Thermal Behaviour of Copolymer derived from o-Toluidine, Biuret and Formaldehyde

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***Abstract* -- Polymer resin o-Toluidine–Biuret–Formaldehyde has been synthesized by the condensation of o-toluidine, biuret and formaldehyde in 1:1:2 molar proportions. The structure of copolymer has been characterized by elemental analysis and various physico-chemical techniques i.e. UV-Visible spectra, FTIR spectra, and proton nuclear magnetic resonance spectra. The morphology of copolymer resin was studied by scanning electron microscopy (SEM). The thermal decomposition behavior of o-TBF copolymer has been studied by using TGA in air atmosphere at a heating rate of 10^0 C/min. The activation energy (Ea) and thermal stability calculated by using the Sharp-Wentworth and Freeman-Carroll methods. Thermodynamic parameters such as entropy change (ΔS), apparent entropy change (S*), free energy change (ΔF) and frequency factor (Z) have also been evaluated on the basis of TGA curves and by using data of the Freeman-Carroll method. The order of reaction (n) was found out to be 0.97.**

***Keywords*--** Synthesis, Copolymer, Thermal degradation, Kinetic parameters, Activation Energy, Freeman-Carroll.Morphology.

I. INTRODUCTION

Due to global applications of polymeric materials polymer science and technology have been developing rapidly and attracted much attention towards the polymer scientists. Polymers have been found to be very useful applications as adhesive, high-temperature flame-resistant fibers, coating materials, semiconductors, catalysts, and ion-exchange resins [1–2]. Polymers are known for their versatile uses and are found to be amorphous, crystalline or resinous in nature. Phenolic resins have been the workhorse as matrix resins in composites for structural and thermal applications in aerospace because of their ease of processability, thermal stability, versatile characteristics and cost effectiveness. Tang and coworkers [3] studied the thermal decomposition kinetics of thermotyropiccopolyesters made from trans-p-hydrocinnamic acid and p-hydrobenzoic acid. Copolymers occupy an intermediate position between organic and inorganic compounds and it is hoped that the study of copolymers will lead to the production of polymer, which are both thermally stable and useful as fabricating materials. Michael et al. studied synthesis, characterization and thermal degradation of 8-hydroxyquinoline–guanidine–formaldehyde terpolymer[4].Rahangdale and coworkers studied thermal degradation of terpolymers derived from 2, 4-dihdroxy-acetophenone, dithioxamide and formaldehyde [5,6].

Copolymer resins are derived from 2,4-dihydroxypropiophenone, biuret, and formaldehyde in hydrochloric acid as catalyst and studied their thermal degradation [7,8]. Thermal degradation of *m*-nitroaniline, *m*-chloroaniline and *m*-aminophenol has been studied by Dash *et al*. [9] and 2-hydroxyacetophenone, oxamide and formaldehyde [10]. Oswal et al synthesized and studied thermal properties of copoly(maleimide-methylmethacrylate), terpoly(maleimide-methylmethacrylate-acrylic acid), and terpoly- (maleimide-methylmethacrylatemethylacrylic acid). The thermal behaviour was studied by TG and DSC techniques [11]. Thermoanalysis and rheological behavior of copolymers of methyl methacrylate, N-phenylmaleimide and styrene studied by G. Jungang et al [12]. In order to synthesize polymers having numerous practical applications, there is a need to investigate the effect of heat on the polymers in order to establish their thermal stability. It must be pointed out that all the methods proposed have been developed by assuming that both activation energy and kinetic model do not change along the process. However, it has concluded from free- model kinetic methods of analysis that the activation energy is a function of the reacted fraction [13-16].

However, the literature studies have revealed that no copolymer has been synthesized using the monomer o-toluidine, biuretand formaldehyde. Therefore, in the present communication we report the synthesis, structural characterization and thermal degradation studies of o-TBF copolymer. The elemental analysis has been carried out to ascertain the molecular formula and the spectral studies have been used to characterize the complete structure of the o-TBF copolymer. After treating the thermal degradation data with Sharp–Wentworth (SW) and Freeman–Carroll (FC) methods, activation energy and kinetic parameters have been evaluated.

