

## Synthesis, Characterization and Thermal Degradation Studies of O-Toluidine-Biuret-Formaldehyde Copolymer

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**ABSTRACT:** The copolymer resin o-Toluidine-Biuret-Formaldehyde (o-TBF) was synthesized by the condensation of o-toluidine and biuret with formaldehyde in the presence of 2M HCl as a catalyst at  $124 \pm 2$  °C for 5 hrs with molar proportion of reactants. Thermogravimetric analysis of o-TBF copolymer has been performed to study the thermal degradation characteristics and to ascertain its thermal stability. In this technique the sample of o-TBF copolymer resin was subjected to the condition of continuous increase in temperature at linear rate. The thermal study of o-TBF copolymer was carried out to study it's mode of decomposition and relative thermal stability. The copolymer resin o-TBF was characterized by UV-visible absorption spectra, FT-IR and proton NMR spectral studies. The thermal activation energy ( $E_a$ ) calculated using above mentioned methods was in good agreement. The Freeman-Carroll and Sharp-Wentworth methods were used to calculate thermal activation energy ( $E_a$ ), order of reaction ( $n$ ), frequency factor ( $Z$ ), entropy change ( $\Delta S$ ), free energy change ( $\Delta F$ ), and apparent entropy change ( $S^*$ ). The thermal activation energy ( $E_a$ ) determined with these methods was in good agreement with each other.

**KEYWORDS:** Synthesis, condensation, thermogravimetric analysis, decomposition, spectral studies, activation energy, kinetic parameters.

### 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. Copolymers resin has become subjects of interest and are found to be amorphous, crystalline or resinous in nature. The thermal degradation study of copolymer resins has become a subject of interest. [1-2] The study of thermal behaviour of copolymer resins in air at different thermal conditions provides information about the nature of different species produced at various temperature due to the degradation of copolymer resins. The copolymer resins having good thermal stability and catalytic activity have enhanced the development of the polymeric materials. A considerable attention has been paid in the past two decades to the synthesis of copolymer resins due to it's exciting features such as high thermal stability. [3-5] S.L.Oswal et al synthesized and studied thermal properties of copolymer (maleimidemethylmethacrylate), trophy(maleimidemethylmethacrylate-acrylicacid) and terpoly(maleimidemethylmethacrylatemethyl-acrylic acid).[6] Synthesis, characterization and ion exchange properties of 4-hydroxyacetophenone, biuret and formaldehyde terpolymer resin were studied by Gurnule and coworkers.[7] Copolymers of salicylic acid, thiourea with trioxane and p-hydroxybenzoic acid, thiourea with trioxane has been reported in the literature. Thermal degradation of m-nitro aniline, m-chloroaniline and m-aminophenol has been studied by Dash et al. [8] and 2-hydroxyacetophenone, oximide and formaldehyde. [9] Many researchers have been studied the applications of copolymer resins of substituted phenols and formaldehyde. [10] This paper deals with the synthesis, characterization and thermal degradation studies of copolymer resin derived from o-toulidine(o-T) and biuret(B) with formaldehyde(F). However, the literature survey have revealed that no copolymer resin has been synthesized by using the said monomers. The sample of the o-TBF copolymer resin was subjected to thermal degradation data with Freeman-Carroll (FC) and Sharp-Wentworth(SW) methods for the calculation of activation energy and kinetic parameters such as entropy change ( $\Delta S$ ), apparent entropy change ( $S^*$ ), free energy change ( $\Delta F$ ), frequency factor ( $Z$ ) and order of reaction ( $n$ ).[11-16]

**MATERIALS AND METHODS:** The entire chemicals used in the synthesis of various new copolymer resins were procured from the market and were chemically pure grade. Whenever required they were further purified by standard methods like thin layer chromatography, re-precipitation and crystallization which are generally used for the analytical purification purpose.

