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Structural and thermokinetic parameters of terpolymeric resin derived from p-hydroxyacetophenone, bis (2-amino- 1, 3, 4 -thiadiazole) and glycerol

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ABSTRACT

The resin PHBG was prepared by polycondensation of p-hydroxyacetophenone, Bis (2-amino-1, 3, 4-thiadiazole) and glycerol in presence of DCC (dicyclohexylcarbodiimide). PHBG was prepared by condensing the monomers p-hydroxyacetophenone and Bis (2- amino -1, 3, 4- thiadiazole) with glycerol using molar ratio 1:1:3. The tentative structure of resin was assigned by elemental analysis, ^{1}H NMR, ^{13} C NMR, FT-IR and UV-VIS spectra. The molecular weight of resin was determined by non aqueous conductometric titration. The thermo kinetic parameters such as apparent entropy (ΔS), frequency factor (A), free energy change (ΔG) and order of reaction were determined by Freeman Carroll (FC) and Sharp Wentworth (SW) methods. The order of degradation determined by FC method was confirmed by SW method.

KeyWords: Polycondensation, Terpolymer, TGA, Resin, Thermokinetic parameters, Thermal degradation.

INTRODUCTION

Considerable interest has been ever seen in the synthesis of terpolymer and their characterization in the last two decades owing to their superiority over the copolymers with reference to electrical insulation, heat and chemical resistivity, thermal stability, high ion exchange capacity, adhesive and high sensing ability. Literature survey has been revealed that various workers have shown immense interest in improving electrical conductivity, thermal stability, and ion exchange capacity by using various functional monomers and varying procedure of synthesis [1]. Various efforts were made by polymer chemist to improve the properties of resins by changing monomer composition in light of industrial applicability in spite of difficulties of low processesability and thermal instability. Many researchers have been characterized the formaldehyde based terpolymeric resins and studied thermal, electrical conductivity and chelating ion exchange property [2-7].Terpolymer occupy the pivotal position in the field of polymer science.The progress in this field has been extremely rapid as they are generally useful in packing materials and coating, electrical sensors, ion exchangers, organometalic semiconductors, activators, catalyst and thermally stable materials [8-13].Much of research work has been carried out on the synthesis and characterization of Bis (2-amino -1, 3, 4 -thiadiazole).The 1, 3, 4-thiadiazole ring is associated with diverse biological activities probably by virtue of incorporating a –N=C-S- linkage [14-16]. 2, 5- disubstituted -1, 3, 4-thiadiazoles which caused N- donor atoms have shown various biological activities [17-18]. Pramanik and co-workers synthesized and characterized some organic semiconducting polymers containing sulphur bridges and suggested that these polymers can be used as rechargeable electrical cells [19].

Thermo gravimetric study of polymer provides information about the degradation pattern during heating and thermal stability. Gurnule *et al* have reported thermodynamic parameters and order of thermal stabilities of tercopolymers by using TGA [20]. Some recent development have made in the field of thermally stable polymers that have grown very rapidly to increase the applicability at elevated temperatures. However the polymer chemists have to face the challenges due to thermal instability and low processability. In this connection many co-workers have made attempt to improve thermal stability by changing the composition of monomers [21]. Aswar *et al* have reported the sequences of thermal stability of chelate polymer predicted on the basis of decomposition temperatures and activation energy was found to be Ni> Mn> Cu>Co>Zn. Whereas kinetic and thermodynamic parameters were calculated from dynamic TGA by the use of Sharp-Wentworth and Freeman-Carroll methods [22]. Masram *et al* reported kinetic study of thermal degradation of resin derived from salicylaldehyde, ethylenediamine and formaldehyde [23].

In literature several methods have been reported for the determination of kinetic parameter from thermal analysis [24-25]. Many co-workers determined various kinetic parameters such as ΔS, ΔF, Z, S* and G* by using Freeman Carroll and Sharp -Wentworth method [26-28].

The present paper deals with the structural analysis of newly synthesized terpolymeric PHBG resin and its thermal study using following methods [29-30].

A) Freeman-Carroll Method: In this the kinetic parameters is determined by following expression,

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

Where dw/dt = Rate of change of weight with time in Min, Wr = difference between weight loss at completion of reaction and at time t., Ea = activation energy, n = order of reaction.