II. EXPERIMENTAL

Materials and Reagents

All the chemicals used were of analytical grade. o-toluidine, biuret and formaldehyde which is purchased from Merck Chemicals, India. Solvents like N,N-dimethylformamide and dimethylsulphoxide purchased from SD Fine Ltd, Mumbai, India, were used after distillation.

Synthesis of 8-HQ5-SASF-II Copolymer

The o-TBFcopolymer was prepared by condensing, o-toluidine, and formaldehyde, (0.1mol) and biuret(0.1 mol) with formaldehyde (0.2mol) in the presence of 2M HCl as a catalyst at 122 ± 2 ^{0}C in an oil bath for 6hr (Figure 1). The brown colored solid product obtained was immediately removed and extracted with diethyl ether to remove excess of o-toluidine,-formaldehyde copolymer, which might be present along with the o-TBFcopolymer. It was further purified by dissolving in 8 % NaOH and then filtered. The copolymer was then reprecipitated by drop wise addition of 1:1 (v/v) conc. HCl / water with constant stirring and filtered. The process was repeated twice. The resulting copolymer sample was washed with boiling water and dried in a vacuum at room temperature. The purified copolymer resin was finely ground to pass through 300-mesh size sieve and kept in a vacuum over silica gel. The yield of the copolymer was found to be about 84 %

Figure 1.Reaction and Suggested Structure of Representative o-TBF-I Copolymer Resin

Analytical and Physicochemical Studies

The elemental analysis was carried out on a Perkin Elmer 2400 Elemental Analyzer instrument. The UV–Visible studies were out carried using Shimadzu UV-1800 Spectrophotometer in the range 200-800 nm. The Infrared spectrum was recorded in the region of 500–4000 cm^{-1} on Shimadzu IR Affinity Spectrophotometer at Department of Chemistry, Kamla Nehru Mahavidyalaya, Nagpur. ^{1}H-NMR studied using BrukerAvance-II FT-NMR Spectrometer in DMSO-d_6 solvent at STIC Analysis, Kochi. All the analytical and spectral studies for the newly synthesized copolymer were carried out at STIC Analysis centre, Kochi.

Instrumentation

The nonisothermalthermogravimetric analysis was performed in air atmosphere with heating rate of 10 $^0C.min^{-1}$ using 5 - 6 mg of samples in platinum crucible from temperature of 40 ^{0}C to 800 ^{0}C and thermograms are recorded for o-TBF sample at STIC, Kochi. With the help of thermogravimetric data the thermal activation energies (Ea) and order of reaction (n) calculated. Also other thermodynamic parameters such as entropy change (ΔS), apparent entropy change (S^*) and frequency factor (z) are determined and reported in the Table 1.

Theoretical considerations

To provide further evidence regarding the degradation system of analyzed compounds, we derived the TG curves by applying an analytical method proposed by Sharp-Wentworth, Freeman- Carroll and Freidman.

Freeman–Carroll method

The straight-line equation derived by Freeman and Carroll [17], which is in the form of

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

Where

dW/dt = rate of change of weight with time.
Wr = Wc-W
Wc = weight loss at completion of reaction.
W = fraction of weight loss at time t.
Ea = energy of activation.
n = order of reaction.

The plot between the terms $\frac{\Delta \log dW/dt}{\Delta \log Wr}$ vs $\frac{\Delta 1/T}{\Delta \log Wr}$ gives a straight line from which slope we obtained energy of activation (Ea) and intercept on Y-axis as order of reaction (n). The change in entropy (ΔS), frequency factor (z), apparent entropy (S^*) can also be calculated by further calculations.

Sharp–Wentworth Method

Using the equation derived by Sharp and Wentworth [18],

$$\log \frac{dC/dT}{1-C} = \log A/\beta - \frac{Ea}{2.303R} \cdot \frac{1}{T} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

Where

dC/dT= rate of change of fraction of weight with change in temperature
β = linear heating rate dT/dt.

By plotting the graph between $\log \frac{dC/dT}{1-C}$ *vs.* $\frac{1}{T}$ we obtained the straight line which give energy of activation (Ea) from its slope.

