



# NON-ISOTHERMAL KINETIC STUDIES OF NOVEL O-TMF COPOLYMER

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## ABSTRACT

The Copolymer (o-TMF) was synthesized by condensation of o-toludine and melamine 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 copolymer resin in present study has been carried out by non-isothermal thermogravimetric analysis technique in which sample is subjected to condition of continuous increase in temperature at linear rate. Thermal study of the resins was carried out to determine their mode of decomposition and relative thermal stabilities. The copolymer (o-TMF) was characterized by FT-IR, <sup>1</sup>H-NMR Spectroscopy. Thermal activation energy (E<sub>a</sub>) calculated with above two mentioned methods are in close agreement. Freeman Carroll and Sharp-Wentworth methods were used to calculate the thermal activation energy (E<sub>a</sub>), the order of reaction (n), entropy Change (ΔS), free energy change (ΔF), apparent entropy change (ΔS), and frequency factor (Z). The thermal activation energy determined with the help of these method was in good agreement with each other.

**Keywords:** Synthesis, condensation, thermogravimetric analysis, activation energy, Kinetic parameter.

## INTRODUCTION

The thermal degradation study of copolymers has become a subject of interest. Study of thermal behaviour of copolymers in air at different temperature provides information about the nature of species produced at various temperatures due to degradation. Copolymers having good thermal stability and catalytic

activity have enhanced the development of polymeric materials. [1-3].

The study of thermal behaviour of copolymers in air at different temperature provides information about the nature of species produced at various temperatures due to degradation. Copolymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. Copolymers of salicylic acid, thiourea with trioxane and *p*-hydroxybenzoic acid, thiourea with trioxane have been reported in the literature [4-7]. Synthesis, characterization and ion exchange properties of 4-hydroxyacetophenone, biuret and formaldehyde terpolymer resin were studied by Gurnule and coworkers [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]. S. L. Oswal *et al.* synthesized and studied thermal properties of copolymer (maleimide methyl methacrylate), terpoly (maleimide methyl methacrylate-acrylic acid) and terpoly (maleimide methyl methacrylate methyl-acrylic acid). The thermal behaviour was studied by TG and DSC techniques. Various researchers have been studied the applications of polymer resins of substituted phenols and formaldehyde [11]. The present paper deals with the synthesis, characterization, and non-isothermal thermogravimetric analysis of copolymer derived from o-toludine and melamine (T) with formaldehyde (F). However, the literature studies have revealed that no copolymer has been synthesized by using the said monomers. Sample is subjected to thermal degradation data with Sharp-Wentworth (SW) and Freeman-Carroll (FC) methods, activation energy and

kinetic parameters such as  $\Delta S$ ,  $Z$ ,  $S^*$  and  $n$  (order of reaction) have been evaluated [12-16].

### MATERIALS AND METHODS

The entire chemical 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-TMF Copolymer Resin

The new copolymer resin o-TMF was synthesized by condensing o-toluidine (0.1 mol) and melamine (0.1 mol) with formaldehyde (0.3 mol) in a mol ratio of 1:1:3 in the presence of 2

M 200 ml HCl as a catalyst at  $126 \pm 2^\circ \text{C}$  for 5h, in an oil bath with occasional shaking, to ensure thorough mixing. The separated copolymer was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove o-toluidine-melamine copolymer which might be present along with o-TMF copolymer. The yellow color resinous product was immediately removed from the flask as soon as reaction period was over and then purified. The reaction and suggested structure of o-TMF is shown in Fig. 1

