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Thermal degradation and kinetic study of terpolymer resin-I derived from p-hydroxybenzaldehyde, succinic acid and ethylene glycol

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ABSTRACT

Resin abbreviated as HBSE-I was synthesized by polycondensation in the presence of polyphosphoric acid as a catalyst using monomers p-hydroxybenzaldehyde (0.1M), succinic acid (0.1M) and ethylene glycol (0.3M) at 120^{0}C. The molecular weight was determined by non-aqueous conductometric titration. Terpolymer was characterized by elemental analysis, FT-IR, ^{1}H NMR and UV-Visible spectroscopy. Thermokinetic parameters were calculated by using Freeman-Carroll (FC) and Sharp-Wentworth (SW) methods in the temperature range 345-446^{0}C. The values of the activation energy (Ea), frequency factor (A), apparent entropy change (ΔS) and free energy change (ΔG) were in good agreement. The order of degradation obtained by the FC method was found to be 1.91 which was further confirmed by SW method.*

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

INTRODUCTION

The synthesized terpolymer showing versatile applications and properties attracted the attention of scientist and introduced the innovation in the polymer chemistry. Terpolymeric resin has been subjects of interest for many decades for day to day application. Terpolymers are used in electrical sensors and electronic devices such as a computer chip and electrical materials [1]. Terpolymeric resins with good thermal stability have enhanced the scope for development of polymeric materials having desired application at elevated temperature [2-13].

Nandekar et al studied the thermal behavior of synthesized copolymer derived from salicylic acid and thiosemicarbazide [14]. Felix et al studied the thermal behavior and decomposition kinetics of Salbutamol under isothermal and non-isothermal conditions [15]. In our laboratory, extensive research work has been carried out and reported on the synthesis, characterization, thermal degradation, electrical conductivity and ion exchange on terpolymer [16-21]. Present communication deals the study of thermal degradation and thermokinetic parameters of HBSE-I 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-I terpolymer resin

The HBSE-I terpolymer resin was synthesized by polycondensation, to a well-stirred and ice-cooled mixture of p-hydroxybenzaldehyde (0.1M), succinic acid (0.1M) and ethylene glycol (0.3M), 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^{0}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-I. 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 76 %. The scheme of synthesis of HBSE-I is shown in figure 1.

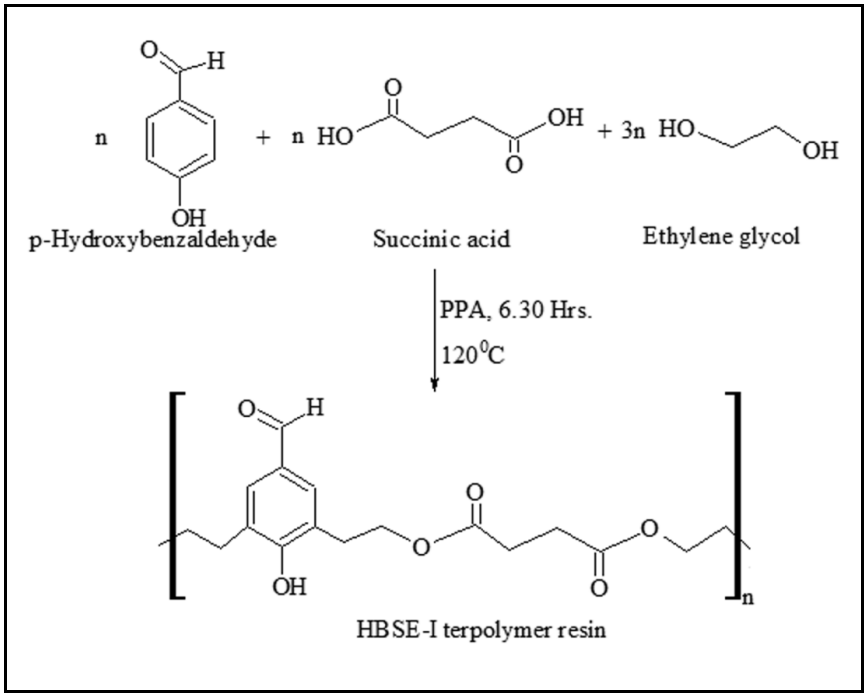

Figure 1 Synthesis scheme of HBSE-I terpolymeric resin

RESULTS AND DISCUSSION

HBSE-I 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 intitrantte alcohol as titrant [22]. 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),

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

$\overline{Mn}$ = $\overline{Dp}$ x Repeat unit weight …….. (2)

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

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

%C		%H		Mol. Formula of repeating unit	Mol. Wt. Of repeating unit	$\overline{Dp}$	Mol. Weight ($\overline{Mn}$)
Cal.	Found	Cal.	Found				
63.75	63.68	6.25	6.19	$C_{17}H_{20}O_6$	320	15	4800

3.2 FT-IR Spectrum

FT-IR spectrum of HBSE-I 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 cm^{-1}. The IR-spectrum of HBSE-I terpolymeric resin is shown in figure 2.

