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Semiconducting behavior and thermokinetic study of terpolymeric resin-I derived from p-hydroxybenzaldehyde, adipic acid and ethylene glycol

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ABSTRACT

Resin abbreviated as HBAE-I was synthesized by polycondensation in presence of PPA using p-hydroxybenzaldehyde (0.1M), adipic acid (0.1M) and ethylene glycol (0.3M). The structure of resin was assigned by elemental analysis, IR, NMR spectroscopy. Resin was found to show semiconducting behavior in the temperature range 302 K to 488 K. The activation energy of conduction was found to be 785.10 J mol^{-1}. The thermokinetic parameters were determined by Freeman-Carroll (FC) and Sharp Wentworth (SW) method in temperature range 265- 685^{0}C. The thermokinetic parameters calculated with aid of these methods were found to be in good agreement.

Keywords: Electrical conductivity, Resin, TGA, Semiconductor, Thermal activation energy.

INTRODUCTION

In recent year considerable interest has been made to improve the quality of polymer by co-polymerization most probably terpolymerisation either by modifying methods or by introduction of variety of functional monomers. The polymer scientists are trying to polymeric resins with improved properties such as thermal stability, durability high chemical resistivity, conductivity and ion exchange capacity in the domain of desired applicability. Semi conducting polymer have been the subjects of study for many decades for day to day application product for example, uses in electrical sensors and electronic device such as a computer chip, electrical materials, industries, etc.

Thermogravimetric study of polymer provides information about the degradation pattern during heating and thermal stability. The thermal stability of the polymer was evaluated by thermogravimetry. The study of thermal behavior of polymers in air at different temperature provides important information about its practical applicability.

Patel et al have measured the electrical resistivity of 2,4-dihydroxy acetophenone- urea-formaldehyde terpolymer over a wide temperature range [1].Pal et al were reported semiconducting behavior of salicylic acid-biuret-formaldehyde and salicylic dithiobiuret trioxane terpolymeric resine [2-3]. Pancholi et al studied electrical conductivity of 2-hydroxyacetophenone-trioxane and this resine rank to be semiconductor [4]. Gurnule et al recently reported semiconducting behavior of salicylic acid-oxamide-trioxane terpolymer [5]. Lingala et al studied the electrical conductivity of resin derived from p-hydroxybenzoic acid-adipamide-formaldehyde and found the conductivities in order of 10^{-12} to 10^{-11} scm^{-1} at room temperature and activation energy in order of 10-22 J/K [6]. Singru et al studied electrical conductivity of p-Cresol-Oxamide-Formaldehyde terpolymer Resin [7].Masram et al reported kinetic study of thermal degradation of resin derived from salicylaldehyde, ethylenediamine and formaldehyde [8]. In earlier communication numbers of studies on terpolymers have been reported in literature [9-23]. In our laboratory, extensive research work has been carried out on synthesis, characterization, thermal degradation, electrical conductivity of terpolymers [24-30].

The present communication deals with the electrical behavior of HBAE-I terpolymeric resin over a wide range of temperature and thermo kinetic parameters was determined by using Freeman- Carroll and Sharp-Wentworth methods.