III. RESULTS AND DISCUSSION

The resin sample was brown in color, insoluble in commonly used solvent, but was soluble in DMF, DMSO, THF, pyridine, concentrated H_2SO_4. No precipitation and degradation occurs of resin in all the solvents. These resins were analyzed for carbon, hydrogen and nitrogen content.

Characterization of Copolymer

Molecular weight of copolymer was estimated by conductometric titration. The number average molecular weight $(\overline{Mn})$ could be obtained by multiplying the $\overline{Dp}$ by the formula weight of the repeating unit [19]. The result of the molecular weight of copolymer samples prepared using higher proportion of two monomers (o-TBF) has the highest molecular weight in the series. The molecular weight for o-TBFis 3518.

The composition of copolymer obtained on the basis of the elemental analysis data was found to be in good correlation to that of the calculated values:

Calculated for $C_{11}H_{14}N_4O_2$: C: 56.41%; H: 5. 98%; N: 23,93%., O: 13.68%, Found for $C_{11}H_{14}N_4O_2$: C: 56.30%; H: 5.92%; N: 23.82%. O: 13.62%,

A broad the UV-visible spectrum of o-TBF copolymer is shown in Figure 2. UV-visible spectra of all the purified copolymer has been recorded in pure DMF. The spectra of this copolymer exhibit two absorption maxima in the region 2400 nm and 280 nm. These observed positions of the absorption bands indicate the presence of carbonyl group (ketonic) processing double bond, which is in conjugation with the aromatic nucleus. The appearance of former band (more intense) can be accounted for $\pi\rightarrow\pi^*$ transition while the later bond (less intense) may be due to $n\rightarrow\pi^*$ electronic transition. The shift from the basic value (viz. 242 nm and 315 nm respectively) may be due to conjugation effect, and presence of phenolic hydroxy group (auxochromes) is responsible for hyperchromic effect i.e. ε_{max} higher values [19-20]. This observation is in good agreement with the proposed most probable structure of this copolymer.

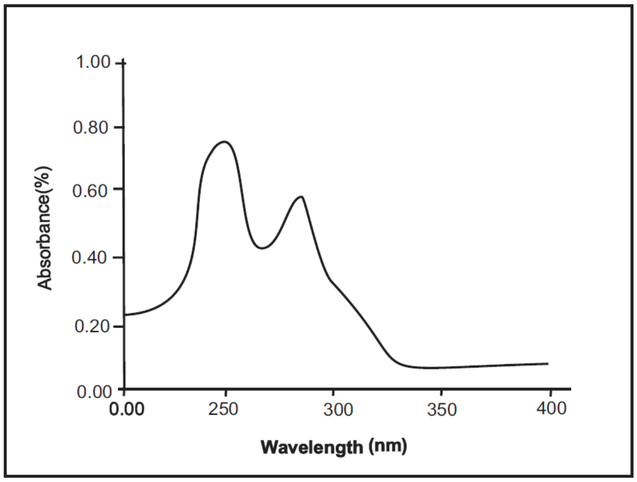

Figure 2.UV-visible spectrum of o-TBFcopolymer.

The IR-spectra of o-TBF copolymer is presented in Figure 3. A band appeared in the region 3436 cm^{-1} may be assigned to the stretching vibration of the phenolic hydroxy groups exhibiting intermolecular hydrogen bonding [21]. The presence of weak peak at 3000 cm^{-1} 2970 cm^{-1} describes the –NH- in semicarbazide moiety may be ascribed in the copolymeric chain [21]. The sharp band displayed at 1631.4 cm^{-1} may be due to the stretching vibration of carbonyl group of both, ketonic moiety [22]. The sharp and weak bond obtained at 1382 cm^{-1} suggests the presence of $–CH_2-$ methylene bridges [22] in the copolymer chain. The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium / weak absorption bands appeared at 592-557, 971.2-970, 1098-1087 and 1162 cm^{-1} respectively. This band seems to be merged with very broad band of phenolic hydroxyl group [22].

