



## Structural and thermal study of terpolymer resin-II derived from p-hydroxybenzaldehyde, succinic acid and ethylene glycol

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### ABSTRACT

Resin abbreviated as HBSE-II was synthesized by polycondensation in the presence of polyphosphoric acid as a catalyst using monomers p-hydroxybenzaldehyde (0.2M), succinic acid (0.1M) and ethylene glycol (0.4M) at 120°C. The molecular weight was determined by non-aqueous conductometric titration. Terpolymer was characterized by elemental analysis, FT-IR, <sup>1</sup>H NMR and UV-Visible spectroscopy. Thermokinetic parameters were calculated by using Freeman-Carroll (FC) and Sharp-Wentworth (SW) methods in the temperature range 405-591°C. The values of the activation energy (E<sub>a</sub>), frequency factor (A), apparent entropy change (ΔS<sup>\*</sup>) and free energy change (ΔG) were in good agreement. The order of degradation obtained by the FC method was found to be 0.3 which was further confirmed by SW method.

**Keywords:** Thermal activation energy, Thermal degradation, Polycondensation, Order of degradation, Free energy, Terpolymer.

### INTRODUCTION

Now a days, terpolymer have more importance in industrial application. These terpolymers can be used as high energy material, antioxidants, fire proofing agent, optical storage data, binders, semiconductors, molding materials, ion-exchanger [1-10].

Present communication deals the study of thermal degradation and thermokinetic parameters of HBSE-II terpolymer by Freeman-Carroll and Sharp-Wentworth methods.

### MATERIALS AND METHODS

#### 2.1 Chemicals

All chemicals used as starting materials in the synthesis of terpolymer were of AR or chemically pure grade. The chemicals such as p-hydroxybenzaldehyde, succinic acid, ethylene glycol, polyphosphoric acid were obtained from s. d. fine chemicals, India.

#### 2.2 Synthesis of HBSE-II terpolymer resin

The HBSE-II terpolymer resin was synthesized by polycondensation, to a well-stirred and ice-cooled mixture of p-hydroxybenzaldehyde (0.2M), succinic acid (0.1M) and ethylene glycol (0.4M), polyphosphoric acid was added slowly as a catalyst with continuous stirring. The reaction mixture was left at room temperature for 30 min and heated in an oil bath at 120°C for 6.30 hrs. The reaction mixture was then cooled, poured on crushed ice and left over night. A reddish brown solid was separated out. The crude product was squeezed with ether so as to remove

succinic acid-glycol copolymer which might be formed along with HBSE-II. The terpolymer was further purified by dissolving in 0.1N NaOH solution and precipitated by dropwise addition of 1:1 HCl with constant stirring. The product was washed several times with hot water and cold water. The product was air dried and kept in vacuum over silica gel. It was collected by filtration and washed with cold water and hot water several times to remove impurities. Yield was found to be 80%. The scheme of synthesis of HBSE-II is shown in figure 1.