B) Sharp-Wentworth method: Following expression is used to evaluate the kinetic parameters.

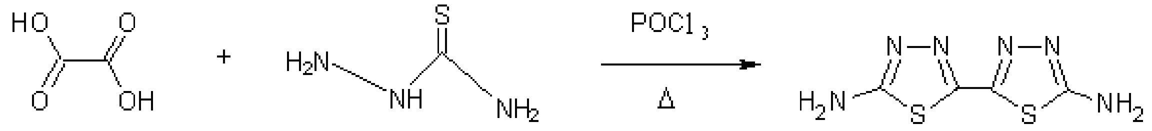
$$\log \frac{(d\alpha / dt)}{(1-\alpha)^n} = \log \frac{A}{\beta} - \frac{Ea}{2.303\,RT} \ldots (2)$$

Where dα/dt is fraction of weight loss with time, n is the order of reaction, A is frequency factor, β is linear heating rate and α is the fraction of amount of reactant.

EXPERIMENTAL SECTION

Materials

The chemicals used for the synthesis were chemically pure and analytical grade.



Oxalic acid Thiosemicarbazide Bis (2-amino-1, 3, 4-thiadiazole)

Fig. 1- Synthesis of Bis (2-amino-1,3,4-thiadiazole)

Synthesis of Bis (2-amino -1, 3, 4 -thiadiazole)

A mixture of oxalic acid (0.04M), thiosemicarbazide (0.04M) and phosphorous oxychloride (0.08M) were heated at 60^0C for 1 hrs. Followed by further heating at 95^oC for 3hrs.The reaction mixture was cooled to 15 ^{0}C. The yellow color product was recovered by adding 8-10ml NaOH solution .The product was collected by filtration and purified by using absolute alcohol and dried at room temp [31]. The reaction scheme is shown in fig.-1

Synthesis of PHBG terpolymer Resin:

The PHBG terpolymer was prepared by condensing p-hydroxyacetophenone (0.1M) and Bis (2-amino-1, 3, 4-thiadiazole) (0.1M) with Glycerol (0.3M) in the presence of dicyclohexylcarbodiimide (DCC) at 120-125^{0}C.in an oil bath for 9 hrs. The yellowish product was washed with hot water and ether to remove unreacted materials. The resin was dried and powdered. The product was squeezed with ether solvent to remove Bis (2-amino-1, 3, 4-thiadiazole), glycerol copolymer which might be formed along with PHBG. It was further purified by dissolving in DMSO then filtered and reprecipitated by distilled water. The resulting polymer sample was washed with boiling water and dried in a vacuum at room temperature. The purified terpolymer washed finely ground to pass through 300 mesh size sieve and kept in a vacuum over silica gel. The yield of the terpolymer was found to be about 79%. The reaction scheme for synthesis of PHBG is shown in fig -2.