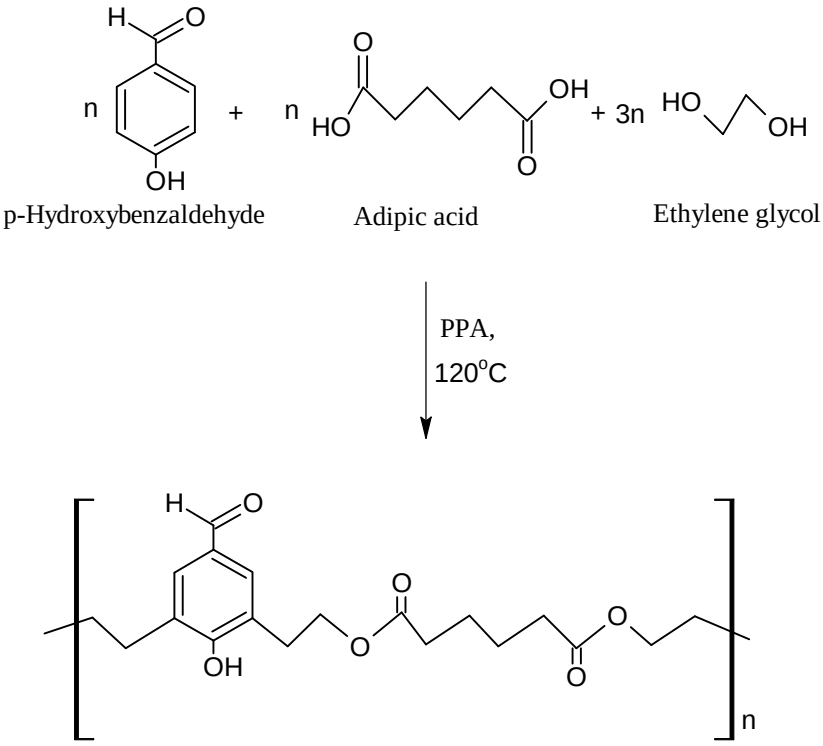
MATERIALS AND METHODS

Chemicals

All chemicals used as starting materials in the synthesis of terpolymer resin were of AR, or chemically pure grade. The Chemicals such as p-hydroxybenzaldehyde, adipic acid, ethylene glycol, polyphosphoric acid were of AR grade manufactured by s.d. Fine chemicals Ltd (Mumbai).

Synthesis of HBAE-I terpolymeric resin

To a well-stirred and ice-cooled mixture of p-hydroxybenzaldehyde (0.1M), adipic acid (0.1M) and ethylene glycol (0.3M), polyphosphoric acid (PPA, 20 gm) was added slowly with continuous stirring as a catalyst. The reaction mixture was left at room temperature for 0.5 h and heated on an oil bath at 120^0C for 5 h. The reaction mixture was than cooled, poured on crushed ice and left over night. Terpolymer resin HBAE-I was synthesized; a brown solid was separated out. It was collected by filtration and washed with cold water and hot water several time to remove unreacted acid and monomer. The polymer was brown in color, Yield (73%). The synthesis reaction of HBAE-I terpolymeric resin is shown in fig 1



p-Hydroxybenzaldehyde Adipic acid Ethylene glycol

HBAE-I Terpolymeric resin

Fig-1 Scheme –Synthesis of HBAE-I Terpolymeric resin

RESULTS AND DISCUSSION

Elemental analysis

The terpolymeric resin was subjected to elemental analysis for C, H, N at CIMFR Unit, Nagpur, by Analytical functional testing Vario MICRO CHN elemental analyzer (Germany). The elemental analysis is presented in following table 1.

Table 1 Elemental analysis of HBAE-I terpolymeric resin

Terpolymer resin	C		H	
HBAE-I	Calculated	Found	Calculated	Found
	59.3	58.8	7.2	7.1

FTIR Spectrum

IR spectra of synthesized terpolymeric resin was recorded at Department of pharmacy, RTM Nagpur University, using FT-IR spectrometer Shimadzu, model no. 8101A in the range of 4600 – 500 cm^{-1}.

The IR-spectra of HBAE-I terpolymeric resin is presented in Fig.2 and the IR-spectrum data are presented in table 2. A broad absorption band appeared in the region 3434 cm^{-1} was assigned to the stretching vibrations of phenolic hydroxyl (-OH) group exhibiting intermolecular hydrogen bonding. The presences of peaks at 2922 cm^{-1} and 2847 cm^{-1} were due to the –C-H- stretch in the aldehyde (doublet due to Fermi resonance). 1671 cm^{-1} due to C=O stretch (ester). A peak at 1655 cm^{-1} assigned to C=O band (aldehyde). The presence of peak at 1603 cm^{-1} was due to aromatic-ring. A peak appeared at 1477 cm^{-1} due to ethylene bridge coupled with aromatic ring. Peak appeared at 1358 cm^{-1} assigned to in plane bending vibration of phenolic –OH. Peak at 1355 cm^{-1} was due to aldehyde C-H bend. . The broad band displayed at 1228 cm^{-1} due to the C (=O)-O stretch (saturated ester) group. 1171 cm^{-1} was due to O-C-C band stretch. 1, 2, 3, 5- tetra substitution of aromatic ring was assigned to the peaks at 1096 and 967 cm^{-1}. The presence of peak at 830 cm^{-1} was due to the -CH_2- (wagging) [31-32].

