



# THERMOKINETIC PARAMETERS OF TERPOLYMER RESIN-II DERIVED FROM P-HYDROXYBENZALDEHYDE, ADIPIC ACID AND ETHYLENE GLYCOL

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## ABSTRACT

Terpolymer abbreviated as HBAE-II was synthesized by polycondensation using monomers p-hydroxybenzaldehyde (0.2M), adipic acid (0.1M) and ethylene glycol (0.4M) in the presence of polyphosphoric acid as catalyst at 120°C. Terpolymer was characterized by elemental analysis, FT-IR, <sup>1</sup>H NMR and UV-Visible spectra. Thermokinetic parameters were calculated by using Freeman-Carroll (FC) and Sharp-Wentworth (SW) methods in the temperature range 399-664°C. The order of the reaction using Freeman-Carroll method was found to be 1.74. The values of the activation energy (E<sub>a</sub>), frequency factor (A), apparent entropy change (ΔS) and free energy changes (ΔG) were in good agreement. The order of degradation reaction determined by the FC method was confirmed by SW method.

**Keywords:** Apparent entropy; Free energy; Thermal degradation; Order of degradation

## 1. Introduction

Terpolymers can be used as high energy material, antioxidants, fire proofing agent, optical storage data, binders, semiconductors, molding materials, ion-exchanger. Terpolymeric resins with good thermal stability have enhanced the scope for development of smart polymeric materials having desired application at elevated temperature [1-10].

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

methods.

## 2. Experimental

### 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 HBAE-II terpolymer resin

The HBAE-II terpolymer resin was synthesized by polycondensation, to a well-stirred and ice-cooled mixture of p-hydroxybenzaldehyde (0.2M), adipic 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 adipic acid-glycol copolymer which might be formed along with HBAE-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 HBAE-II is shown in figure 1.

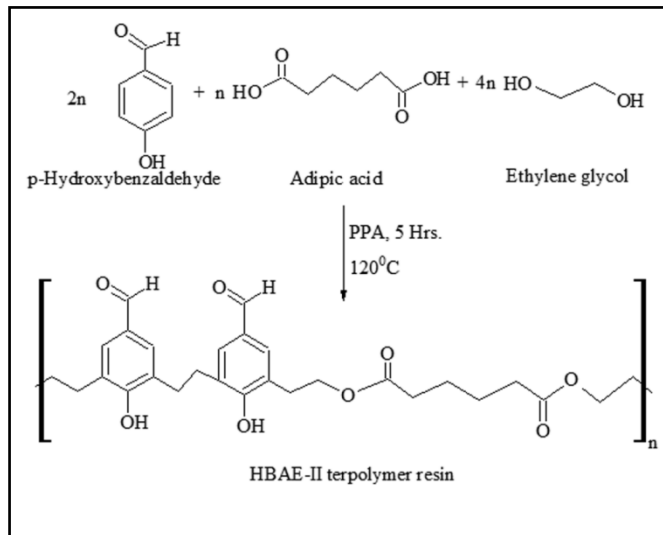


Figure 1 Synthesis scheme of HBAE-II terpolymeric resin

**3. Results and Discussion**

HBAE-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.

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

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

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

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

%C		%H		Mol. Formula of repeating unit	Mol. Wt. Of repeating unit	$\overline{Dp}$	Mol. Weight ( $\overline{Mn}$ )
Cal.	Found	Cal.	Found				
67.74	67.70	6.45	6.37	(C <sub>28</sub> H <sub>32</sub> O <sub>8</sub> ) <sub>n</sub>	496	15.9~16	7936

**3.2 FT-IR Spectrum**

FT-IR spectrum of HBAE-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 cm<sup>-1</sup>. The IR-spectrum of HBAE-II terpolymeric resin is shown in figure 2.