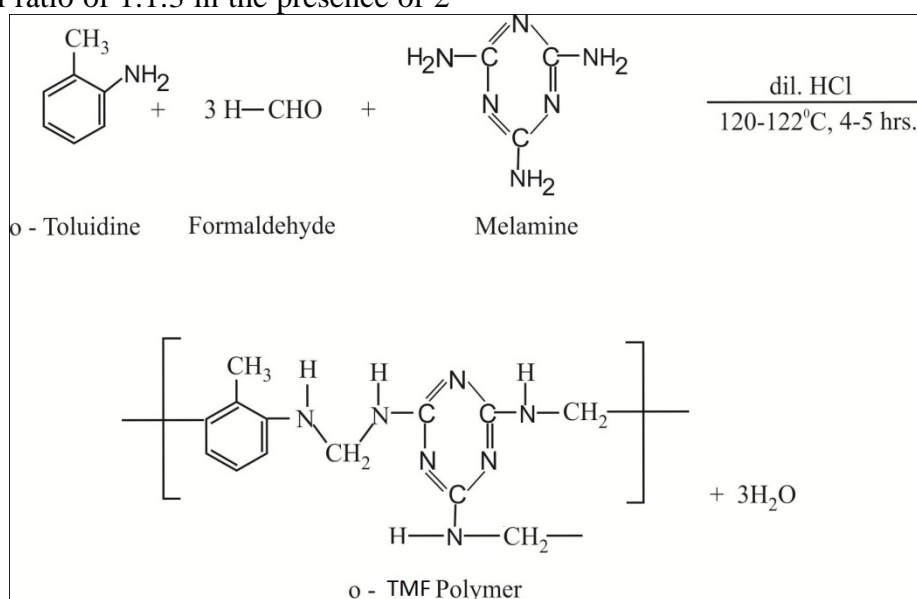


Fig.1: Synthesis of o-TMF Copolymer Resin.

The copolymer was purified by dissolving in 10% aqueous sodium hydroxide solution, 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 reprecipitation was repeated twice. The copolymer sample o-TMF thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desiccator over silica gel.

#### Thermogravimetric Analysis :

The non-isothermal thermogravimetric analysis was performed in air atmosphere with heating rate of  $10^\circ \text{C} \cdot \text{min}^{-1}$  from temperature range of  $50^\circ \text{C}$  to  $600^\circ \text{C}$  using Perkin Elmer Diamond TGA analyzer in argon environment. The thermograms were recorded at

Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Vallabh Vidyanagar, Gujarat. 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. A plot of percentage mass loss versus temperature is shown in the Fig. 4 for a representative o-TMF copolymer. From the TG curves, the thermoanalytical data and the decomposition temperatures were determined for different stages. To obtain the relative thermal stability of the copolymer, the method described by Sharp-Wentworth and Freeman-Carroll adopted.

### RESULTS AND DISCUSSION

The newly synthesized purified o-TMF copolymer resin was found to be yellow in

color. 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-TMF copolymer resin is 190 °C and the yield of the copolymer resin was found to be 89 %.

A broad band appeared in the region 2800-3200 $\text{cm}^{-1}$  may be assigned to the stretching vibrations of phenolic hydroxy (-OH) groups exhibiting intermolecular hydrogen bonding. The sharp band displayed at 1600-1680  $\text{cm}^{-1}$  may be due to the stretching vibrations of carbonyl group (C=O) and 1600-

1400  $\text{cm}^{-1}$  may be due to (C=S) moiety. The presence of -NH in melamine moiety may be assigned due to sharp band at 2800-3000  $\text{cm}^{-1}$ . A strong sharp peak at 1625-1500  $\text{cm}^{-1}$  may be ascribed to aromatic skeletal ring. The bands obtained at 1400 - 1200  $\text{cm}^{-1}$  suggest the presence of methylene bridges in the polymer chain. The weak band appearing at 720 - 760  $\text{cm}^{-1}$  is assigned to C - OH bond. 1,2,4,6 tetrasubstitution of aromatic ring is recognized from the bands appearing at 902, 1084, 1201, and 1290  $\text{cm}^{-1}$  respectively.