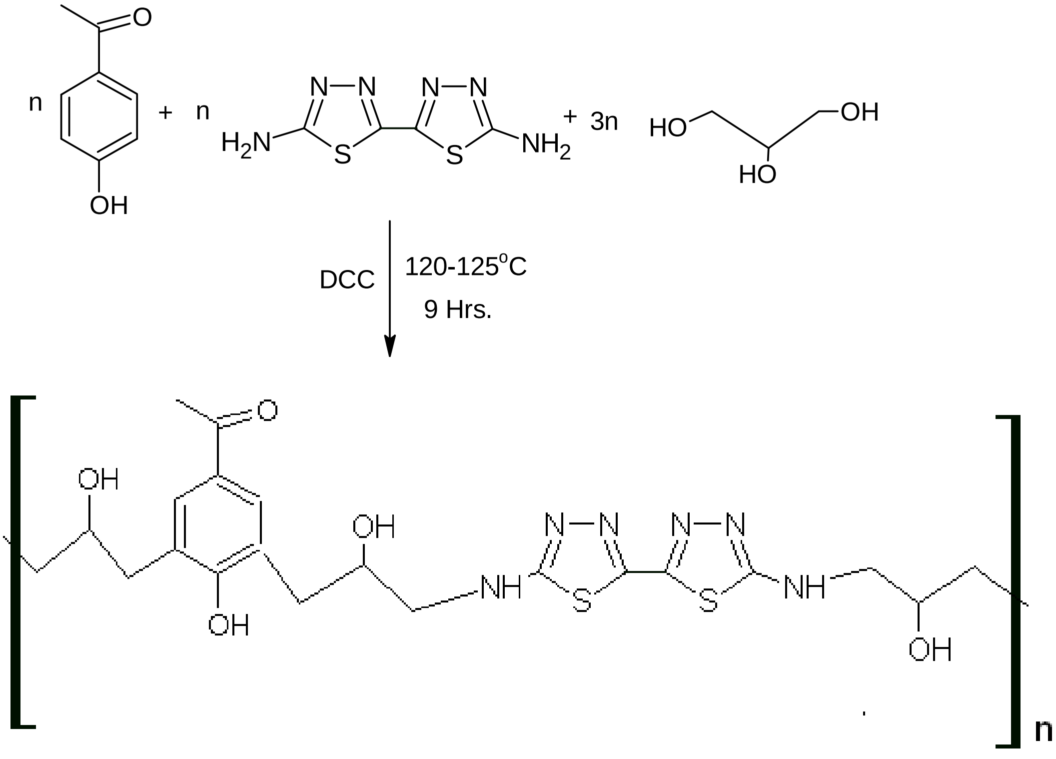


Fig. 2- Synthesis of PHBG terpolymer resin

Table 1: Synthetic details of PHBG resin

parameters/conditions	Specifications
Terpolymeric ligand	PHBG
Parahydroxy acetophenone	0.1M
Bis(2-amino-1,3,4 -thiadiazole)	0.1M
Glycerol	0.3M
Catalyst (DCC)	10 g.
React.Temp (^{0}C)	120-125
Time (hrs)	9.0
Yield (%)	79

RESULTS AND DISCUSSION

Elemental Analysis and molecular weight of PHBG resin:

The elemental analysis (C, H, N, S) of terpolymeric resin was carried out at Sophisticated Analytical Instrumental Facility (SAIF), Indian institute of Technology (IIT) Bombay. The average degree of polymerization of resin sample was determined by titrating 25ml of 0.1% solution of resin in DMF against 0.1M KOH solution in absolute alcohol, conductometrically [32-33]. The conductance was plotted against the miliequivalents KOH per 100gm. of resin. The inspection of plot revealed that there were many breaks in the plot. The Dp was calculated by using following equation,

$$\overline{DP} = \frac{\textit{Milliequivalent of base required for complete neutralisation}}{\textit{Milliequivalentof base required for smallest interval}}$$

The molecular weight of repeating unit was determined from elemental analysis data as shown in following table 2. The molecular weight of resin was determined by using following relation,

Mn=DP x Molecular weight of the repeating unit.

The repeating Unit weight was obtained from elemental analysis.
The elemental analysis and molecular weight determination data of PHBG resin are given in following Table 2.

Table 2: Elemental Analysis and molecular weight determination of PHBG resin

Resin	%C		%H		%N		%S		DP	Molecular weight (M_n)	Mol. Formula of repeating unit	Molecular Weight of repeating unit
	Cal	Found	Cal	Found	Cal	Found	Cal	Found				
PHBG	51.21	50.39	5.28	5.76	14.22	14.85	13.01	13.19	12	5904	$C_{21}H_{26}N_6S_2O_5$	492

IR spectra data of PHBG resin: FT- IR spectra are shown in fig.3 and data are tabulated in table.3 [34-35].

