respectively.

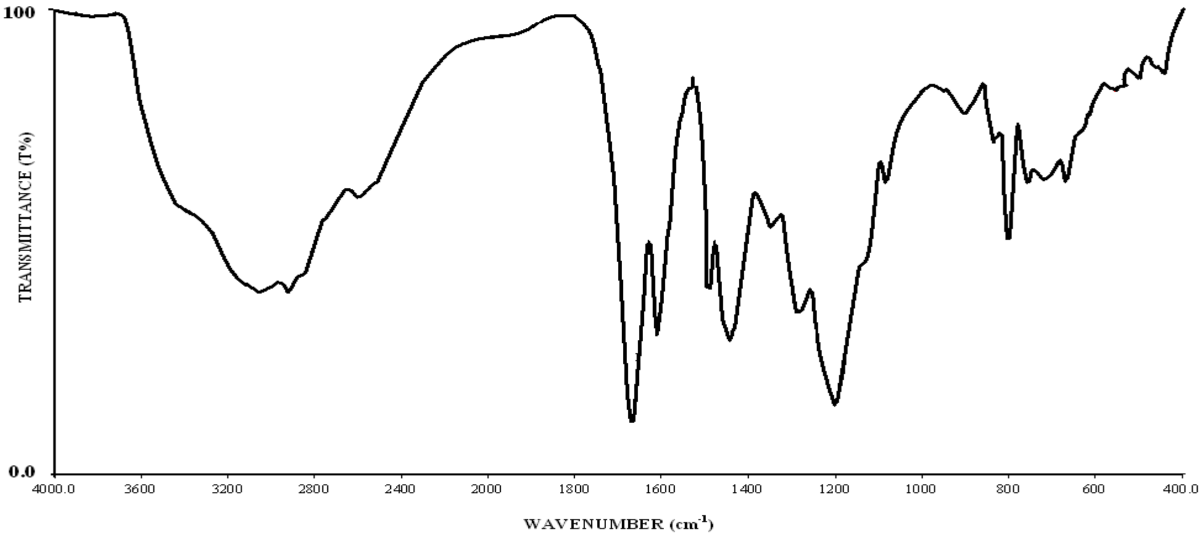

Fig.2: FT-IR Spectra of SATF-II Copolymer

NMR Spectra:

Weak signal in the range of 7.8 ppm is attributed to phenolic -OH proton. The NMR spectra of SATF-II copolymer resins show a weak multiplate signal (unsymmetrical pattern) in the region 6.8 (δ) ppm which is due aromatic protons. A medium singlet peak appeared at 3.9 (δ) ppm may be assigned to methyl protons of Ar-CH_2-NH group. Intense signal appeared in the region 2.5 (δ) ppm may be due to Ar–CH_2-NH .Triplet signal appeared in the region 3.77 (δ) ppm can be assigned to amido proton of –CH_2-NH-CO- linkage.