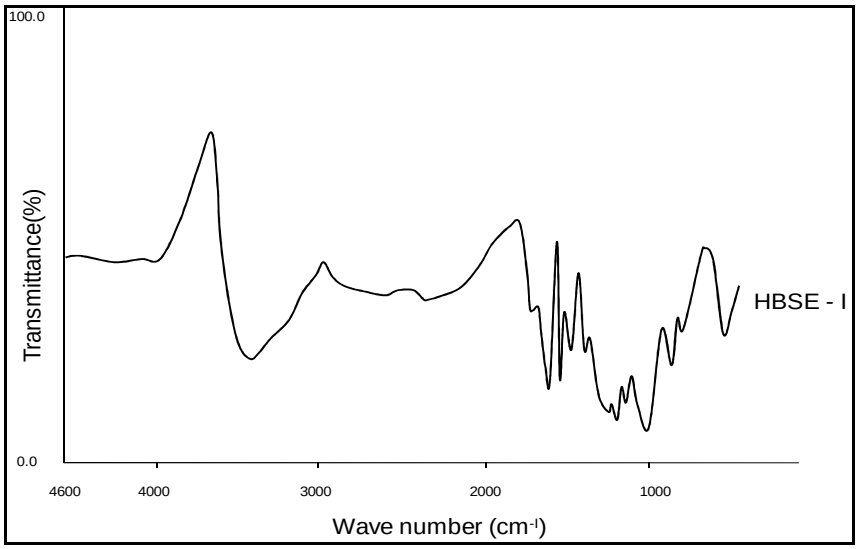

Figure 2 FT-IR spectrum of HBSE-I terpolymer

A broad absorption band appeared in the region 3437 cm^{-1} was assigned to the stretching vibrations of phenolic (-OH) group exhibiting intermolecular hydrogen bonding. The presence of peaks at 2920 cm^{-1} and 2845 cm^{-1} were due to the –C-H- stretch in the aldehyde (doublet due to Fermi resonance). A peak at 1674 cm^{-1} was due to C=O stretch (ester). A peak appeared at 1654 cm^{-1} was due to the C=O band (an aldehyde). A Peak at 1603 cm^{-1} was due to aromatic-ring present in HBSE-I. A peak appeared at 1479 cm^{-1} was due to methylene bridge coupled with aromatic ring. Peaks appeared at 1421 cm^{-1} and 1359 cm^{-1} were assigned to the plane bending vibration of phenolic –OH. A peak appeared at 1356 cm^{-1} was due to aldehyde C-H bend. The broad band displayed at 1219 cm^{-1} was due to the C-O-C stretch (saturated ester) group. A peak at 1167 cm^{-1} was due to O-C-C band stretch in HBSE-I. 1, 2, 3, 5-tetra substitution of aromatic ring was assigned due to the peaks at 1093 cm^{-1} and 972 cm^{-1}. The presence of peak at 831 cm^{-1} was due to the -CH_2- (wagging) [23-24]. FT-IR spectral data of HBSE-I terpolymer is tabulated in table 2.

Table 2 FT-IR frequencies of HBSE-I terpolymer

Observed frequency (cm^{-1})	Assignment
3437 (b)	-OH bonded (phenolic)
2920 (w), 2845 (w)	C-H stretching in aldehyde (doublet due to Fermi resonance)
1674 (w)	C=O stretch (ester)
1654 (w)	C=O band (aldehyde)
1603 (s)	Aromatic-ring
1479 (w)	CH_2 bending
1421 (w), 1359 (w)	-OH bending (phenol)
1356 (w)	Aldehydic C-H bending
1219 (b)	C-O-C stretch (saturated ester)
1167 (w)	The O-C-C band stretch
1093 (w), 972 (b)	1,2,3,5 tetra substituted aromatic ring
831 (w)	-CH_2-wagging

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

3.3 ^{1}H NMR Spectrum

^{1}H NMR spectrum of HBSE-I terpolymer using DMSO-d^6 solvent was scanned on NMR spectrophotometer SAIFNM100820A, at Sophisticated Test and Instrumentation Center, Cochin University, Kerala, India. The ^{1}H NMR spectrum of HBSE-I terpolymer is shown in figure 3.