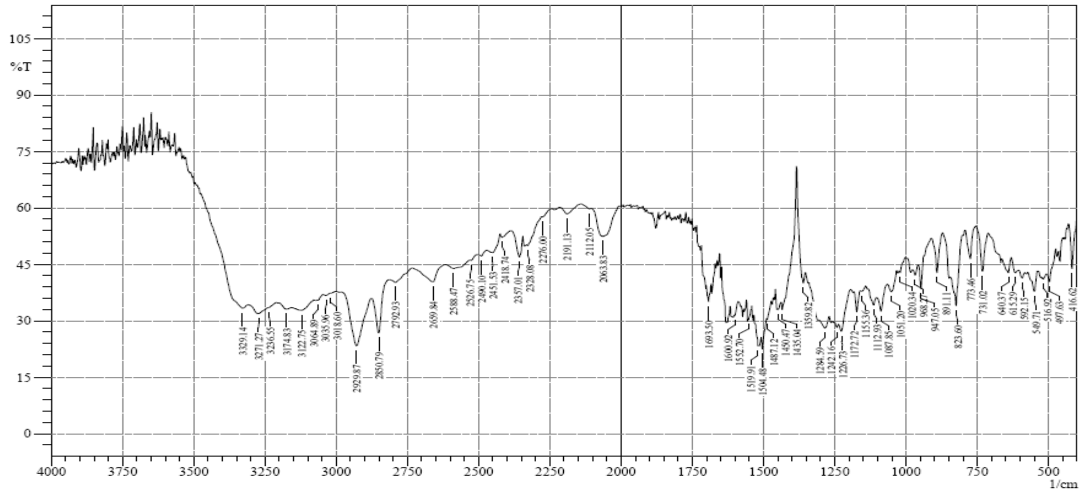


Fig. 3- IR spectrum of PHBG resin

Spectral analysis

IR spectra of synthesized terpolymeric resins were recorded at Department of pharmacy; RTM Nagpur University, Nagpur Using FT-IR spectrophotometer Shimadzu, Model No-8101A. ^{1}H NMR spectra of terpolymeric resin using DMSO-d^6 solvent were scanned on BRUKER AC II 400 NMR spectrophotometer SAIF, Punjab University, Chandigarh. UV-VIS spectra of terpolymer resin in DMSO solvent recorded by UV-VIS Double Beam Spectrophotometer Shimadzu, Model No-1701 fitted with automatic pen chart recorder at Department of Pharmacy, RTM Nagpur University, Nagpur.

Table 3: FT- IR Spectral data of PHBG resin

IR (frequency number in cm^{-1})	Nature of fragment assigned	IR (frequency number in cm^{-1})	Nature of fragment assigned
3329-3350,1552	-NH-Str.	3064,3035	Aromatic-CH-Str.
3236	H-Bonded alcoholic-OH	2929	CH-Str.
3271	H-Bonded Phenolic-OH	1693	C=O aryl Ketone
3174-3122	CH-Str.in –$COCH_3$. PHAP* moiety	1600	C=C aromatic ring.
1450	C-S-C-Str.BAT* moiety	1112	C-CO-CH_3 def. PHAP* moiety
1359	C-N Str. Aromatic sec .amine	947,823	2,2- disubstituted Bis thiadiazole ring
1226	C-O-Str. phenolic	1172	1,2,3,5-tetrasubstituted aromatic ring

**PHAP-(Parahydroxy acetophenone), BAT*- (Bis-(2-amino-1, 3, 4-thiadiazole).*

The absorption bands at 3329cm^{-1}, 1552cm^{-1} were assigned to N-H stretching and bending vibration in secondary amine. The broad band at 3271$cm^{-1}$was assigned to phenolic group .The band displayed at 3174cm^{-1}, 3122cm^{-1} were due to C-H stretching in –$COCH_3$ moiety. The peaks at 3064cm^{-1} are due to aromatic ring. The sharp band displayed at 1693cm^{-1} was assigned to –C=O moiety. The absorption at 1600 cm^{-1} was assigned to C==C aromatic ring in PHAP. The band obtained at 1450cm^{-1} was due to the presence of –C-S-C- stretching in BAT. A sharp band appears at 1359cm^{-1} show the presence of –C-N stretching in aromatic secondary amine. The weak band at 1112cm^{-1} was assigned to-C-CO-CH_3-deformation in PHAP moiety. Moreover the absorption at 1172cm^{-1} was attributed to the 1,2,3,5-tetra substituted aromatic ring [36] and 947, 823cm^{-1} attributed to 2, 2'- disubstituted Bis-thiadiazole ring.