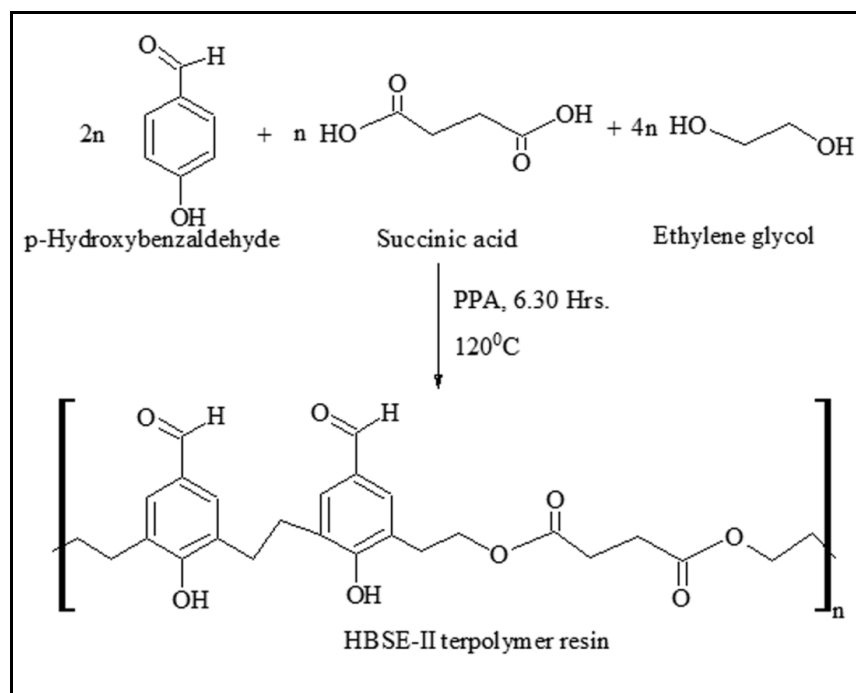


Figure 1 Synthesis scheme of HBSE-II terpolymeric resin

## RESULTS AND DISCUSSION

HBSE-II terpolymer was reddish brown in color and soluble in DMSO and NaOH solution where as insoluble in acids and common organic solvents.

### 3.1 Elemental analysis and molecular weight determination ( $\overline{Mn}$ )

Elemental analysis has been carried out in CIMFR unit, Nagpur by analytical functional testing Vario MICRO CHN elemental analyzer. The number average molecular weight ( $\overline{Mn}$ ) was determined by non-aqueous conductometric titration in DMSO using 0.1M KOH in alcohol as titrant [11]. From the graph of specific conductance against miliequivalents of KOH, first and last breaks were noted. The degree of polymerization ( $\overline{Dp}$ ) and the number average molecular weight ( $\overline{Mn}$ ) have been calculated using equations (1) and (2),

$$\overline{Dp} = \frac{\text{Total Meq. of base required for last break}}{\text{Meq. of base required for first break}} \quad (1)$$

$$\overline{Mn} = \overline{Dp} \times \text{Repeat unit weight} \quad (2)$$

The repeating unit weight was obtained from elemental analysis. The elemental analysis and molecular weight determination data of HBSE-II terpolymer are tabulated in table 1.

Table 1 Elemental analysis data,  $\overline{Dp}$  and molecular weight of HBSE-II

%C		%H		Mol. Formula of repeating unit	Mol. Wt. Of repeating unit	$\overline{Dp}$	Mol. Weight ( $\overline{Mn}$ )
Cal.	Found	Cal.	Found				
66.67	66.62	5.98	5.87	$(C_{26}H_{28}O_8)_n$	468	19.4~19	8892

### 3.2 FT-IR Spectrum

FT-IR spectrum of HBSE-II terpolymer was recorded at department of pharmacy, R.T.M. Nagpur University, Nagpur using FT-IR spectrometer, Shimadzu, model no. 8101A in the range of 4600-500  $\text{cm}^{-1}$ . The IR-spectrum of HBSE-II terpolymeric resin is shown in figure 2.