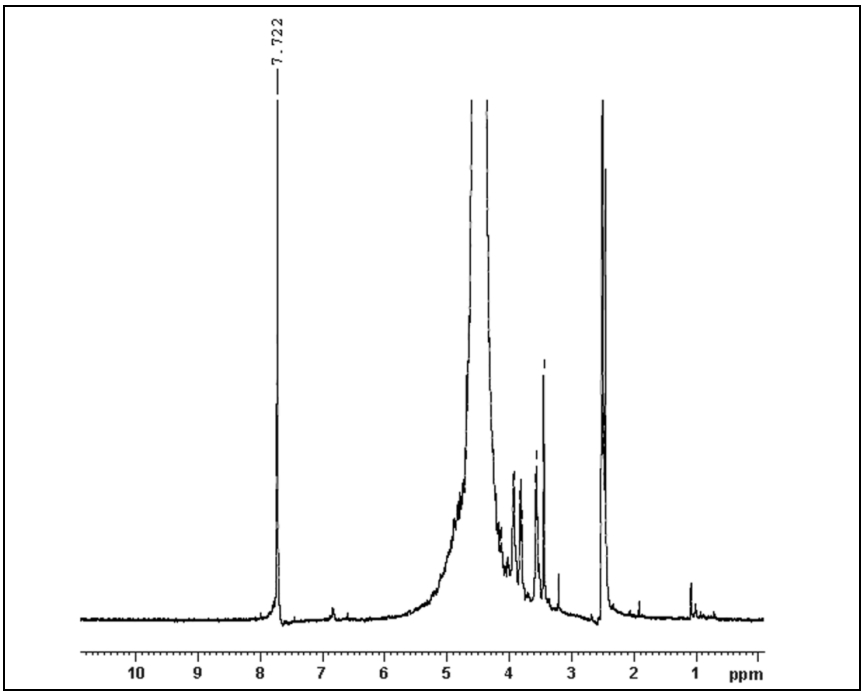

Figure 3 ^{1}H NMR spectra of HBSE– I terpolymer

The δ in 1.1 δppm was of -C**H**$_2$- in HBSE-I. The signal at 2.5 δppm was due to DMSO solvent. Signal at 3.8 δppm was attributed to C**H**-OH moiety. The signal at 6.9 δppm was due to aromatic ring protons in HBSE-I. The signal at 7.7 δppm was due to the aldehydic proton [25]. ^{1}H NMR spectrum data are tabulated in table 3.

Table 3 ^{1}H NMR spectrum data of HBSE– I terpolymer

Chemical shift δ ppm	Nature of proton assigned
1.1	-C**H**$_2$-
2.5	DMSO solvent
3.8	C**H**-OH
6.9	Aromatic proton (Aromatic-**H**) (asymmetrical substitution pattern)
7.7	-C**H**O

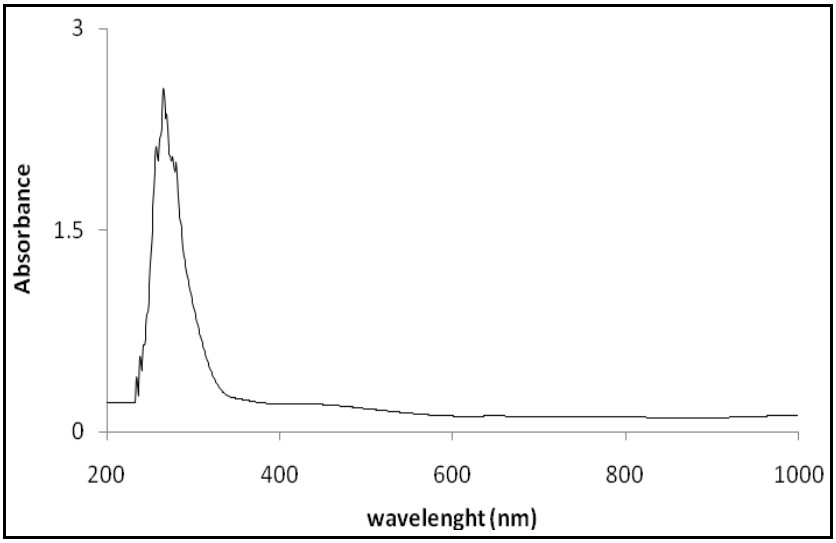

Figure 4 UV-Visible spectrum of HBSE-I terpolymer

3.4 UV-Visible spectrum

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

A peak at 257.5 nm was assigned to n-**σ*** transition for ether (–O–) group and peak at 265.0 nm was assigned to **σ*** transition for aromatic ring. n-**σ*** transitions at 280.0 nm was due to -CHO group [26]. The UV-Visible spectrum data are tabulated in table 4.