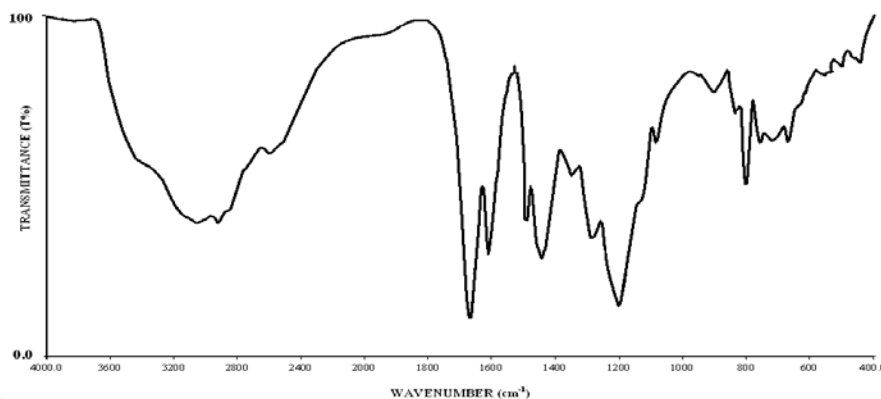


Fig.2: FT-IR Spectra of o-TMF Copolymer

#### NMR Spectra:

Weak signal in the range of 7.8 ppm is attributed to phenolic -OH proton. The NMR spectra of o-TMF copolymer resins show a weak multiplet signal (unsymmetrical pattern) in the region 6.8 (δ) ppm which is due aromatic protons. A medium singlet peak appeared at 3.9

(δ) ppm may be assigned to methyl protons of Ar-CH<sub>2</sub>-NH group. Intense signal appeared in the region 2.5 (δ) ppm may be due to Ar-CH<sub>2</sub>-NH. Triplet signal appeared in the region 3.77 (δ) ppm can be assigned to amido proton of -CH<sub>2</sub>-NH-CO- linkage.

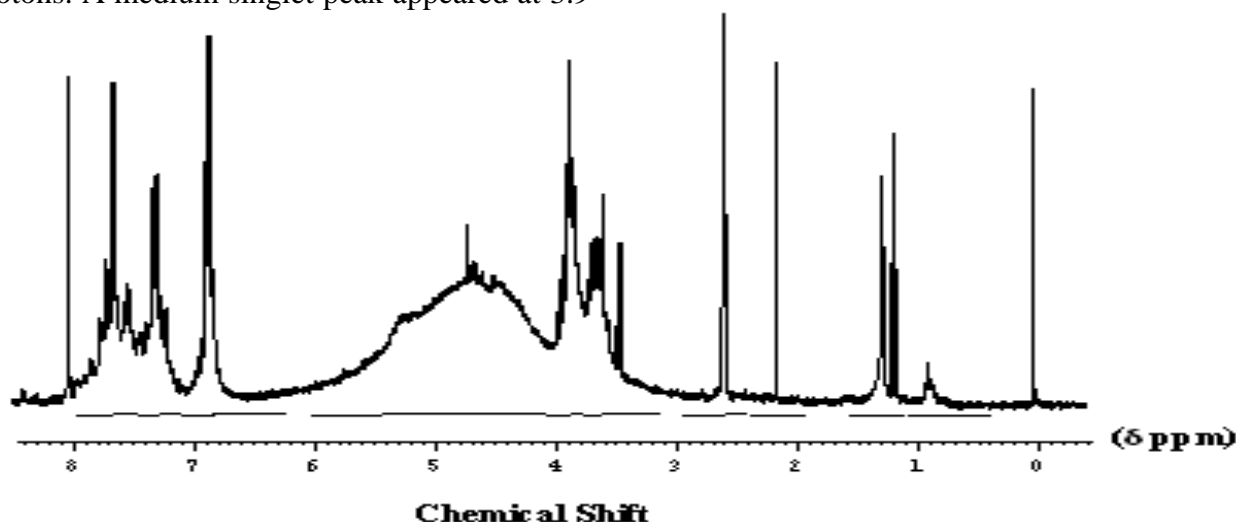


Fig.3: NMR Spectra of o-TMF copolymer

#### Thermogravimetry:

The thermogravimetric data provide information regarding the thermal stability of a polymer. The thermograms were obtained by

heating resin sample in air at 10<sup>0</sup>C/min. The results of percentage weight loss of the copolymer resins depicts three steps decomposition in the temperature range 140-

600°C and are furnished in Figure 4. The slow decomposition between 0-180°C corresponds to 5.0 % loss which may be attributed to loss of water molecule against calculated 4.8 % present per repeat unit of the polymer. The first step decomposition start from 180-260°C which represents loss of methyl group (38.00 % found and 37.86 % cal.). The second step decomposition start from 260-520°C corresponding to 78.00 % removal of aromatic nucleus and methylene bridge against calculated 78.4 %. The third step decomposition side chain from 480-580°C corresponding to removal of melamine moiety (100.00 % found and 98.4 % cal.).

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 & 2. 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 and Freeman-Carroll. The 'average Ea' calculated by Freeman-Carroll (24.51 KJ/mole) and 'average Ea' by Sharp-Wentworth (24.85 KJ/mole) is nearly same.