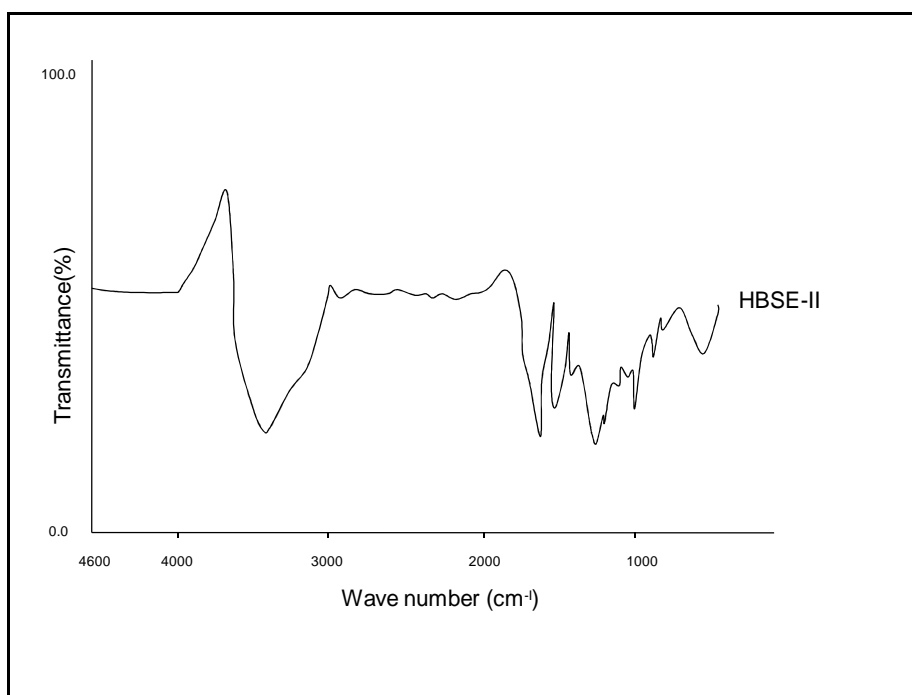


Figure 2 FT-IR spectrum of HBSE-II terpolymer

A broad absorption band appeared in the region  $3434 \text{ cm}^{-1}$  was assigned to the stretching vibrations of phenolic (-OH) group exhibiting intermolecular hydrogen bonding. The presence of peaks at  $2921 \text{ cm}^{-1}$  and  $2843 \text{ cm}^{-1}$  were due to the -C-H- stretch in the aldehyde (doublet due to Fermi resonance). A peak at  $1680 \text{ cm}^{-1}$  was due to C=O stretch (ester). A peak appeared at  $1655 \text{ cm}^{-1}$  was due to C=O band (aldehyde). A Peak at  $1603 \text{ cm}^{-1}$  was due to aromatic-ring present in HBSE-II. A peak appeared at  $1476 \text{ cm}^{-1}$  was due to methylene bridge coupled with aromatic ring. Peaks appeared at  $1420 \text{ cm}^{-1}$  and  $1360 \text{ cm}^{-1}$  were assigned to the plane bending vibration of phenolic -OH. A peak appeared at  $1357 \text{ cm}^{-1}$  was due to aldehyde C-H bend. The broad band displayed at  $1220 \text{ cm}^{-1}$  was due to the C-O-C stretch (saturated ester) group. A peak at  $1178 \text{ cm}^{-1}$  was due to O-C-C band stretch in HBSE-II. 1, 2, 3, 5- tetra substitution of aromatic ring was assigned due to the peak at  $966 \text{ cm}^{-1}$ . The presence of peak at  $831 \text{ cm}^{-1}$  was due to the -CH<sub>2</sub>- (wagging) [12-13]. FT-IR spectral data of HBSE-II terpolymer is tabulated in table 2.

Table 2 FT-IR frequencies of HBSE-II terpolymer

Observed frequency ( $\text{cm}^{-1}$ )	Assignment
3434(b)	-OH bonded (phenolic)
2921(w), 2843(w)	C-H stretching in aldehyde (doublet due to Fermi resonance)
1680(w)	C=O stretch (ester)
1655(w)	C=O band (aldehyde)
1603(s)	Aromatic-ring
1476(w)	CH <sub>2</sub> bending
1420(w), 1360(w)	-OH bending (phenol)
1357(w)	Aldehydic C-H bending
1220(b)	C-O-C stretch (saturated ester)
1178(w)	O-C-C band stretch
966(b)	1,2,3,5 tetra substituted aromatic ring
831(w)	-CH <sub>2</sub> -wagging

(m) = medium, (b) = broad, (s) = sharp, (w) = weak

### 3.3 <sup>1</sup>H NMR Spectrum

<sup>1</sup>H NMR spectrum of HBSE-II terpolymer using DMSO-d<sub>6</sub> solvent was scanned on NMR spectrophotometer SAIFNM100820A, at Sophisticated Test and Instrumentation Center, Cochin University, Kerala, India. The <sup>1</sup>H NMR spectrum of HBSE-II terpolymer is shown in figure 3.