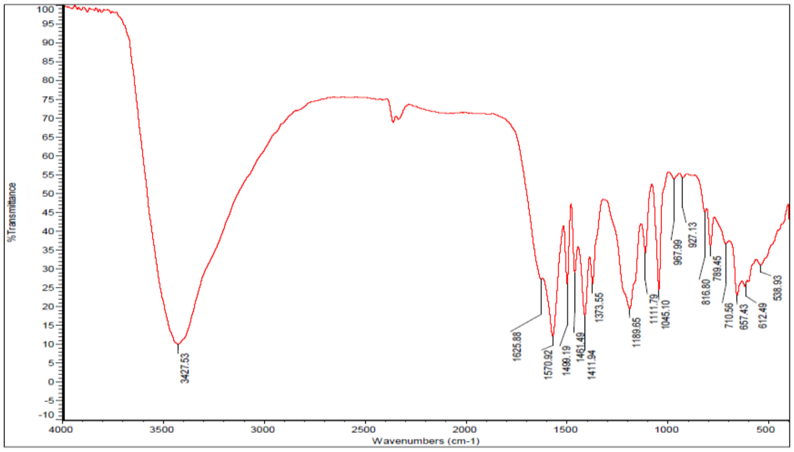

Figure 3.FT-IR spectrum of o-TBFcopolymer

^{1}H-NMR spectra of o-TBF copolymer is shown in Figure 4. Proton NMR spectra of all four o-TBF copolymer resins were scanned in DMSO-d_6 solvent. The spectra are given in Fig. 3.21 and the spectral data are given in Table 3.25. From the spectra it is revealed that all four o-TBF copolymer resins give rise to different pattern of 1H NMR spectra, since each of o-TBF copolymer possesses set of proton having different electronics environment. The chemical shift (□) ppm observed is assigned on the basis of data available in the literature [23]. The singlet obtained in the region of 4.67-4.65 (□) ppm may be due to the methylene proton of Ar-CH-N moiety [23]. The signal in the region 7.45-7.43 (□) ppm are attributed to protons of -NH bridge [24]. The weak multiplate signal (unsymmetrical pattern) in the region of 8.98-8.96 (□) ppm may be attributed to aromatic proton (Ar-H) [23]. The signal appeared at 9.05 to 9.03 (□) ppm may be due to phenolic hydroxyl group protons [24]. The much downfield chemical shift fore phenolic -OH indicate clearly the intramolecular hydrogen bonding of -OH group [24].

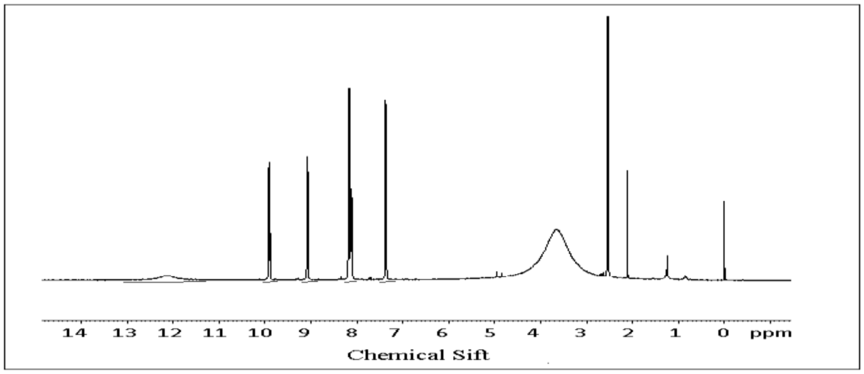

Figure 4 ^{1}H NMR Spectrum of o-TBFcopolymer

Scanning electron microscope (SEM)

The SEM micrographs of o-TBF copolymer resin are shown in Fig.5. The white bars at the bottom of micrographs represent the scale. The micrographs were represented at two different magnifications. The SEM micrographs of o-TBF copolymer resin sample exhibits spherulites with deep corrugation. The spherulites are typical crystalline formation and they grow in high viscous and concentrated solution. In the present case, the spherulites are complex polycrystalline formation composed of simplest structural formula having smoothest surface free from defects of growth. The crystals are smaller in surface area with less closely packed structure. Thus the spherulites morphology of resin exhibit crystalline structure of resin with deep corrugation which is clearly visible in SEM photographs of resin. These evidences indicate that more or less the resin shows amorphous character with less close packed surface having deep pits. The resin thus possesses amorphous nature and showing higher exchange capacity for metal ions. Thus SEM study shows that the o-TBFcopolymer resin has crystalline and some amorphous characters. Thus it has the transition structure between crystalline and amorphous. The surface morphology of the composite shows an excess of active sites and different pores present on the surface compared to copolymer. This indicates that increase in the surface area led to larger number of cavity formation in the composite. Hence, from the images, it is concluded that composite has formed very firmly with the synthesized polymer and activated charcoal with larger surface area and more active sites which are responsible for better metal ion removal capacity.