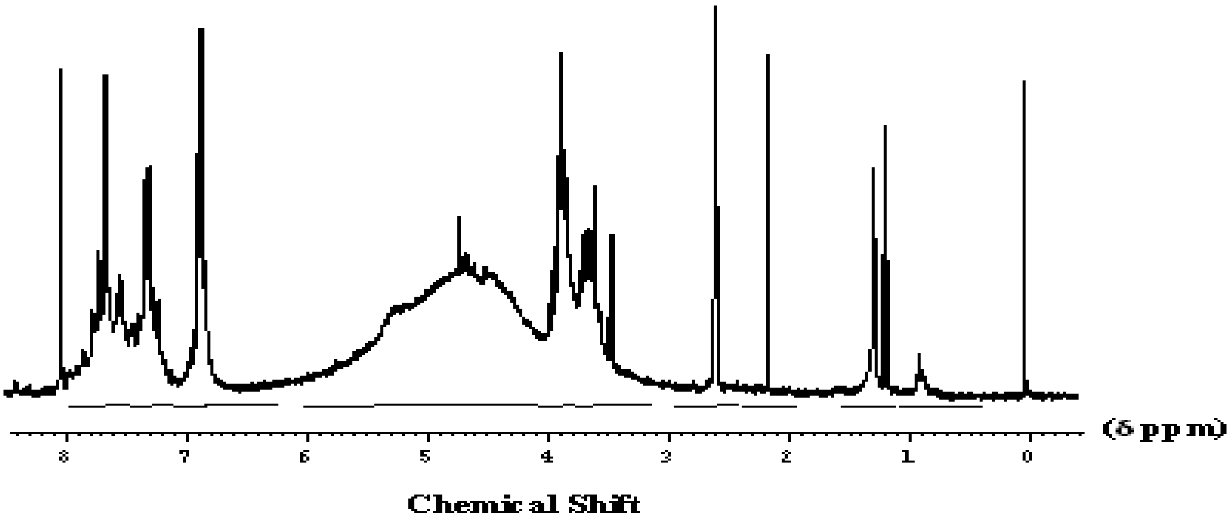

Fig.3: NMR Spectra of SATF-II copolymer

Thermogravimetry:

The thermogravimetric data provide information regarding the thermal stability of a polymer. The thermograms were obtained by heating resin sample in air at 10^0 C/min. The results of percentage weight loss of the copolymer resins depicts three steps decomposition in the temperature range 140-600ºC and are furnished in Figure 4. The slow decomposition between 0-180ºC corresponds to 5.0 % loss which may be attributed to loss of water molecule against calculated 4.8 % present per repeat unit of the polymer. The first step decomposition start from 180-260ºC which represents loss of hydroxyl group and acid group (38.00 % found and 37.86 % cal.). The second step decomposition start from 260-520ºC corresponding to 78.00 % removal of aromatic nucleus and methylene bridge against calculated 78.4 %. The third step decomposition side chain from 480-580ºC corresponding to removal of Thiosemicarbazide moiety (100.00 % found and 98.4 % cal.).

With the help of thermogravimetric 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 1& 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 (24.51 KJ/mole) and ‘average Ea’ by Sharp- Wentworth (24.85 KJ/mole) is nearly same.

Sharp -Wentworth method:

Using the equation derived by Sharp and Wentworth [1],

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

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 J mol^{-1} K^{-1}) and T is the absolute temperature. The plots (figure 2) give the activation energies at different stages of degradation reaction take place.

Freeman-Carroll method:

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

$$[\Delta \log (dw / dt)] / \Delta \log Wr = (-E / 2.303R) .\ \Delta (1/ T) / \Delta \log Wr + n \text{ -----------------(1)}$$

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.

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

(i) Entopy Change:

$$\text{Intercept} = [\log KR/h\phi E] + S / 2.303\ R \text{ ------------------- (2)}$$

Where, K = 1.3806 x 10-16 erg/deg/mole, R = 1.987 Cal/deg/mole
h = 6.625 x 10-27 erg sec. , ϕ = 0.166
S = Change in entropy, E = Activation energy from graph.

(ii) Free Energy Change:

$$\Delta F = \Delta H - T\Delta S \text{ \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ } (3)$$

Where, ΔH = Enthalpy Change = activation energy
T = Temperature in K
S = Entropy change from (i) used.

(iii) Frequency Factor:

$$Bn = \text{Log } ZEa / \phi R \text{ ---------------------------------- } (4)$$
$$B1 = \log [\ln 1/1-\alpha] - \log P(x) \text{ ------------------- } (5)$$

Where, Z = frequency factor, B = calculated from equation (5)
Log P(x) = calculated from Doyle s table corresponding to activation energy.