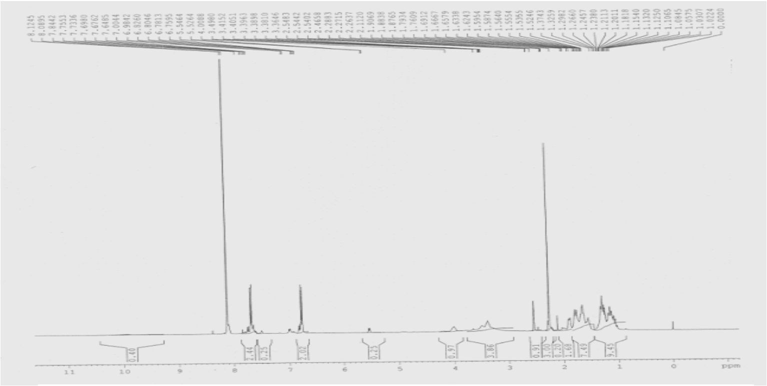


Fig. 4(a)- ^{1}H NMR spectrum of PHBG resin

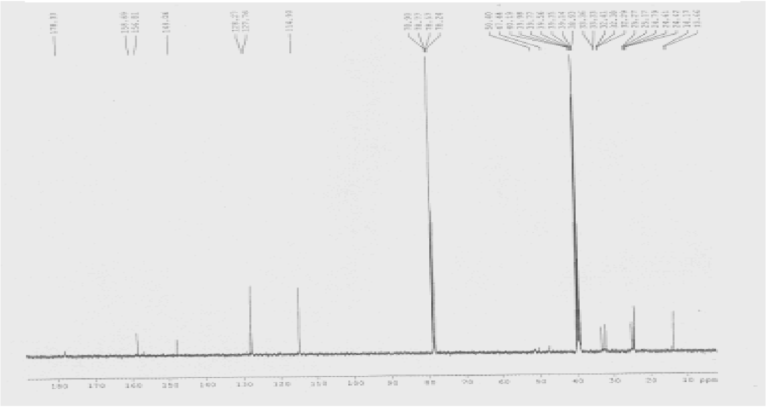


Fig. 4(b)- ^{13}C NMR spectrum of PHBG resin

^{1}H NMR and ^{13}C NMR Spectra of PHBG resin:.

The ^{1}HNMR and ^{13}C NMR spectra is shown in fig.4 (a) and fig.4(b) and various signals are assigned as given in table-4. [37].

Table 4: ^{1}H NMR and ^{13}C NMR data of PHBG resin

PHBG ^{1}H NMR δpm	**Nature of proton assigned**	**PHBG ^{13}C NMR δ ppm**	**Nature of Carbon assigned**
8.09	Aromatic Ring protons	13.65,14.17	CO-**C**H_3
7.67	C-N**H**$_2$	47.5	**C**-OH(phenolic)
5.52	Ar-O**H**	78.53	**C**-OH (alcoholic)
4.01	Alcoholic-O**H**	178.36	**C**=O
3.67-3.49	C**H**-OH	127,128.23	Carbon in Bis thiadiazole ring
2.46	C**H**$_2$-NH	148,156,158.74	Carbon in benzene ring
2.54	-COC**H**$_3$	24.45	Aromatic- **C**H_2
5.7	Phenolic-O**H**	32.31	-NH-**C**H_2
3.3	N-**H** Variable		

In ^{1}H NMR spectrum of PHBG terpolymer resin show signals at 3.67 and 3.49 δ ppm were attributed to C**H**-OH moiety. The signal at 2.46 δ ppm was due to –C**H**$_2$-NH in PHBG terpolymeric resin. The multiplet at 8.09 δ ppm represents aromatic ring protons in PHAP. Signal at 2.54 δ ppm was assigned to –COC**H**$_3$ in PHAP. Signal at 3.3 δ ppm was assigned to secondary amine proton in BAT moiety. Singlet at 4.01 δ ppm was due to in secondary alcoholic –OH in PHBG terpolymeric resin.