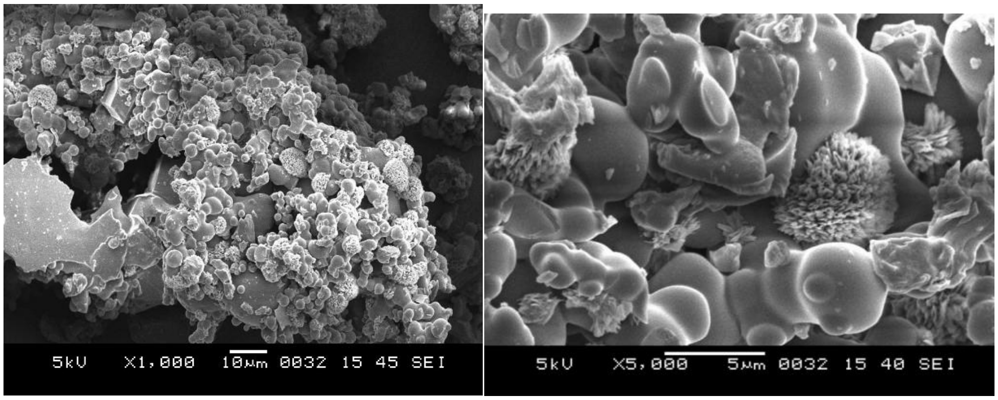

Figure 5: SEM Photographs of o-TBF-I Copolymer Resin

Thermogravimetric Analysis of the Copolymer

The thermal stability of copolymer is evaluated by dynamic thermo-gravimetric analysis in air atmosphere with heating rate of 10^0C.min^{-1}.

Thermogram of TG of o-TBF copolymer is shown in Figure 5. Thermogram of copolymer depicts three steps decomposition after loss of water molecule in the temperature range 40 ^{0}C – 800 ^{0}C. The initially decomposition takes place between 40^0C - 150 ^{0}C corresponds to 3.29 % loss which may attributed to loss of a water molecule against calculated 3.71 % present per repeat unit of the polymer. The first step decomposition starts from 150^0C – 320 ^{0}C which represents degradation of two sulphonic acid group and two hydroxyl groups (36.70% experimental and 36.20 % calculated). The second step which is start from 320^0C - 480^0C corresponding to 59.20 % loss of aromatic ring along with two methylenic groups against calculated 59.72 %. The third step starts from 480 ^{0}C – 710 ^{0}C corresponding to loss of toludine ring and biuretmoiety (85.03% experimental and 85.61% calculated).

Thermoanalytical Data

A plot of percentage mass loss versus temperature is shown in the Figure 5 for a representative o-TBF copolymer. To obtain the relative thermal stability of the copolymer, the method described by Sharp-Wentworth, Freeman-Carroll and Freidman was adopted. The thermal stability of copolymer, based on the initial decomposition temperature, has also been used here to define their relative thermal stability, neglecting the degree of decomposition.