Table 4 UV-Visible spectrum data of HBSE-I terpolymer

Transition	Wavelength (nm)	The group assigned
n-□*	257.5	Ether linkage (–O–)
□□□*	265.0	Aromatic ring
n-□*	280.0	-CHO group

3.5 Thermogravimetric Analysis

The thermogram of HBSE–I 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 [27-31].

3.5.1 Freeman-Carroll method:

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

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

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

Wr = Difference between weight loss at completion of reaction, and at time t, Ea = Energy of activation and n = Order of reaction. The plot of $\frac{\Delta \log(\ dw\ /\ dt\ )}{\Delta \log\ Wr}$ verses $\frac{\Delta\ (1\ /\ T\ )}{\Delta \log\ Wr}$ is a straight line, with a slope of (-Ea/2.303R). Energy of activation (Ea) determined from the slope and order of reaction (n) obtained with the help of intercept.

3.5.2 Sharp-Wentworth method:

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

Equation (4) has been used to evaluate the kinetic parameters. Where, (dα/dt) = Fraction of weight loss with time, β = Linear heating rate, A = Frequency factor, α = Fraction of molecule decomposed. By plotting the graph between $\log\ \frac{(d\alpha\ /\ dt\ )}{(1-\alpha)^n}$ verses $\frac{1}{T}$, 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 (ΔS*) and change in free energy (ΔG) calculated by further calculations.

Thermogram of HBSE-I terpolymer is shown in figure 5. The HBSE-I terpolymer was allowed to heat up to 1000^0C in argon atmosphere at a linear heating rate of 10^oC min^{-1}. The decomposition of HBSE-I terpolymer resin was studied between 345-446^0C. FC and SW plots are shown in figure 6 and figure 7 respectively. Thermokinetic parameters are tabulated in table 5.