(iv) Apparent Entropy Change:

$$S^* = 2.303 \log Zh / KT^* \text{ ------------------------- } (6)$$

Z = from relation (4)
T* = temperature at which half of the compound is decomposed from it total loss

Table 1: Results of Thermogravimetric Analysis of SATF-II copolymer

Coplymers	Half Decomposition Temp.T*K	Activation Energy (kJ/mol)	
		F.C	S.W
SATF-II	433	24.51	24.85

Table.2: Kinetic Parameters of SATF-II copolymer

Coplymers	Entropy Change -ΔS(J)	Free Energy Change ΔF (kJ)	Frequency factor Z (S^{-1})	Apparent Entropy Change (S*)	Order of reaction (n)
SATF-II	300.67	165.71	438	-23.97	0.92

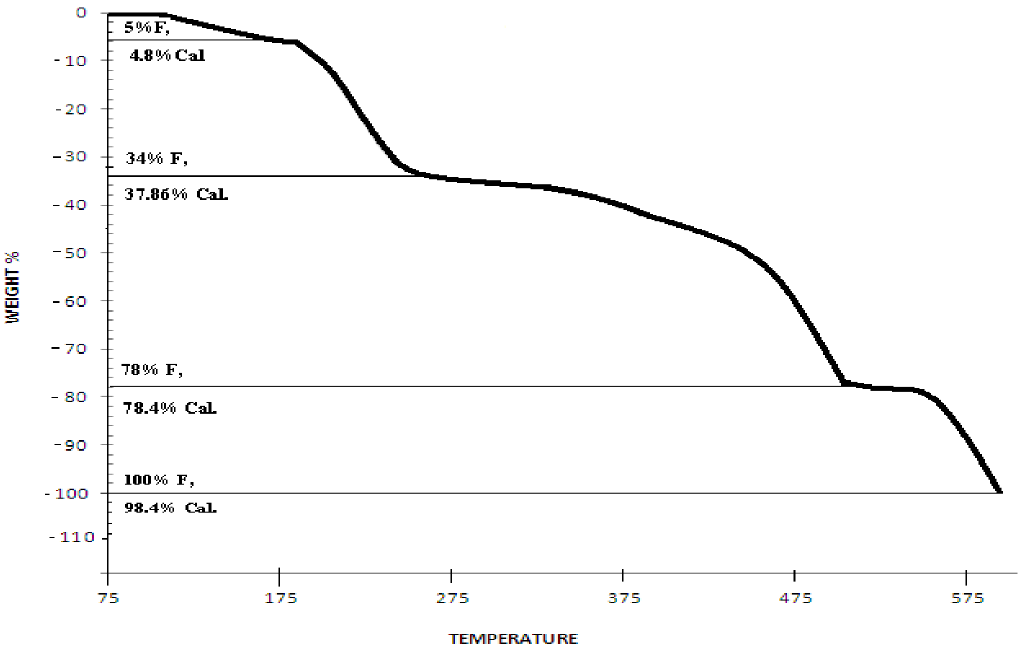

Fig. 4: Decomposition Pattern of SATF-II copolymer Resin.