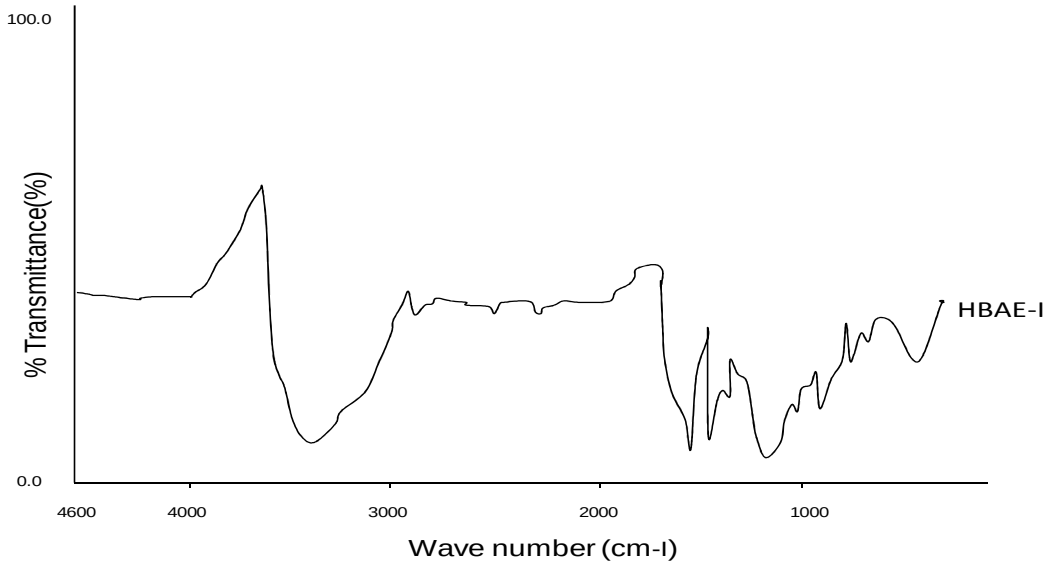


Fig-2 IR spectra of HBAE-I terpolymer resin

Table 2. IR frequencies of HBAE-I terpolymer resin

Observed frequency(cm^{-1})	Assignment
3434	-OH bonded (phenolic)
2922,2847	C-H streching in aldehyde (doublet due to Fermi resonance)
1671	C=O stretch (ester)
1655	C=O band (aldehyde)
1603	Aromatic-ring
1477	CH_2 bending (Ethylene bridge)
1423, 1358	-OH bending (phenol)
1355	Aldehydic C-H bending
1228	C(=O)-O stretch(saturated ester)
1171	O-C-C band stretch
1096, 967	1,2,3,5 tetra substituted aromatic ring
830	-CH_2-wagging

Electrical conductivity

The DC conductivities of HBAE-I resin was study for temperature range 302 K to 488 K. The value of specific conductance was determined from specific resistance. The powdered sample of HBAE-I was palatalized by hydraulic press at pressure of 17 lb $inch^{-2}$. The surface of pallet was made conducting by applying graphite paste. The diameter and thickness was measured. The solid state conductivity as function of temperature was recorded by two probe method. The electrical conductivity varies exponentially with the absolute temperature according to the well know relationship,

$\sigma = \sigma^{o} \exp.(-Ea/KT)$

where, σ= Electrical conductivity at temperature T
σ^{o} = Electrical conductivity at temperature T→σ ∞ i.e., constant.
Ea= Activation energy of electrical conductance
K= Boltzmann constant
T= Absolute temperature

The plot of log σ versus 1/T was found to be linear in the temperature range under study, as shown in fig.3 which indicate that the Wilson's exponential law was obeyed. This indicates the semiconducting nature of the HBAE-I terpolymeric resin. The electrical activation energy (Ea) of electrical conductance was found to be 785.10 $Jmol^{-1}$. The electrical conductivity for HBAE-I resin was found in the range of $0.7603x10^{-6}$ to $0.9930x10^{-6}$ Scm^{-1} for temperature range 302K to 488K.