In ^{13}C NMR spectrum of PHBG terpolymer resin, signal at 14.17 δ ppm was assigned to –**C**H_3. Signal at 47.5 δ ppm are due to –**C**-OH. Signals at 78.53 δ ppm was attributed to –OH in alcoholic proton in PHBG. Signal at 178.36 δ ppm was due to carbonyl carbon (–**C**=O) in PHAP. Signals at 127.74 and 128.23 δ ppm were due to carbons in BAT moiety. Signal at 156 δ ppm was assigned to carbons in benzene ring. Signal at 24.45 δ ppm was due to carbon in Ar –**C**H_2– moiety. Signal at 32.31 δ ppm was assigned to carbon in –NH-**C**H_2 moiety.

UV-VIS spectra of PHBG resin:

The UV-VIS spectral data is given in following fig.5. And related data is given in Table5.[38]

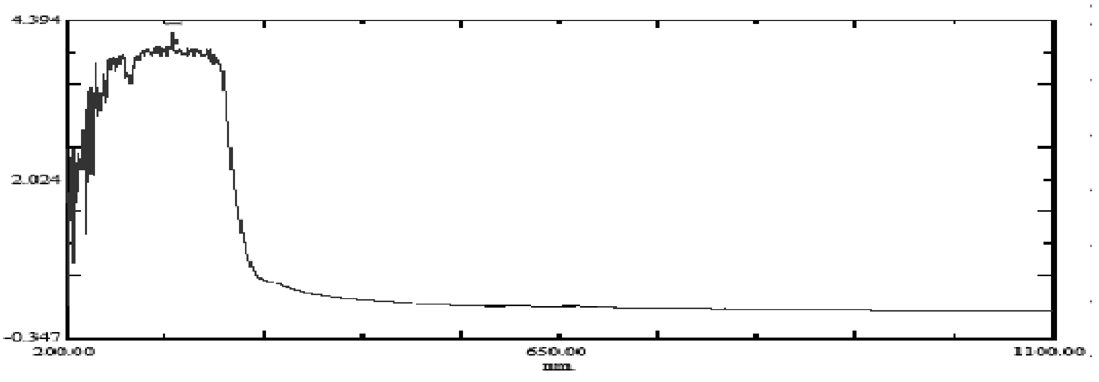


Fig. 5- UV-VIS spectrum of PHBG resin

Table 5: UV-VIS data of PHBG resin

Resin	Transition	Wavelength (nm)	Group / moiety assigned
PHBG	*n-σ^**	215	*C-**S**-C BAT moiety*
		222	C-**N**H- Thiadiazole moiety
		225.7	C-OH Phenol moiety
		230	C-OH glycerol moiety
	$\pi-\pi^*$	237.5	Aromatic ring(PHAP)
		252.5	BAT moiety
	n-π^*	282.5	C-NH- moiety
		298	C-OH glycerol moiety
		327.4	C-OH Phenolic OH
		357.5	N-N BAT moiety

Inspection of UV-VIS spectra of terpolymeric PHBG resin reveals three types of transition *n-σ^** (ranging from 215-230nm), $\pi-\pi^*$ transition (ranging from 237-252nm) similarly the broad band of n-π^* transition (ranging from 282-357nm) [38]. The important UV-VIS absorptions are assigned to the moiety of resin as shown in given above table 5.

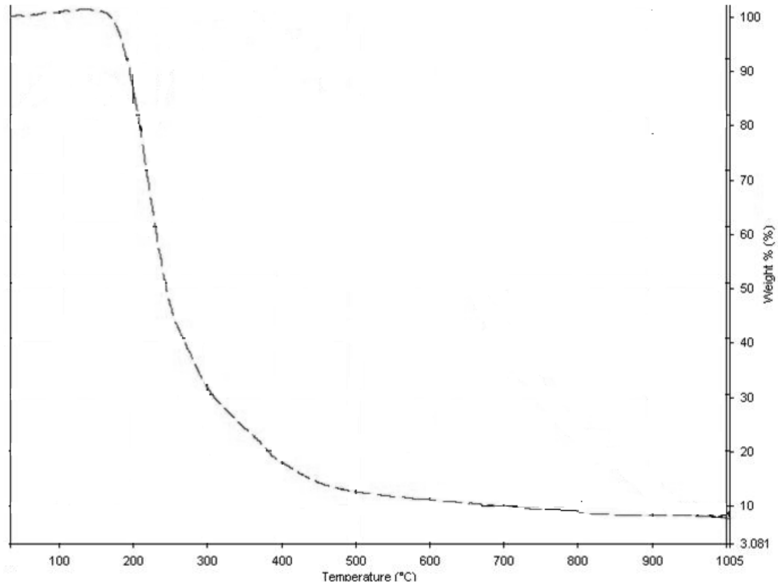


Fig. 6- Thermogram of PHBG resin

Thermo gravimetric analysis of PHBG terpolymeric resin:

The thermo gram of PHBG terpolymer resin as shown in figure 6, was recorded at Dept. of Material Science, VNIT Nagpur, using Perkin Elmer Diamond TGA/DTA analyzer in argon environment. The resin was allowed to heat up to 800^{o}C at linear heating rate of 10^{0}C min^{-1}. The initial weight loss up to 150^{0}C was due to the loss of water [39]. The decomposition of resin starts from 180^{0}C to 284^{0}C. The order of decomposition was found to be 0.66 orders by Freeman-Carroll method, which was further confirmed by Sharp- Wentworth method. The FC and SW method plots are shown in figure 7 and figure 8 respectively. The thermo kinetics parameters determined by these two methods are shown in table.

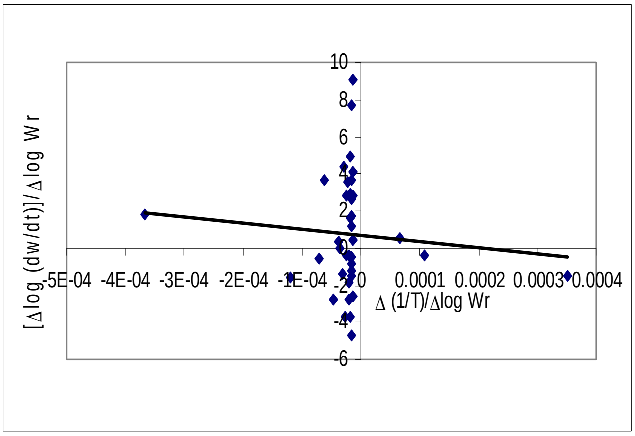


Fig. 7- Freeman- Carroll plot of PHBG resin

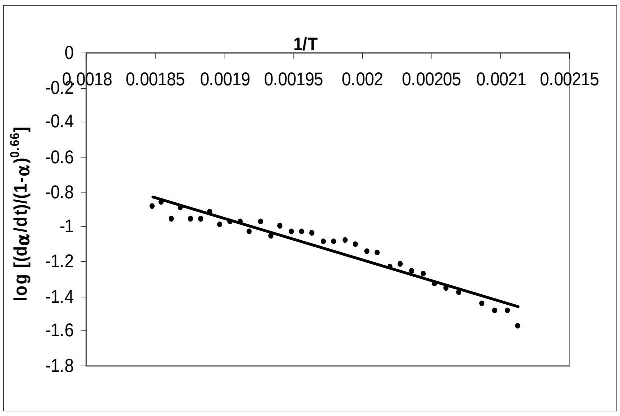


Fig. 8 - Sharp –Wentworth plot of PHBG resin

Table 6: Thermo kinetic parameters of PHBG resin

Resin	Parameters	Freeman-Carroll method	Sharp-Wentworth method
PHBG	Temperature range	473 - 555 K	473 - 555 K
	Activation energy, Ea (kJ)	47.77	45.51
	Frequency factor, A (min^{-1})	1.563×10^4	3.145×10^4
	Apparent entropy, ΔS (JK^{-1})	-117.26	-106.91
	Free energy, ΔG (kJ)	108.64	101.01
	Order of reaction, n	0.66	0.66

CONCLUSION

The elemental analysis and spectral studies such as UV-VIS, IR, ^{1}H NMR, ^{13}C NMR data is in good agreement to the above assigned tentative structure of PHBG terpolymeric resin shown in figure 2. The activation energy obtained by FC method is slightly higher than that obtained by SW method. The values of frequency factor, apparent entropy and free energy are in good agreement. The order of degradation reaction is in a fraction (0.66) due to solid state degradation. The low value of activation energy and high value of frequency factor suggest that the resin is thermally unstable between above mentioned temperature range.

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