**Synthesis of o-TBF copolymer resin :** The new copolymer resin o-TBF was synthesized by condensing o-toluidine (0.2 mol) and biuret (0.1 mol) and formaldehyde (0.3 mol) in molar ratio of 2:1:3 in the presence of 2M (200 ml) HCl as a catalyst at  $122^{\circ}\text{C} \pm 2^{\circ}\text{C}$  for 5 hrs in the round bottom flask attached with water condenser and was heated in an oil bath with occasional shaking to ensure thorough mixing. The temperature of oil bath was controlled by dime stat. The resinous cream product obtained was removed immediately as soon as the condensation reaction was over. The reaction and the suggested structure of o-TBF is shown in Fig.1

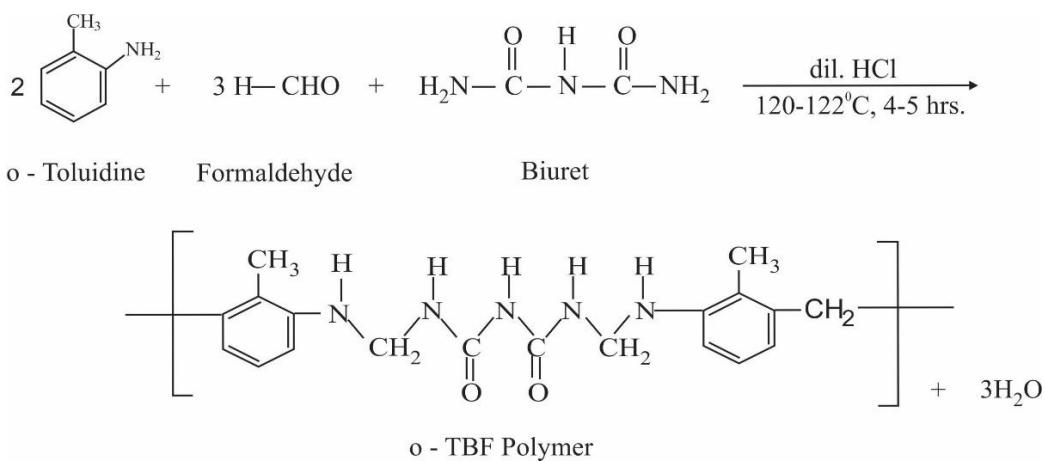


Fig. 1 : Synthesis of o-TBF Copolymer Resin.

The separated copolymer resin was washed with hot water and methanol to remove unreacted starting materials and monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove 4-hydroxybenzoic acid-formaldehyde copolymer which might be present along with o-TBF copolymer. The product so obtained was further purified by reprecipitation technique. For this purpose the copolymer resin was dissolved in 10% aqueous sodium hydroxide solution, stirred well, filtered, and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v concentrated hydrochloric acid/distilled water) with constant and rapid stirring to avoid lump formation. The process of re-precipitation was repeated twice. The copolymer sample o-TBF thus obtained was filtered and washed several times with hot water, dried in air, powdered and kept in vacuum desiccators over silica gel.

**Thermogravimetric analysis:** The thermogravimetric analysis of o-TBF copolymer was performed in air atmosphere with heating rate of  $10^{\circ}\text{C}.\text{min}^{-1}$  from temperature range of  $50^{\circ}\text{C}$  to  $600^{\circ}\text{C}$  using Perkin Elmer Diamond TGA analyser in argon environment. The thermogram were recorded at Sophisticated Instrumentation Centre for Applied Research and testing, Vallabh vidyanagar, Gujrat, based on the initial decomposition temperature, has also been used here to define their relative thermal stability neglecting the degree of decomposition. A plot of percentage mass loss versus temperature is shown in the Fig. 4 for representative o-TBF copolymer resin. From the TG curves, the thermoanalytical data and the decomposition temperature were determined for different stages. To obtained the relative thermal stability of the o-TBF copolymer resin, the method described by Sharp-Wentworth and Freeman-Carroll adopted.