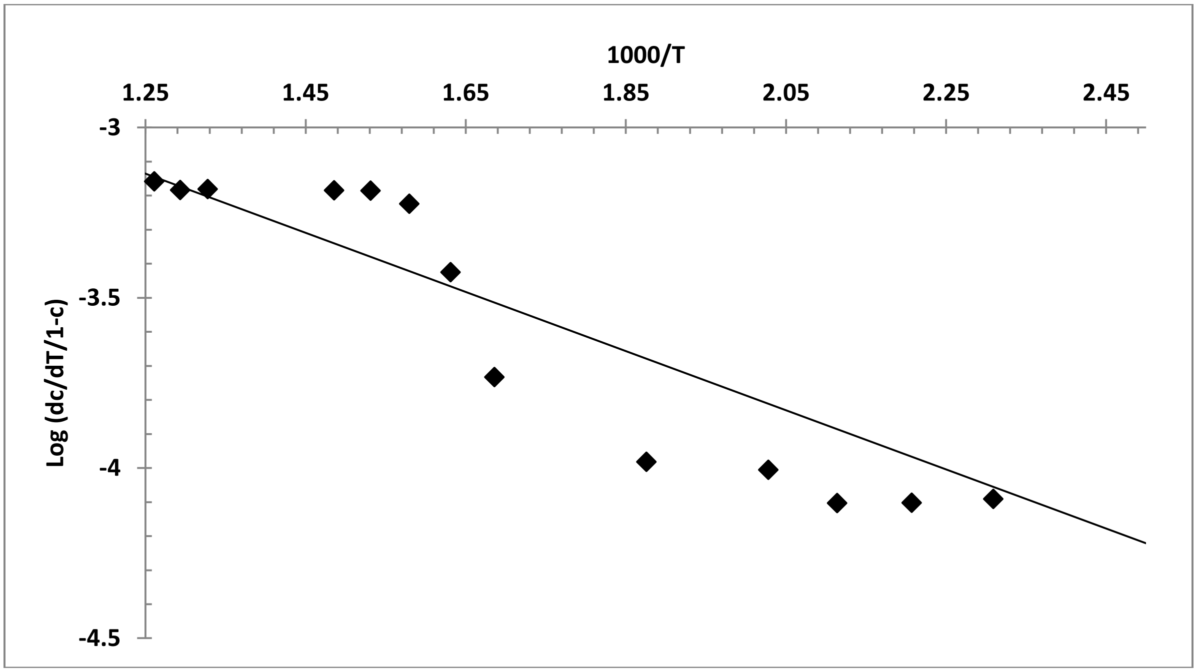

Fig. 5: Sharp-Wentworth plot of SATF-II copolymer

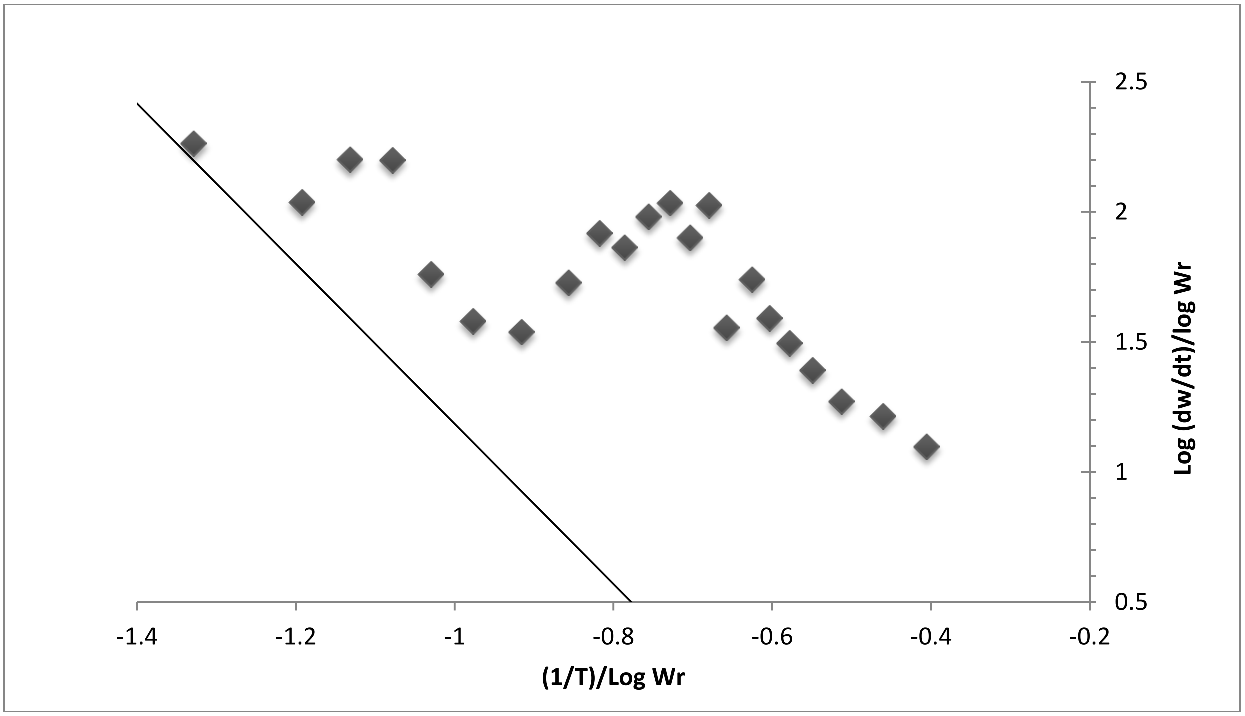

Fig. 6: Thermal activation energy plot of SATF-II copolymer

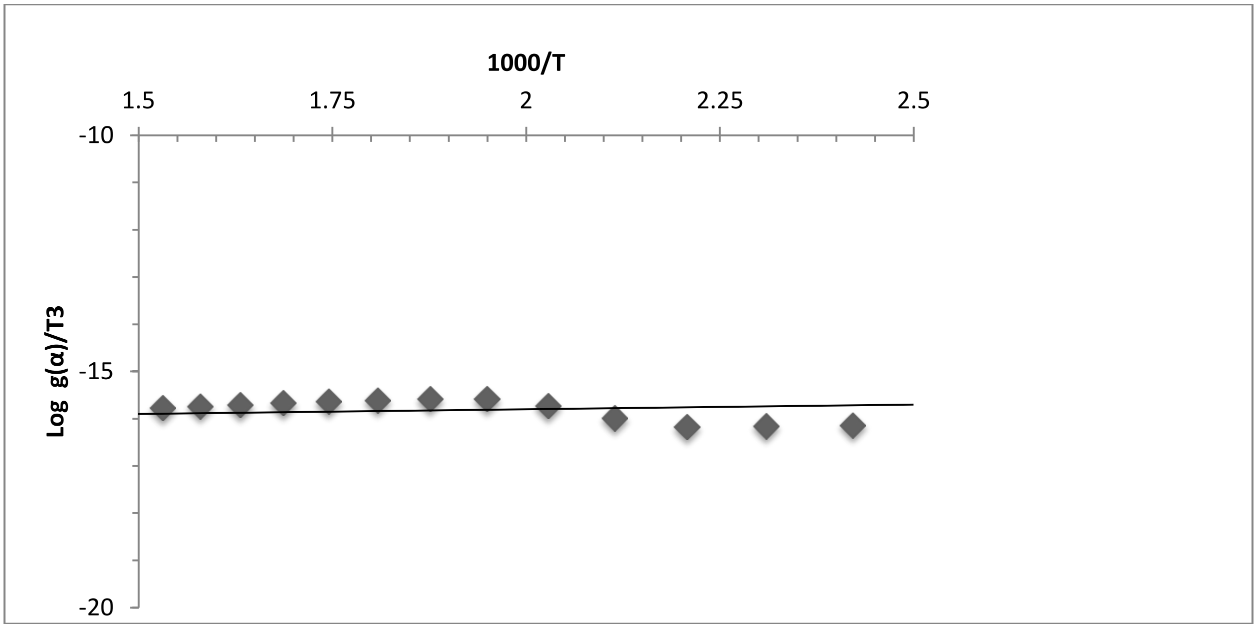

Fig. 7: Freeman-Carroll plot of SATF-II copolymer

CONCLUSION

A copolymer, SATF-II based on the condensation reaction of Salicylic acid, thiosemicarbazide formaldehyde in the presence of acid catalyst was prepared. From the FT-IR and ^1H NMR spectral studies the proposed structure of the SATF-II copolymer has been determined. In TGA the energy of activation evaluated from the Sharp-Wentworth and Freeman-Carroll methods are found to be nearly equal and the kinetic parameters obtained from Freeman-Carroll method are found to similar, indicating the common reaction mode. However, it is difficult to draw any unique conclusion regarding the decomposition mechanism. Low values of collision frequency factor (Z) may be concluded that the decomposition reaction of Salicylic acid, thiosemicarbazide, formaldehyde copolymer can be classified as ‘slow reaction’. The decomposition reaction was started at higher temperature, indicating a copolymer SATF-II is thermally stable at higher temperature..

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