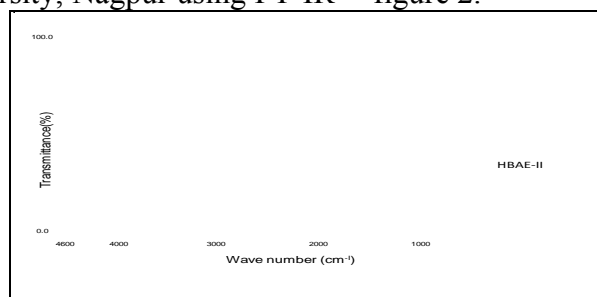


Figure 2 FT-IR spectrum of HBAE-II terpolymer

In HBAE-II, A broad absorption band appeared in the region 3433 cm<sup>-1</sup> was assigned to the stretching vibrations of phenolic hydroxyl (-

OH) group exhibiting intermolecular hydrogen bonding. The presences of peaks at 2921 cm<sup>-1</sup> and 2848 cm<sup>-1</sup> were due to the -C-H- stretch in

the aldehyde (doublet due to Fermi resonance). 1673  $\text{cm}^{-1}$  due to C=O stretch (ester). A peak at 1654  $\text{cm}^{-1}$  assigned to C=O band (aldehyde). The presence of peak at 1603  $\text{cm}^{-1}$  was due to aromatic-ring. A peak appeared at 1480  $\text{cm}^{-1}$  due to ethylene bridge coupled with aromatic ring. Peak appeared at 1420 and 1355  $\text{cm}^{-1}$  assigned to in plane bending vibration of phenolic -OH. Peak at 1354  $\text{cm}^{-1}$  was due to aldehyde C-H bend. The broad band displayed at 1229  $\text{cm}^{-1}$  due to the C (=O)-O stretch (saturated ester) group. 1171  $\text{cm}^{-1}$  was due to O-C-C band stretch. 1, 2, 3, 5- tetra substitution

of aromatic ring was assigned to the peaks at 1098 and 965  $\text{cm}^{-1}$ . The presence of peak at 828  $\text{cm}^{-1}$  was due to the -CH<sub>2</sub>- (wagging) [12-13].

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

<sup>1</sup>H NMR spectrum of HBAE-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 HBAE-II terpolymer is shown in figure 3.

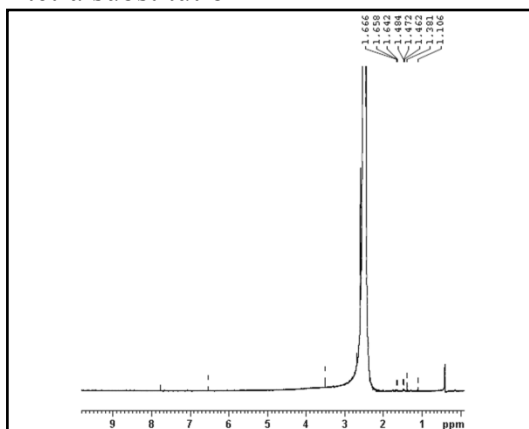


Figure 3 <sup>1</sup>H NMR spectra of HBAE- II terpolymer

In HBAE-II, The  $\delta$  in the range 1.4 ppm was of -CH<sub>2</sub>- in HBAE-II. The signal at 2.4  $\delta$  ppm was due to DMSO solvent. Signal at 3.6  $\delta$  ppm was attributed to CH-OH moiety. The signal at 6.6  $\delta$  ppm was due to aromatic ring protons in HBAE-II. The signal at 7.8  $\delta$  ppm was due to the aldehydic proton [14].

### 3.4 UV-Visible spectrum

UV-Visible spectrum of HBAE-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 HBAE-II terpolymer is shown in figure 4

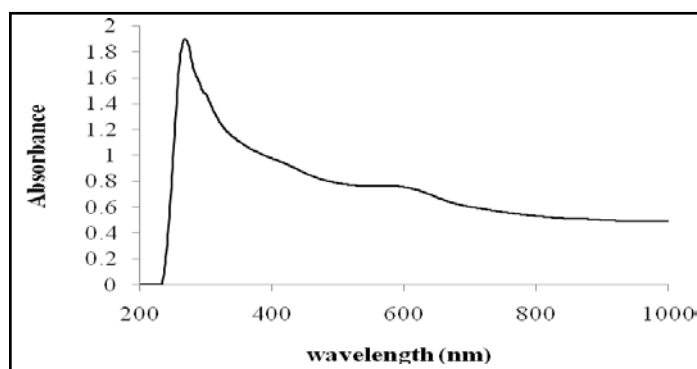


Figure 4 UV-Visible spectrum of HBAE-II terpolymer

In HBAE-II, A peak at 253 nm was assigned to n- $\sigma^*$  transition for ether (-O-) group and peak at 266 nm was assigned to n- $\sigma^*$  transition for aromatic ring. n- $\pi^*$  transitions at 296 nm was due to -CHO group.