## II. RESULTS AND DISCUSSION

The newly synthesized purified o-TBF copolymer resin was found to be cream in colour. The copolymer is soluble in solvents such as DMF, DMSO and THF while insoluble in almost all other organic solvents. The melting point of o-TBF copolymer resin is  $150^{\circ}\text{C}$  and the yield of the copolymer resin was found to be 81%. A broad absorption band appeared in the region  $3506\text{-}3507\text{ cm}^{-1}$  may be assigned to the stretching vibrations of phenolic hydroxyl ( $-\text{OH}$ ) groups exhibiting intramolecular hydrogen bonding [9, 11, 12]. The peak, at  $3397\text{-}3399\text{ cm}^{-1}$  and at  $1556\text{-}1557\text{ cm}^{-1}$  indicate the presence of  $>\text{NH}$  stretching (amide/imides) [12, 32, 156]. The peak at  $3080\text{-}3081\text{ cm}^{-1}$  ( $-\text{CH}$  stretching),  $2566\text{-}2567\text{ cm}^{-1}$  ( $-\text{CH}$  stretching of  $-\text{CH}_2$  group),  $1312\text{-}1313\text{ cm}^{-1}$  ( $-\text{CH}_2$  banding wagging and twisting),  $1302\text{-}1303\text{ cm}^{-1}$  ( $-\text{CH}_2$  plane banding), indicate the presence of methylene ( $-\text{CH}_2$ ) group [90, 99] and methylene bridge in copolymer chain. The bands appeared at  $3102\text{-}3104\text{ cm}^{-1}$  (Aryl C-H stretching) and  $1550\text{-}1552\text{ cm}^{-1}$  (substituted aromatic ring) may be ascribed to aromatic Skeletal ring [28, 30]. The band at  $2.55\text{-}3.60\text{ cm}^{-1}$  indicate the presence of aromatic  $-\text{CH}_3$  group. The band at  $2.0\text{-}3.0$  indicate that the presence of aromatic  $-\text{CH}_2$  group. The band at  $856\text{-}857\text{ cm}^{-1}$  indicates the presence of tetra substituted aromatic ring, 1,2,3 substitution in aromatic ring was confirmed by the bands appeared at  $956\text{-}958\text{ cm}^{-1}$ ,  $1070\text{-}1072\text{ cm}^{-1}$ ,  $1140\text{-}1142\text{ cm}^{-1}$ . The band of  $-\text{NH}$  stretching ( $3397\text{-}3399\text{ cm}^{-1}$ ) seems to be merged with very broad band of phenolic hydroxyl group.