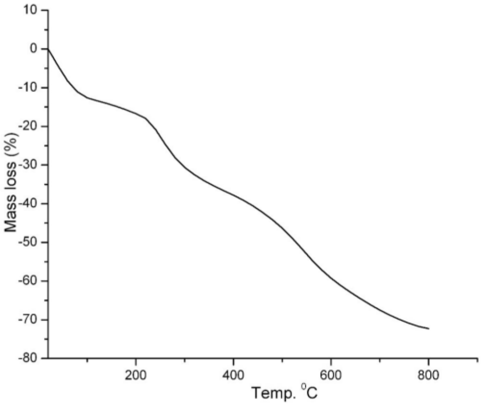

Figure 5. Thermal degradation of o-TBFcopolymers

Thermogram of the o-TBF -I copolymer is presented in Fig. 4.9 which exhibitsthree step decomposition in the temperature range 40 - 640 0C, after loss of watermolecule (4.08 % found and 4.20 % calculated). First step decomposition starts from190 - 480 0C corresponding to the gradual mass loss of 39.97 % found and 39.95 %calculated which may be due to degradation of side chain attached to the aromatic benzene ring i.e., CH3 group. The second step decomposition starts from 480 - 510 ^{0}Ccorresponding the rapid mass loss of 63.81 % found and 63.08 % calculated whichrepresents the degradation of aromatic nucleus with methylene group. The third stepdecomposition starts from 510 - 640 0C corresponding to the removal of all the biuretmoiety with observed mass loss of 98.23 % against calculated 100 %. [25].

A representative thermal activation energy plot of Sharp-Wentworth (Figure 6), Freeman-Carroll (Figure 7-8) and Freidman (Fig. 9) method for the copolymer has been shown. Thermodynamic parameters such as entropy change (ΔS), frequency factor (z), apparent entropy change (S^*) calculated on the basis of thermal activation energy (Ea) using equations (3), (4), (5). These values are given in (Table 1).

i. Entropy Change (ΔS):

$$Intercept = log\frac{kR}{h\phi Ea} + \frac{\Delta S}{2.303R} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Where, k = 1.3806 x 10^{-16} erg.deg^{-1}.mol^{-1},
R = 1.987 cal.deg^{-1}.mol^{-1},
h = 6.625 x 10^{-27}erg.sec,
ϕ = 0.166,
ΔS = entropy change,
Ea = activation energy from graph.

ii. Frequency Factor (z):

$$B_{2/3} = \frac{\log z.Ea}{R\phi} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4)}$$

$$B_{2/3} = \log 3 + \log[1\text{-}3\sqrt{1-\alpha}] - \log p(x) \ldots\ldots\ldots\ldots\ldots\ldots (a)$$

Where, z = frequency factor,
B = calculated from eq [a],
$\log p(x)$ = calculated from Doyle table corresponding to activation energy.

iii. Apparent entropy change (S*):

$$S^* = 2.303R \log \frac{zh}{RT*} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Where, T^* = temp at which half of the compound decomposed.

The abnormally low value of frequency factor, it may be concluded that decomposition reaction of o-TBF copolymer can be classed as a ‘slow’ reaction. There is no other obvious reason [26, 27]. Fairly good straight-line plots are obtained using the two methods. This is expected since the decomposition of copolymer is known not to obey first order kinetic perfectly [28-31].

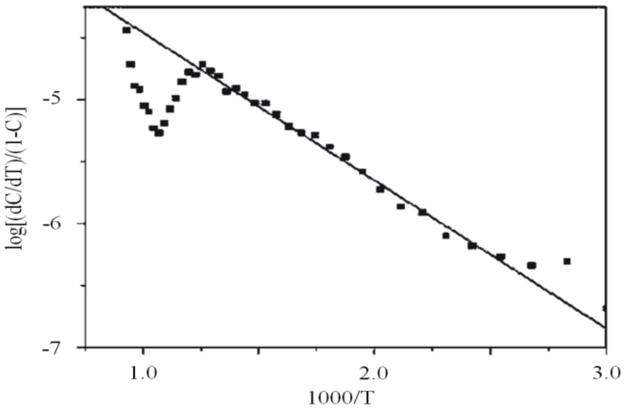

Figure 6.Activation energy plot by Sharp–Wentworth plot for o-TBFcopolymer.