### 3.5 Thermogravimetric Analysis

The thermogram of HBAE-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),

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

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

W<sub>r</sub> = Difference between weight loss at completion of reaction, and at time t, E<sub>a</sub> = Energy of activation and n = Order of reaction.

The plot of  $\frac{\Delta \log(dw/dt)}{\Delta \log W_r}$  verses  $\frac{\Delta(1/T)}{\Delta \log W_r}$  is a straight line, with a slope of (-E<sub>a</sub>/2.303R). Energy of activation (E<sub>a</sub>) determined from the slope and order of reaction (n) obtained with the help of intercept.

.....(3)

**3.5.2 Sharp-Wentworth method:**

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

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 (-E<sub>a</sub>/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 HBAE-II terpolymer is shown in figure 5. The HBAE-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 HBAE-II terpolymer resin was studied between 399-664°C. FC and SW plots are shown in figure 6 and figure 7 respectively. Thermokinetic parameters are tabulated in table 5.

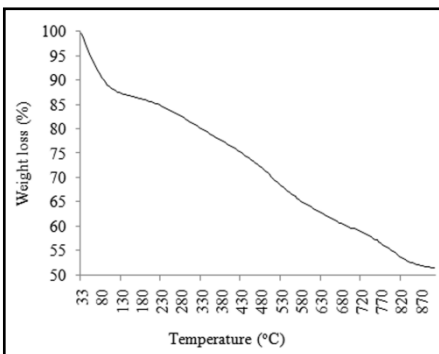


Figure 5 Thermogram of HBAE-II terpolymeric resin

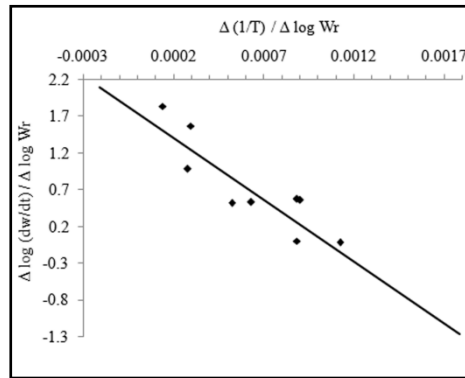


Figure 6 Freeman – Carroll plot of HBAE-II terpolymeric resin

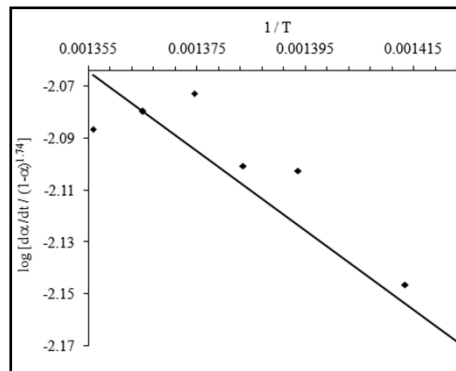


Figure 7 Sharp-Wentworth plot of HBAE-II terpolymeric resin

Table 5 Thermokinetic Parameters of HBSE-II Terpolymeric resin

Thermokinetic Parameters	HBAE-II	
Temperature range (°C)	399-664°C	
Method	FC	SW
Activation energy (E <sub>a</sub> ) in kJ	31.53	29.25
Frequency factor (A) in min <sup>-1</sup>	10.16	10.15
Apparent entropy change (ΔS*) in J/K	-233.04	-233.05
Free energy change (ΔG) in kJ	197.69	197.7
Order of reaction (n)	1.74	1.74

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].

#### 4. Conclusions

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 HBAE-II terpolymeric resin. HBAE-II terpolymer resin is found to be thermally stable below 110°C. The thermal activation energies (E<sub>a</sub>), 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 =1.74 calculated from the intercept of FC-plot satisfy SW-equation with good approximation hence confirms the said order of degradation. Abnormal low values of frequency factor were due to 'slow' degradation the decomposition reaction of HBAE-II 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.

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