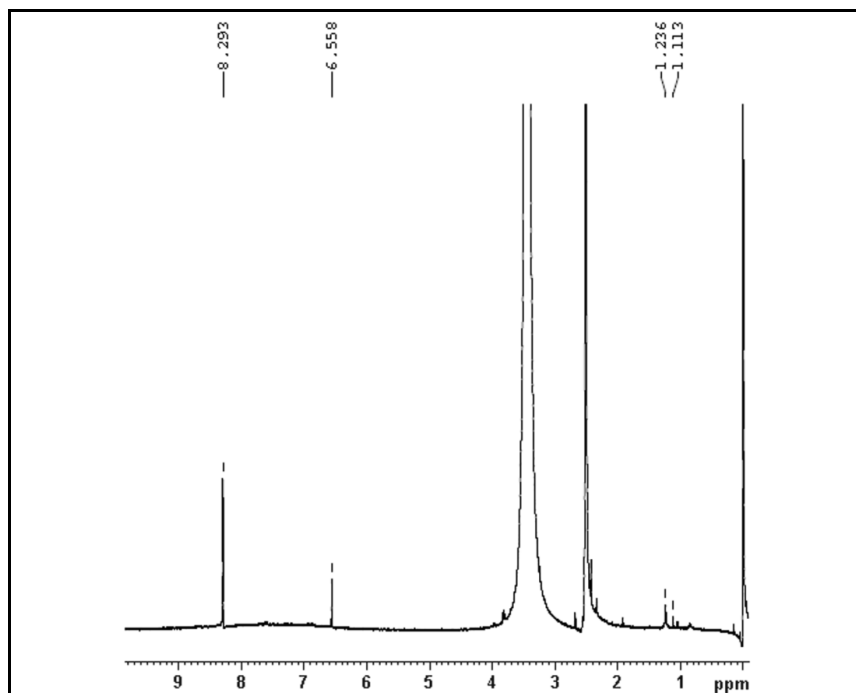


Figure 3  $^1\text{H}$  NMR spectra of HBSE- II terpolymer

The  $\delta$  in the range 1.2 ppm was of  $-\text{CH}_2-$  in HBSE-II. The signal at 2.3  $\delta$  ppm was due to DMSO solvent. Signal at 3.8  $\delta$  ppm was attributed to  $\text{CH-OH}$  moiety. The signal at 6.5  $\delta$  ppm was due to aromatic ring protons in HBSE-II. The signal at 8.2  $\delta$  ppm was due to the aldehydic proton [14].  $^1\text{H}$  NMR spectrum data are tabulated in table 3.

Table 3  $^1\text{H}$  NMR spectrum data of HBSE-II terpolymer

Chemical shift $\delta$ ppm	Nature of proton assigned
1.2	$-\text{CH}_2-$
2.3	DMSO solvent
3.8	$\text{CH-OH}$
6.5	Aromatic proton (Aromatic-H) (asymmetrical substitution pattern)
8.2	$-\text{CHO}$