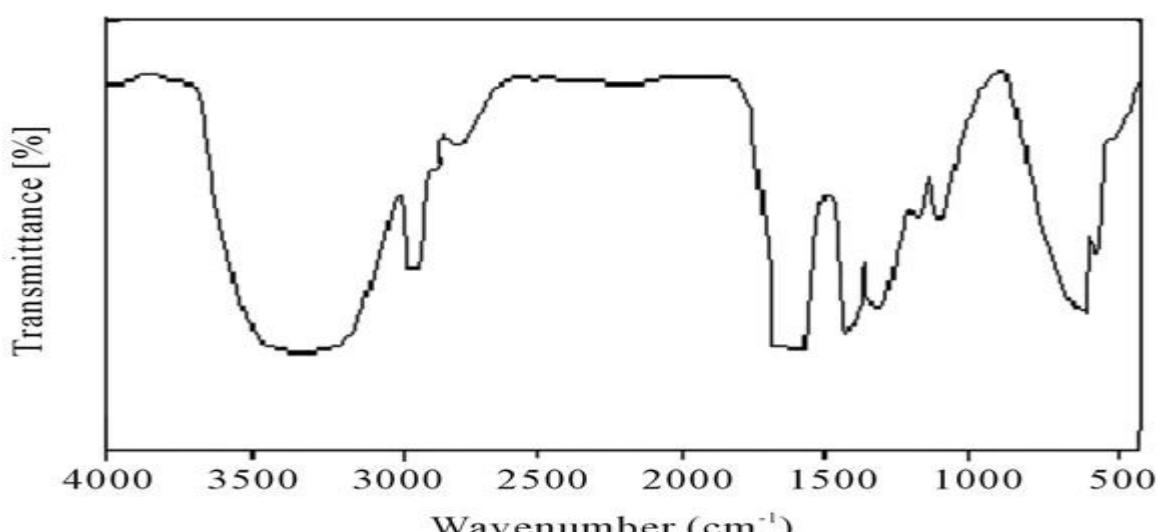


Fig. 2 : FT-IR Spectra of o-TBF copolymer resin

**NMR Spectra :** The chemical shift ( $\delta$ ) ppm observed is assigned on the basis of data available in the literature [159, 160]. The singlet obtained in the region of 4.67-4.65 ( $\delta$ ) ppm may be due to the methylene proton of Ar-CH-N moiety [19, 20, 26]. The signal in the region 7.45-7.43 ( $\delta$ ) ppm are attributed to protons of -NH bridge [20, 21]. The weak multiplate signal (unsymmetrical pattern) in the region of 8.98-8.96 ( $\delta$ ) ppm may be attributed to aromatic proton (Ar-H) [14, 30, 32]. The signal appeared at 9.05 to 9.03 ( $\delta$ ) ppm may be due to phenolic hydroxyl group protons [35, 41, 65]. The much downfield chemical shift fore phenolic -OH indicate clearly the intramolecular hydrogen bonding of -OH group.

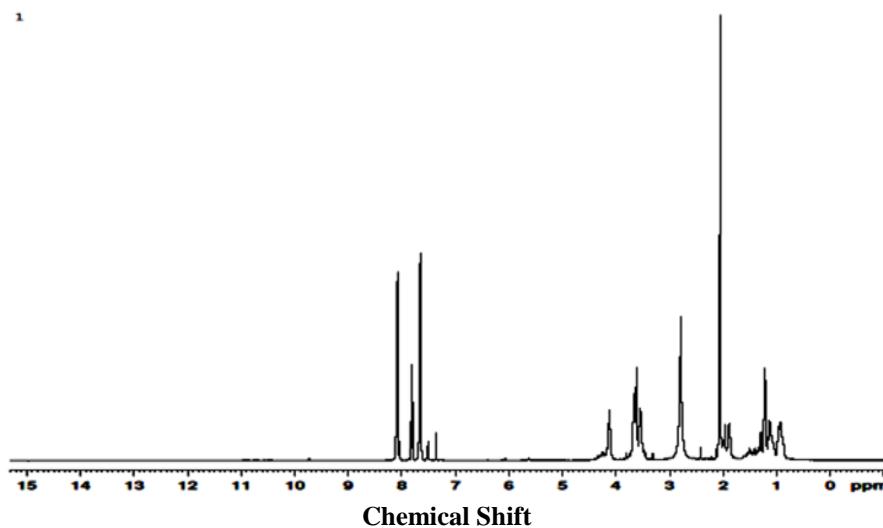


Fig. 3 : NMR Spectra of o-TBF copolymer resin

**Thermogravimetry:** The thermogravimetric data of o-TBF copolymer resin provide information regarding the thermal stability of a polymer. The thermograms were obtained by heating o-TBF resin sample in air at 10 °C per min. The result of percentage weight loss of the copolymer o-TBF copolymer resin exhibits three steps decomposition in the temperature range 40 - 620 °C and are furnished in figure 4. The slow decomposition between 0-80 °C corresponds to 2.82% loss which may be attributed to loss of water molecule against calculated 2.69% present per repeat unit of the polymer. The first step decomposition starts from 80 - 510 °C corresponding to the gradual mass loss of 48.23 % found and 48.50 % calculated which may be due to degradation of side chain attached to the aromatic benzene ring i.e., CH<sub>3</sub> group. The second step degradation starts from 510 - 560°C corresponding the rapid mass loss of 74.98 % found and 74.55 % calculated which represents the degradation of aromatic nucleus with methylene group. The third step decomposition starts from 560 - 620 °C corresponding to

the removal of all the biuret moiety with observed mass loss of 99.60 % against calculated 100 %. Using thermogravimetric data the thermal activation energies (Ea) and order of reaction (n) calculated. Also other thermodynamic parameters such as entropy change ( $\Delta S$ ), apparent entropy change ( $S^*$ ) and frequency factor (Z) are determined and reported in the table 1 and 2. To provide further evidence regarding the degradation system of analysed compounds, we derived the TG curves by applying an analytical method proposed by Sharp-Wentworth and Freeman-Carroll. The ‘average Ea’ calculated by Freeman-Carroll (30.18 KJ/mol) and ‘average Ea’ by Sharp-Wentworth (29.68 KJ/mol) is nearly same.