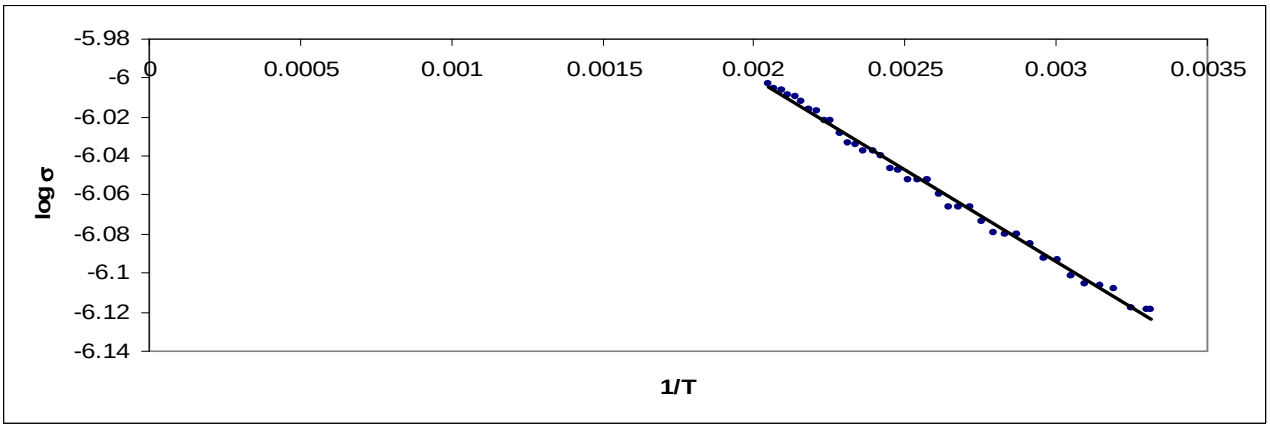


Fig.3. Wilson's plot of HBAE-I terpolymeric resin

Thermo gravimetric analysis

The thermogram of HBAE –I terpolymeric resin was recorded at department of Material Science, VNIT, Nagpur, using Perkin Elmer Diamond TGA/DTA analyzer. Thermokinetic parameters of HBAE-I were determined by using Freeman- Carroll and Sharp-Wentworth methods. To provide evidence regarding the degradation system of analyzed compounds, TG curves derived by applying an analytical method proposed by Freeman- Carroll and Sharp-Wentworth [33-34].

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

$$\frac{\Delta \log\ dw\ /\ dt}{\Delta \log\ Wr} = n - \frac{Ea}{2.303\ R} \cdot \frac{\Delta (1/T)}{\Delta \log\ Wr} \quad \ldots\ldots\ldots \quad .(1)$$

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

Wr = Wc-W

Wc = Weight loss at completion of reaction
W = Total weight loss up to time t
Ea = Energy of activation
n = Order of reaction

$\frac{\Delta \log\ dw\ /\ dt}{\Delta \log\ Wr}$ was plotted against $\frac{\Delta 1/T}{\Delta \log\ Wr}$. The activation energy of degradation (Ea) was obtained by slope and the order of reaction (n) was determined with the aid of intercept.

The thermokinetic parameters can be determined by Sharp – Wentworth method using equation,

$$\log \frac{(d\alpha / dt)}{(1-\alpha)^n} = \log \frac{A}{\beta} - \frac{Ea}{2.303\ RT} \quad \text{.....(2)}$$

Where,
dα/dt = Rate of change of fraction of weight with change in temperature
β = Linear heating rate dT/dt.
A = Frequency factor

A straight line graph was obtained when $\log \frac{d\alpha / dt}{(1-\alpha)^n}$ was plotted against $\frac{1}{T}$, the activation energy (Ea) was obtained from slope and with the help of intercept the frequency factor (A) was obtained. The change in entropy (ΔS), change in free energy (ΔG) can also be calculated by further calculations. The thermogram of HBAE-I resin was scanned up to 1005^0C in inert atmosphere at linear heating rate of 10^oC min^{-1}. The thermogram reveals that initial weight loss up to 115^0C due to loss of water. The decomposition of resin between 265-685^0C was studied .FC and SW plots are shown in fig 5 and fig 6 respectively.

The order of decomposition obtained by FC method was found to be 0.93 which was further confirmed by SW method and thermokinetic parameters are tabulated in table 3. Thermal activation energies of degradation were found to be 35.09 KJ (FC method) and 31.69 KJ (SW method).