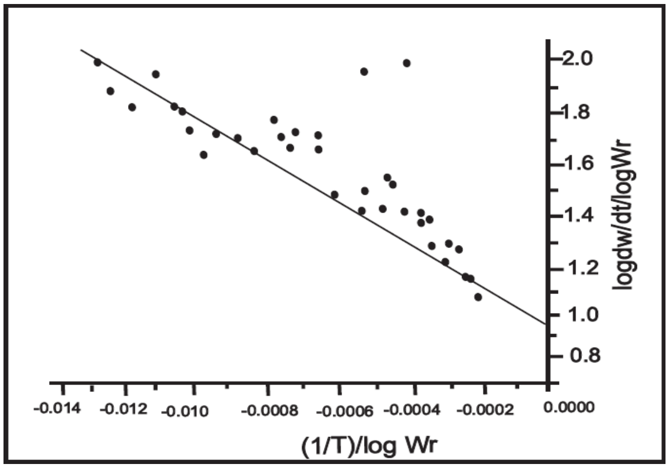

Figure 7.Activation energy plot by Freeman-Carroll of o-TBFcopolymer

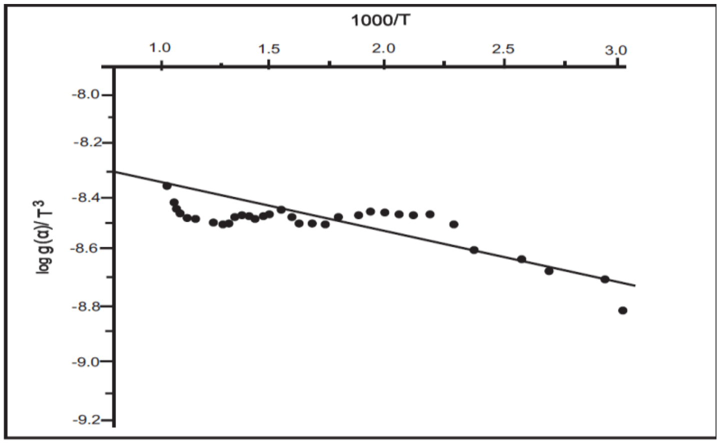

Figure 8.Freeman–Carroll plot of o-TBFcopolymer

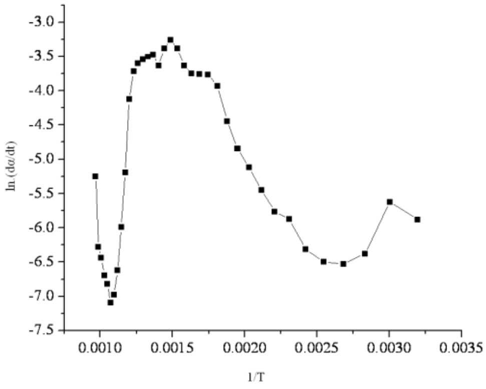

Figure 9. Activation energy plot by Freidman plot for o-TBFcopolymer

IV. CONCLUSIONS

The o-TBFcopolymer based on the condensation polymerization of o-toluidine and biuret with formaldehyde in the presence of acid catalyst has been prepared. From the elemental analysis, UV-visible, FT-IRand ^{1}H NMR spectral studies the proposed structure of the o-TBFcopolymer has been determined. In TGA the kinetic parameters evaluated from the Sharp-Wentworth and Freeman-Carroll methods are found to be similar, indicating the common reaction mode. The resins undergoes degradation at high temperature, indicates that the copolymer resins under study are thermally stable at elevated temperature. Low value of frequency factor may be concluded that the decomposition reaction of o-toluidine -biuret-formaldehyde polymer can be classified as ‘slow reaction’. The activation energy calculated from Sharp Wentworth and Freeman Carroll methods are good agreement with each other.

Table1.
Thermogravimetrical Parameters Corresponding to Heating Rate of 10^0C/min. of o-TBFcopolymer

Copolymer	T* (^{0}C)[a]	ΔS	Z	S*	n
o-TBF	510	−82.02	112.2	-124.16	0.97

[a] Half decomposition temperature

Table 2.
Comparison of Activation Energy (Ea) of Degradation at Different Stages by Different Methods of o-TBFCopolymer

Copolymer	Stages	Temp Range	Group loss	Wt. loss (%)	Activation (Ea) (KJ/mol.)	
					Sharp-Wentworth	Freeman-Carroll
o-TBF	1st	40−190	H_2O molecule entrapped	4.07	28.85	29.06
	2nd	150-320	degradation of –CH_3group	39.96		
	3rd	320-480	Loss ofaromatic nucleus andmethylene linkage	63.80		
	4th	480-710	loss of biuret moiety	98.22		

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