**Sharp -Wentworth method:**

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

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 dc/dt)/(1-c) vs 1/T we obtained the straight line which give energy of activation (Ea) from its slope. Where β is the conversion at time t, R is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and T is the absolute temperature. The plots (figure 2) give 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  
 $[\Delta \log (dw / dt)] / \Delta \log W_r = (-E / 2.303R) \cdot \Delta (1/ T) / \Delta \log W_r + n$  -----(1)

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

$W_r = W_c - W$

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  $[\Delta \log (dw/dt)] / \Delta \log W_r$  Vs  $\Delta (1/T) / \Delta \log W_r$  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 (S), frequency factor (z), apparent entropy (S\*) can also be calculated by further calculations.

**(i) Entopy Change:**

Intercept =  $[\log KR/h\phi E] + S / 2.303 R$  ----- (2)

Where, K = 1.3806 x 10<sup>-16</sup> erg/deg/mole, R = 1.987 Cal/deg/mole

h = 6.625 x 10<sup>-27</sup> erg sec., φ = 0.166

S = Change in entropy, E = Activation energy from graph.

**(ii) Free Energy Change:**

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

Where,

ΔH = Enthalpy Change = activation energy

T = Temperature in K

S = Entropy change from (i) used.

**(iii) Frequency Factor:**

$B_n = \log Z E_a / \phi R$  -----(4)

$B_1 = \log [ \ln 1 / (1-\alpha) ] - \log P(x)$  -----(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:**

$S^* = 2.303 \log Z h / K T^*$  ----- (6)

Z = from relation (4)

T\* = temperature at which half of the compound is decomposed from it total loss

Table. 1: Results of Thermogravimetric Analysis of o-TMF copolymer

Copolymers	Half Decomposition Temp. T*K	Activation Energy (kJ/mol)	
		F.C	S.W
o-TMF	433	24.51	24.85

Table.2: Kinetic Parameters of o-TMF copolymer

Copolymers	Entropy Change $-\Delta S(J)$	Free Energy Change $\Delta F$ (kJ)	Frequency factor $Z$ ( $S^{-1}$ )	Apparent Entropy Change ( $S^*$ )	Order of reaction (n)
o-TMF	300.67	165.71	438	-23.97	0.92

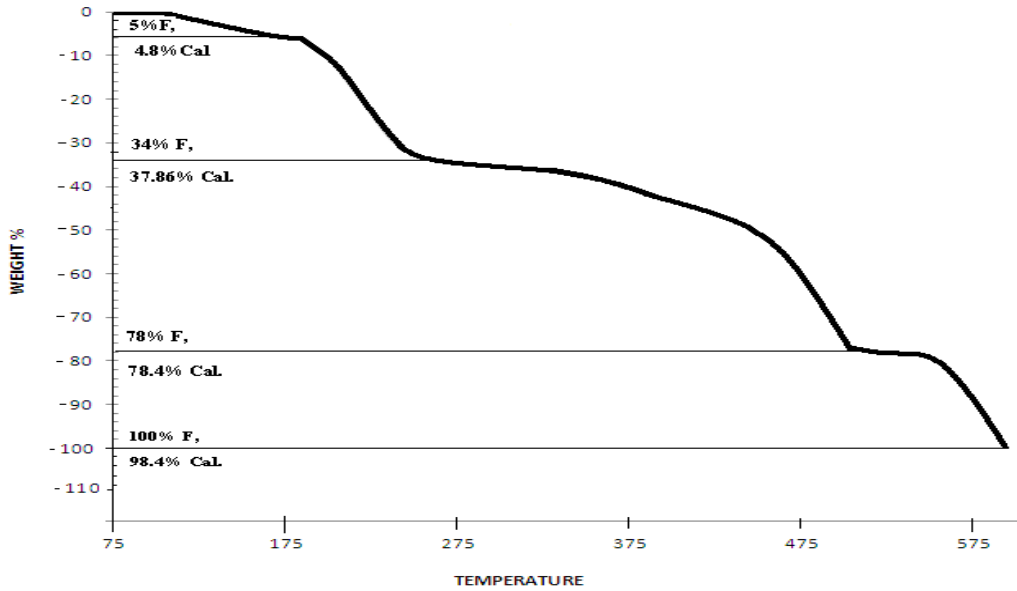


Fig. 4: Decomposition Pattern of o-TMF copolymer Resin.