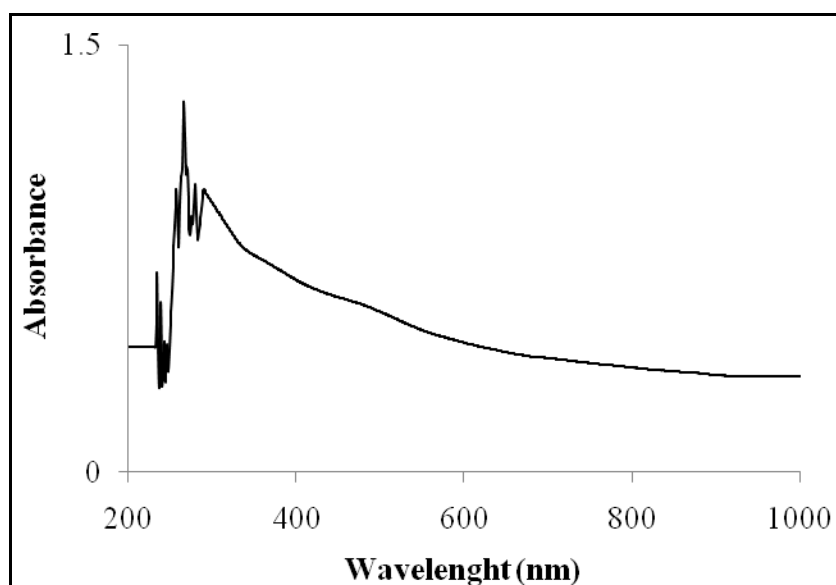


Figure 4 UV-Visible spectrum of HBSE-II terpolymer

### 3.4 UV-Visible spectrum

UV-Visible spectrum of HBSE-II terpolymer in DMSO solvent recorded by UV-Visible double beam spectrophotometer, Shimadzu, model-1800 at the department of nanotechnology, Shivaji Science College, Nagpur. The electronic spectrum of the HBSE-II terpolymer is shown in figure 4.

A peak at 259.0 nm was assigned to  $n-\sigma^*$  transition for ether (-O-) group and peak at 265.5 nm was assigned to  $\pi-\pi^*$  transition for aromatic ring.  $n-\pi^*$  transitions at 281.0 nm was due to -CHO group [15]. The UV-Visible spectrum data are tabulated in table 4.

**Table 4 UV-Visible spectrum data of HBSE-II terpolymer**

Transition	Wavelength (nm)	The group assigned
$n-\sigma^*$	259.0	Ether linkage (-O-)
$\pi-\pi^*$	265.5	Aromatic ring
$n-\pi^*$	281.0	-CHO group

### 3.5 Thermogravimetric Analysis

The thermogram of HBSE-II was recorded at Department of Material Science, VNIT, Nagpur using Perkin Elmer Diamond TGA/DTA analyzer. TG parameter calculated by applying an analytical method proposed by Freeman-Carroll and Sharp-Wentworth [16-19].

#### 3.5.1 Freeman-Carroll method:

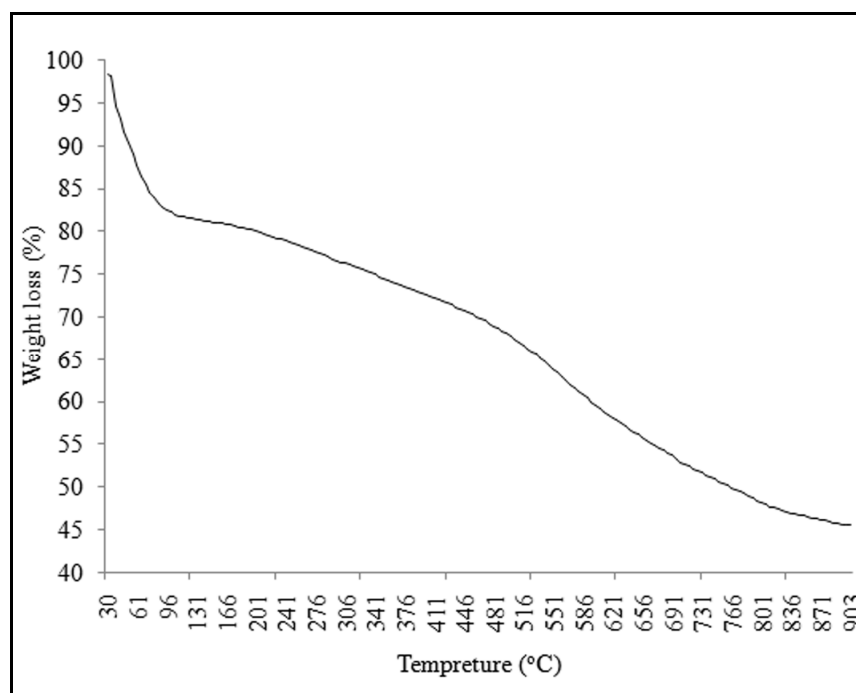
In this method, activation energy and order of degradation are related to equation (3),

$$\frac{\Delta \log( dw / dt )}{\Delta \log W_r} = \left[ - \frac{Ea}{2.303 R} \right] \times \frac{\Delta (1 / T)}{\Delta \log W_r} + n, \quad (3)$$