**Sharp-Wentworth method :**

Using the equation derived by Sharp and Wentworth ,  
 $\log [(dc/dt)/(1-c)] = \log (A/\beta) - [Ea/2.303R] \cdot 1/T$

Where,

$dc/dT$  = rate of change of fraction of weight with change in temperature

$\beta$  = linear heating rate  $dT/dt$ .

By plotting the graph between  $(\log dc/dt) / (1- c)$  vs  $1/T$  we obtained the straight line which give energy of activation (Ea) from its slope.

Where,

$\beta$  is the conversion at time t,

R is the gas constant( $8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$ ) and

T is the absolute temperature.

The plots (fig. 2) gives the activation energies at different stages of degradation reaction take place.

**Freeman-Carroll method :**

The straight line equation derived by Freeman and Carroll, which is in the form of ‘n’ as,

$$[\Delta \log (dw/dt)] / \Delta \log Wr = \left( -\frac{E}{2.303R} \right) \cdot \Delta(1/T) / \Delta \log Wr + n \quad \dots\dots\dots(1)$$

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  $[\Delta \log (dw/dt)] / \Delta \log Wr$  versus  $\Delta(1/T) / \Delta \log Wr$  gives a straight line. From the slope we get energy of activation (Ea) and intercept on Y- axis gives the order of reaction (n). The change in entropy (S), frequency factor (z), apparent entropy ( $S^*$ ) can also be calculated by further calculations.

**i) Entropy Change :**

$$\text{Intercept} = [\log KR/h\phi E] + \Delta S / 2.303 R \quad \dots\dots\dots(2)$$

Where,

K =  $1.3806 \times 10^{-16}$  erg/deg/mole

R = 1.987 Cal/deg/mole

$h = 6.625 \times 10^{-27}$  erg sec.

$\phi = 0.166$

$\Delta S$  = Change in entropy

E = Activation energy from the graph.

**ii) Free Energy Change**

$$\Delta F = \Delta H - T\Delta S \quad \dots\dots\dots(3)$$

Where,

$\Delta H$  = Enthalpy Change = activation energy

T = Temperature in K

$\Delta S$  = Entropy change from (i) used.

**iii) Frequency Factor**

$$B_{2/3} = \log Z E_a / \phi R \dots\dots\dots (4)$$

$$B_{2/3} = \log 3 + \log [1 - 3 \sqrt{1 - \alpha}] - \log P(x) \dots\dots\dots (5)$$

Where,

Z = frequency factor

B = calculated from equation (5)

$\log P(x)$  = calculated from Doyle's table corresponding to activation energy.

#### iv) Apparent Entropy Change

$$S^* = 2.303 \log Z_h / K T^* \dots\dots\dots (6)$$

Z = from relation (4)

$T^*$  = temperature at which half of the compound is decomposed from its total loss.

Table 1 : Activation Energy and Decomposition Temperature of o-TBF copolymer resin

Copolymers	Half Decomposition Temp. (°K)	Activation energy (kJ mole <sup>-1</sup> )	
		FC	SW
o-TBF	529	30.18	29.68

Table 2 : Kinetic Parameters of o-TBF copolymer resin

Copolymers	Entropy change	Free energy change	Frequency factor	Apparent entropy change	Order of reaction
	$\Delta S(J)$	$\Delta F(KJ)$	$Z(S^{-1})$	$S^*(KJ)$	$n$
o-TBF -I	-232.55	212.23	463.0	-657.04	0.96