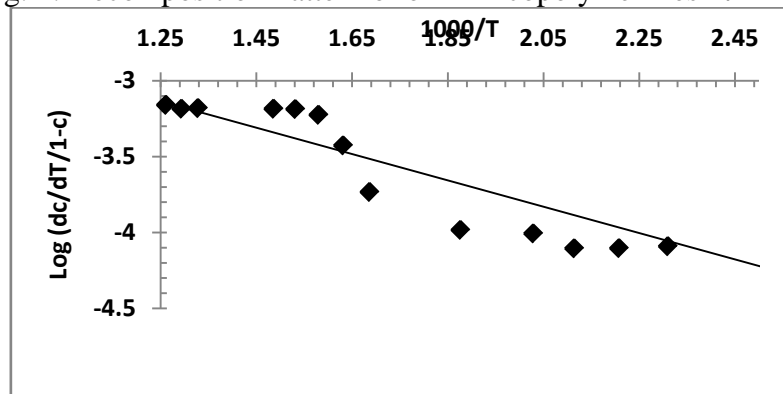


Fig. 5: Sharp-Wentworth plot of o-TMF copolymer

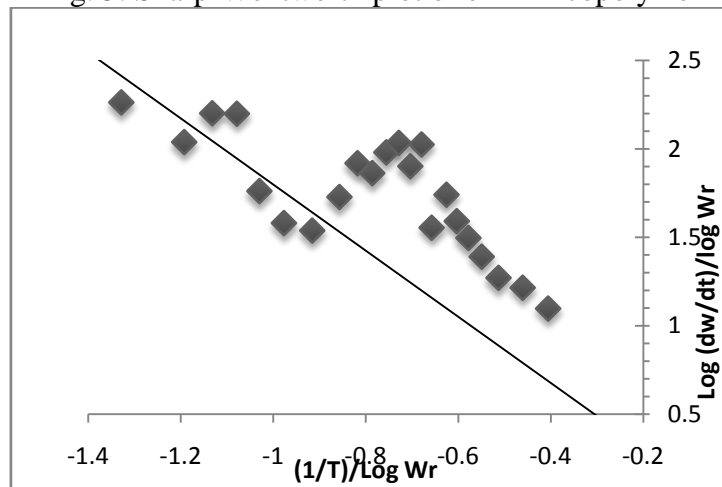


Fig. 6: Thermal activation energy plot of o-TMF copolymer

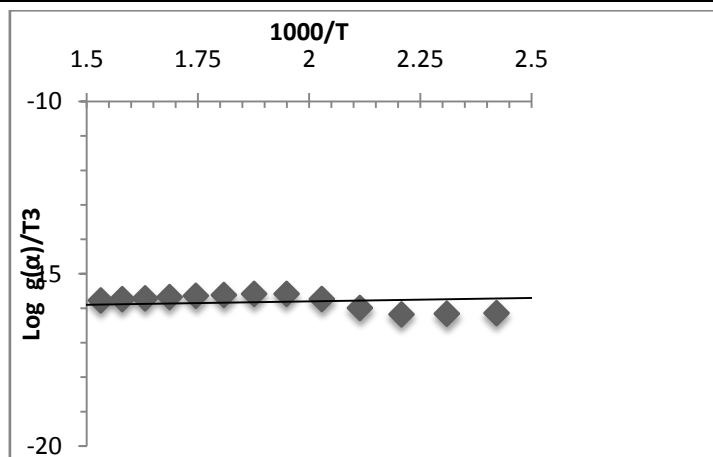


Fig. 7: Freeman-Carroll plot of o-TMF copolymer

### CONCLUSION

A copolymer, o-TMF based on the condensation reaction of o-toulidine, melamine 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-TMF copolymer 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 the Freeman-Carroll method are found to be 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-toulidine-melamine-formaldehyde copolymer can be classified as 'slow reaction'. The decomposition reaction was started at higher temperature, indicating a copolymer o-TMF is thermally stable at higher temperature.

### ACKNOWLEDGEMENTS

Authors are thankful to the STIC Cochin for carrying out spectral analysis, and also to the SICART, Vallabhvidyanagar, Gujrat for carrying out the thermal analysis.

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