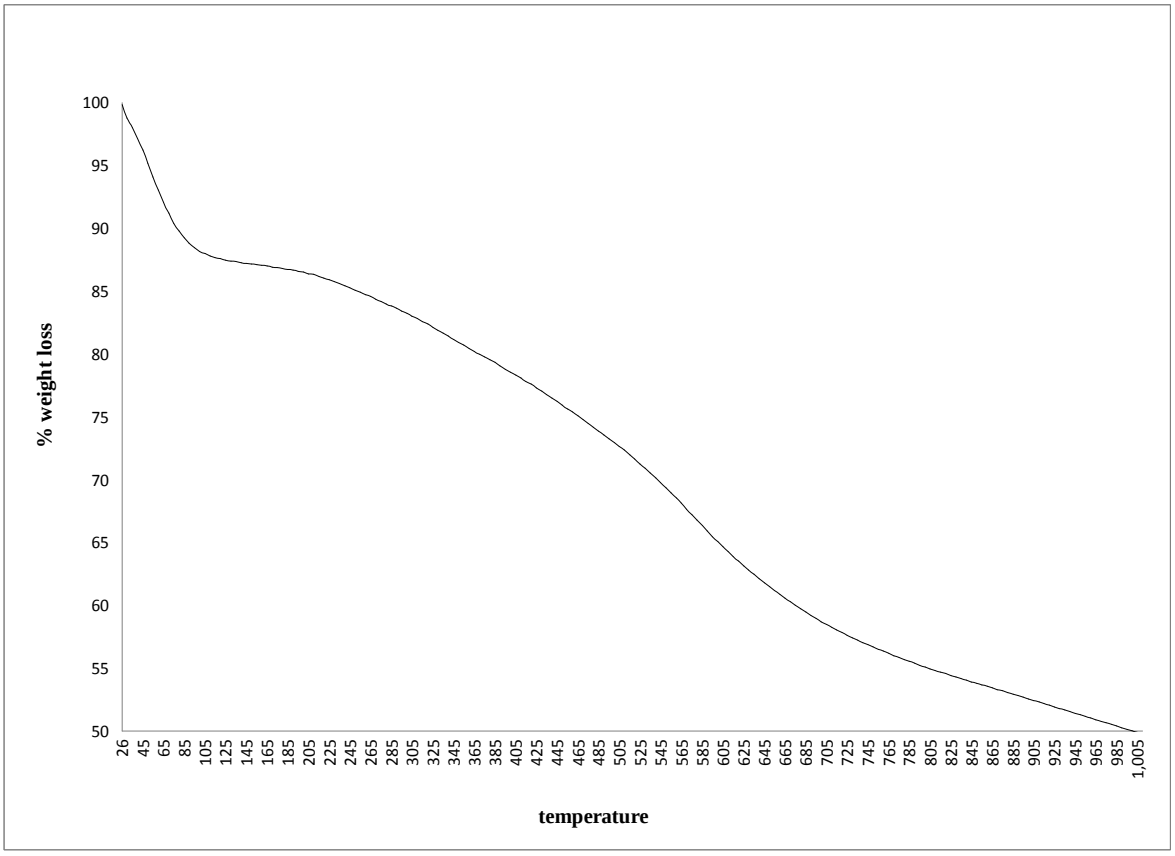


Fig.4. Thermogram of HBAE-I terpolymeric resin

Table 3. Thermokinetic Parameters of HBAE-I terpolymeric resin

Parameters	FC method	SW method
Thermal activation energy, Ea(KJ)	35.09	31.69
Frequency factor, A(min^{-1})	12.09	11.08
Apparent entropy, ΔS(J/K)	-232.42	-233.14
Free energy, ΔG (KJ)	220.58	217.77
Order of degradation, (n)	0.93	0.93
FC method = Freeman-Carroll method, SW method = Sharp-Wentworth method		