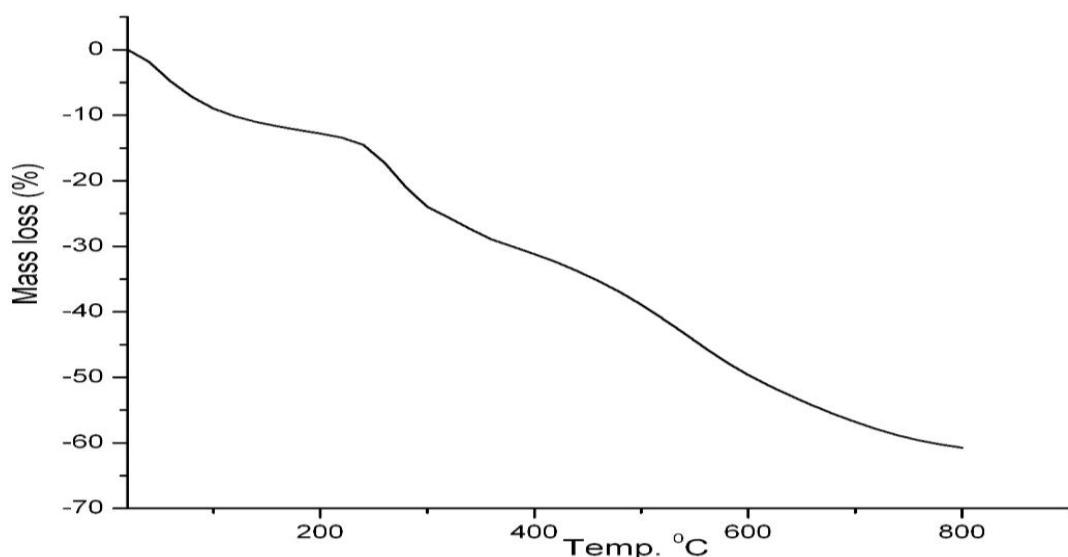


Fig. 4 : Decomposition pattern of o-TBF copolymer resin

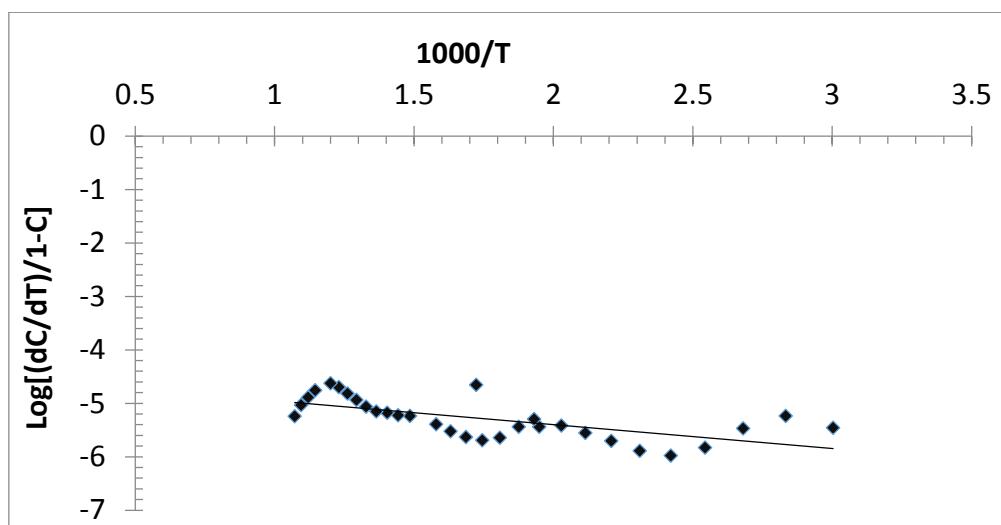


Fig. 5 : Sharp-Wentworth plot of o-TBF copolymer resin

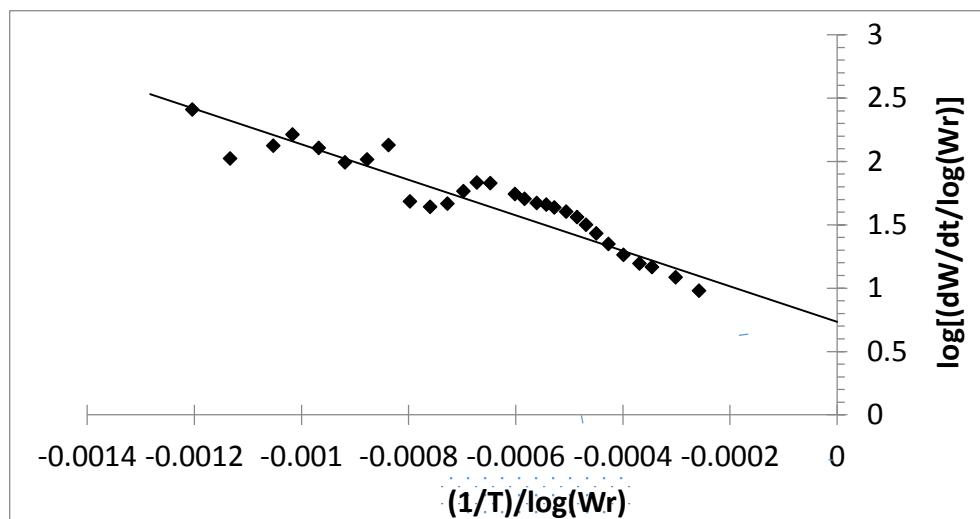


Fig. 6 : Thermal activation energy plot of o-TBF copolymer resin

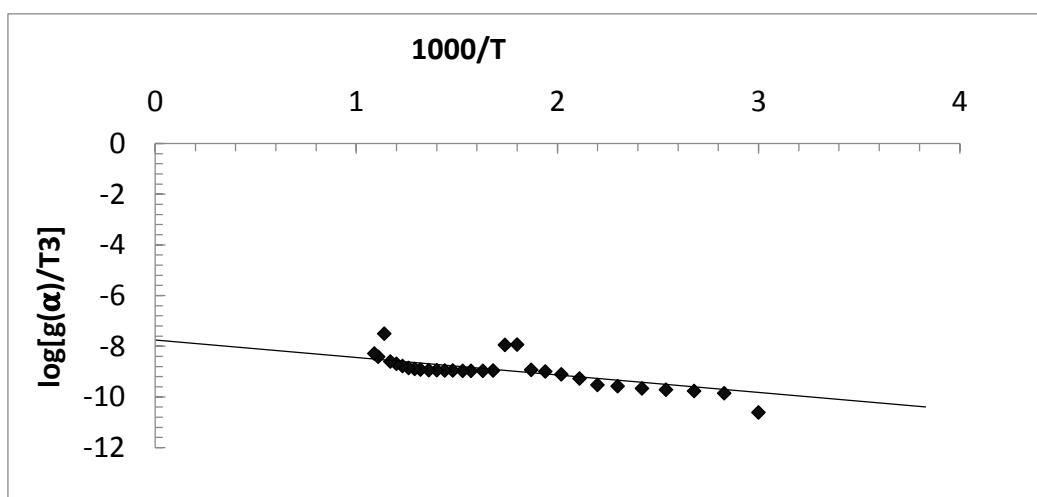


Fig. 7 : Freeman - Carroll plot of o-TBF copolymer resin

### III. CONCLUSION

A copolymer resin o-TBF is based on the condensation reaction of o-toluidine, biuret and formaldehyde in the presence of acid catalyst was prepared. From the FT-IR and  $^1\text{H}$  NMR spectral studies the proposed structure of the o-TBF copolymer resin has been determined. In TGA the energy of activation evaluated from the Sharp-Wentworth and Freeman-Carroll methods are found to be nearly equal and the kinetic parameters obtained from Freeman-Carroll method are found to similar, indicating the common reaction mode. However it is difficult to draw any unique conclusion regarding the decomposition mechanism. Low values of collision frequency factor ( $Z$ ) may be concluded that the decomposition reaction of o-toluidine-biuret-formaldehyde copolymer resin can be classified as ‘slow reaction’. The decomposition reaction was started at higher temperature, indicating a copolymer o-TBF is thermally stable at higher temperature.

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