Where,  $(dw/dt)$  = Rate of change in weight with time,

$W_r$  = Difference between weight loss at completion of reaction, and at time  $t$ ,  $E_a$  = Energy of activation and  $n$  = Order of reaction. The plot of  $\frac{\Delta \log( dw / dt )}{\Delta \log W_r}$  versus  $\frac{\Delta (1 / T)}{\Delta \log W_r}$  is a straight line, with a slope of  $(-E_a/2.303R)$ .

Energy of activation ( $E_a$ ) determined from the slope and order of reaction ( $n$ ) obtained with the help of intercept.



**Figure 5 Thermogram of HBSE-II terpolymeric resin**

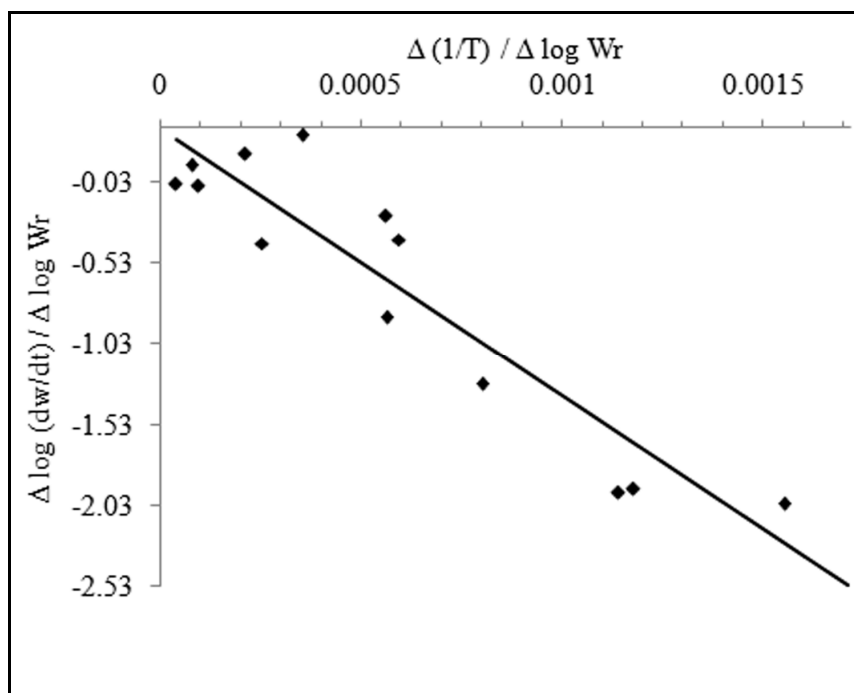


Figure 6 Freeman – Carroll plot of HBSE-II terpolymeric resin

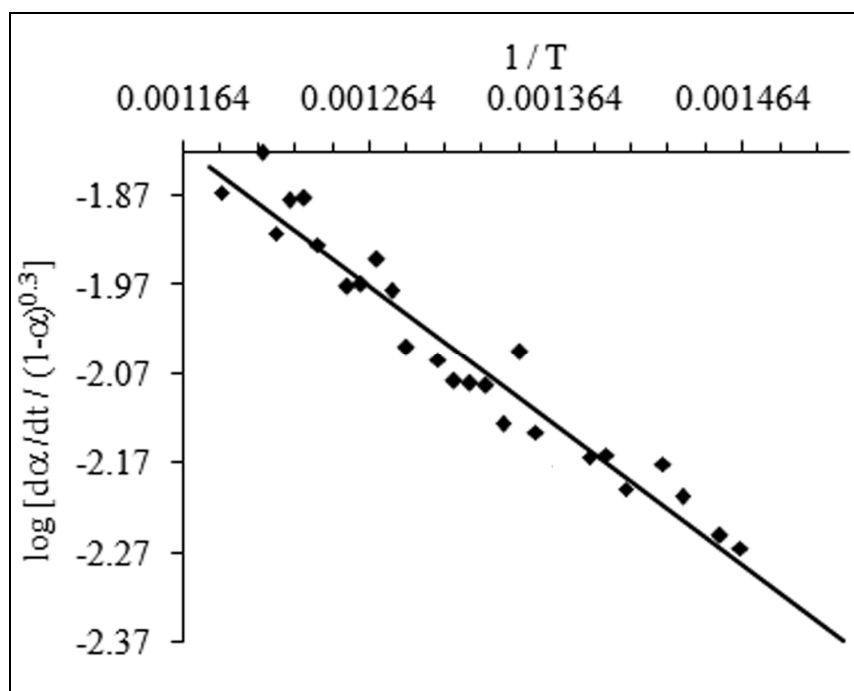


Figure 7 Sharp-Wentworth plot of HBSE-II terpolymeric resin

### 3.5.2 Sharp-Wentworth method:

$$\log \frac{(d\alpha/dt)}{(1-\alpha)^n} = \log \frac{A}{\beta} - \frac{Ea}{2.303 RT} \quad (4)$$

Equation (4) has been used to evaluate the kinetic parameters. Where,  $(d\alpha/dt)$  = Fraction of weight loss with time,  $\beta$  = Linear heating rate,  $A$  = Frequency factor,  $\alpha$  = Fraction of molecule decomposed. By plotting the graph between  $\log \frac{(d\alpha/dt)}{(1-\alpha)^n}$  versus  $\frac{1}{T}$ , the straight line graph obtained with a slope of  $(-Ea/2.303R)$  from which activation energy calculated and frequency factor ( $A$ ) evaluated from intercept. The change in apparent entropy ( $\Delta S^*$ ) and change in free energy ( $\Delta G$ ) calculated by further calculations.