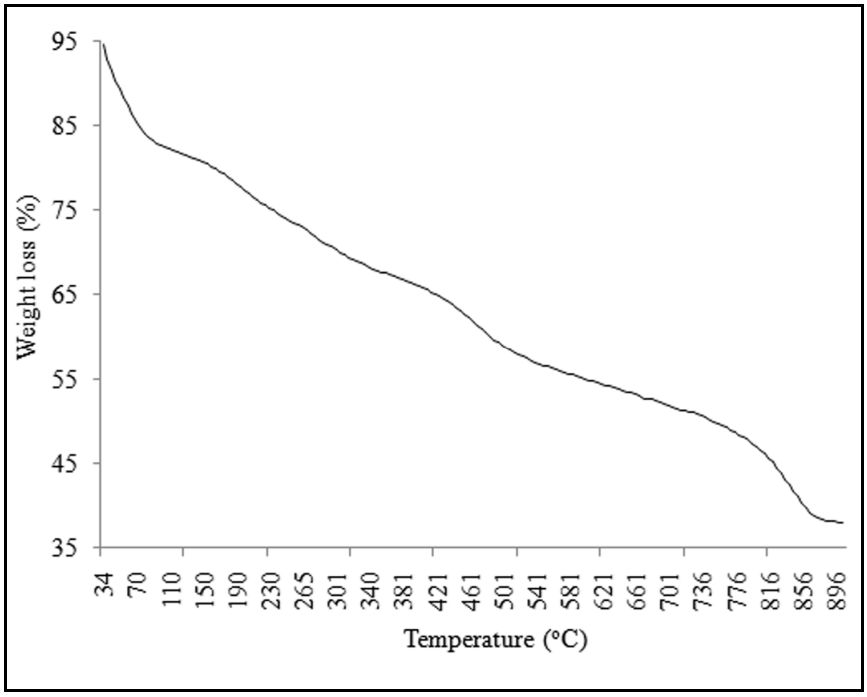

Figure 5 Thermogram of HBSE-I terpolymeric resin

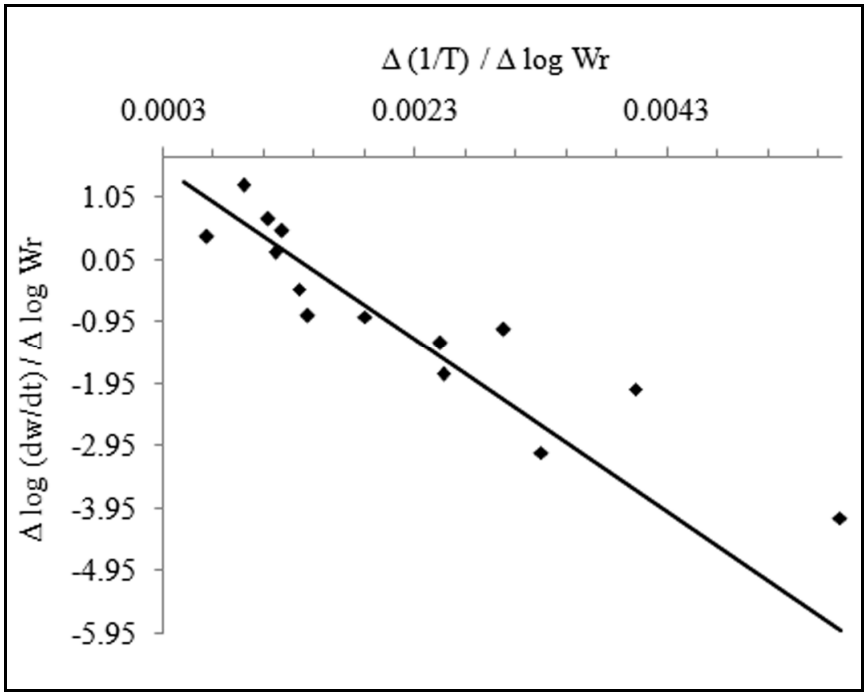

Figure 6 Freeman – Carroll plot of HBSE-I terpolymeric resin

Table 5 Thermokinetic Parameters of HBSE-I Terpolymeric resin

Terpolymer	**HBSE-I**	
Temperature range (°C)	345°C – 446°C	
Method	FC	SW
Activation energy (Ea) in kJ	31.50	28.95
Frequency factor (A) in min^{-1}	12.37	12.32
Apparent entropy change (ΔS*) in J/K	-229.33	-229.36
Free energy change (ΔG) in kJ	160.66	158.15
Order of reaction (n)	1.91	1.91

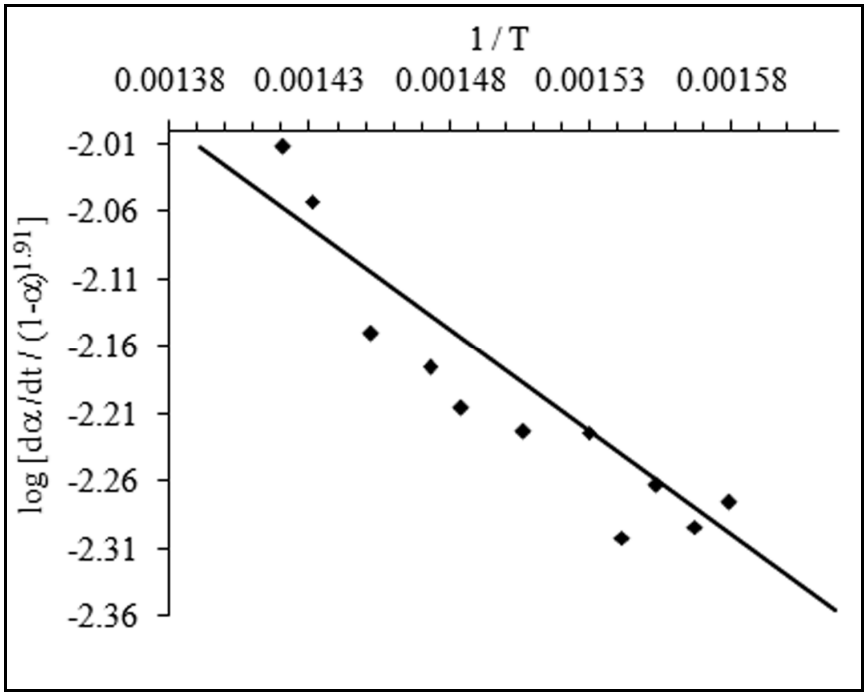

Figure 7 Sharp-Wentworth plot of HBSE-I terpolymeric resin

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 [32-34].

CONCLUSION

The results so obtained reveals following important conclusions

1) The elemental analysis, FT-IR, ^{1}H NMR and UV-Visible spectroscopy study, is in good agreement with the assigned tentative structure of HBSE-I terpolymeric resin.
2) 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.
3) Abnormal low values of frequency factor were due to 'slow' degradation the decomposition reaction of HBSE-I terpolymer. The negative values for entropy indicated that the activated polymer has a more ordered structure than the reactants and the reaction was slower than normal. This was further supported by the low value of frequency factor.
4) The order of degradation n= 1.91 calculated from the intercept of FC-plot satisfy SW-equation with good approximation hence confirms the said order of degradation.
5) HBSE-I terpolymer resin is found to be thermally stable below 150^{0}C.

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