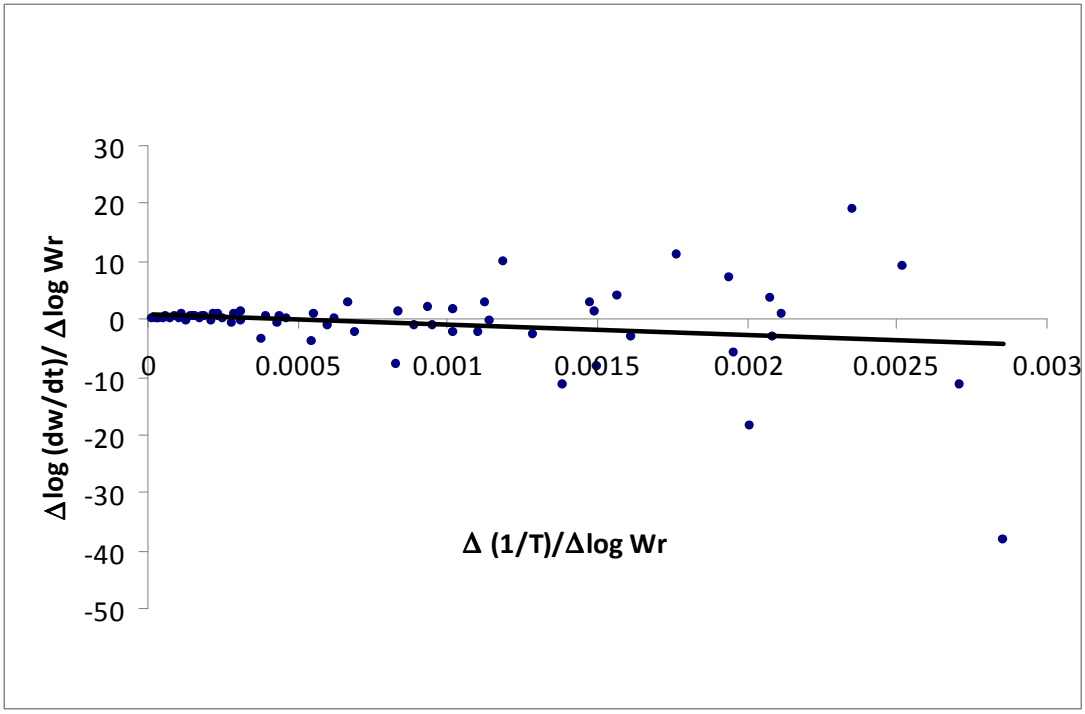


Fig.5. Freeman –Carroll plot of HBAE-I terpolymeric resin

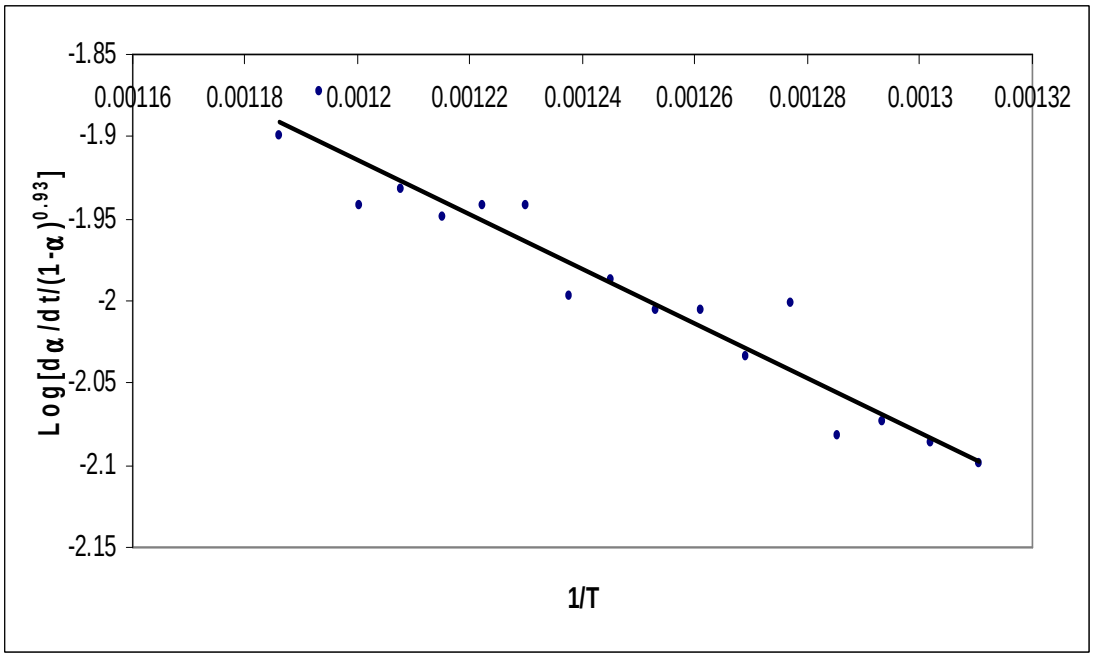


Fig.6. Sharp-Wentworth plot of HBAE-I terpolymeric resin

CONCLUSION

The elemental analysis and IR spectrum data are in good agreement with assigned tentative structure of HBAE-I terpolymeric resin. The plot of log σ versus 1/T found linear for temperature range 302K to 488K consequently Wilson's exponential law is obeyed. The linear plot implies the semiconducting behavior of HBAE-I terpolymeric resin. The electrical conduction is due to hopping of π electrons at the unsaturation centers in the polymeric matrix, as evident from the nature of plot. Thermokinetic parameters such as thermal activation energy, entropy and free energy obtained by Freeman-Carroll and Sharp-Wentworth methods are in good agreement. The high value of energy of activation energy and low value of frequency factor of thermal degradation indicate that resin is thermally stable.

The order of degradation obtained by FC method is confirmed by SW method. The fractional order (0.93) is attributed to solid state degradation.

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