Thermogram of HBSE-II terpolymer is shown in figure 5. The HBSE-II terpolymer was allowed to heat up to 1000°C in argon atmosphere at a linear heating rate of 10°C min<sup>-1</sup>. The decomposition of HBSE-II terpolymer resin was studied between 405-591°C. FC and SW plots are shown in figure 6 and figure 7 respectively. Thermokinetic parameters are tabulated in table 5.

**Table 5 Thermokinetic Parameters of HBSE-II Terpolymeric resin**

Thermokinetic Parameters	HBSE-II	
Temperature range (°C)	405°C – 591°C	
Method	FC	SW
Activation energy (Ea) in kJ	26.41	29.97
Frequency factor (A) in min <sup>-1</sup>	10.17	10.18
Apparent entropy change (ΔS*) in J/K	-233.38	-233.37
Free energy change (ΔG) in kJ	202.37	205.21
Order of reaction (n)	0.3	0.3

Thermokinetic parameters have been calculated on the basis of thermal activation energy. It has been found that from table 5, the values of thermokinetic parameters were comparable indicating common reaction mode [20-21].

### CONCLUSION

The results so obtained reveals following important conclusions:

The elemental analysis, FT-IR, <sup>1</sup>H NMR and UV-Visible spectroscopy study, is in good agreement with the assigned tentative structure of HBSE-II terpolymeric resin.

The thermal activation energies (Ea), apparent entropy change (ΔS\*) and free energy (ΔG) are determined by Freeman-Carroll and Sharp-Wentworth methods are in good agreement. The order of degradation n = 0.3 calculated from the intercept of FC-plot satisfy SW-equation with good approximation hence confirms the said order of degradation.

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