# Thermokinetic study of Terpolymer Resin derived from p-Toluenesulfonic acid, m-Cresol and Formaldehyde

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**ABSTRACT**

*The resin-I (abbreviated as PTSMF-II) was synthesized by polycondensation reaction of p-toluensulfonic acid (0.05M), m-cresol (0.1M) and formaldehyde (0.2M), in presence of an acid catalyst (1M HCl). The structure of resin was determined by its elemental analysis, UV-VIS, IR data. Non-aqueous conductometric titration technique was employed to determine the molecular weight of the terpolymer. In the present paper investigation of the thermokinetic parameters such as apparent entropy ($\Delta S$), frequency factors (A), free energy change ($\Delta G$). The order of degradation reaction determined by Freeman Carroll (FC) and Sharp Wentworth (SW) methods.*

**Keywords:** Terpolymer, Polycondensation, TGA, Thermokinetic parameters, Thermal degradation,
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## INTRODUCTION

Knowledge of thermal properties have been used since biblical times moreover some evidences had been found in Iron Age [1]. The thermal degradation of polymer remains a major concern of researchers an alternative method for studying the decomposition of polymers, dedication towards research, scientist have introduced the recent innovations in the polymer chemistry. Terpolymer resins having better thermal stability, this property has enhanced the scope for development of some polymeric materials. Thermo gravimetric studies of polymer provide

information about the degradation pattern during heating and thermal stability. Phenolic resins have a large number of practical applications in insulating materials, electronic controls, aerospace industry, and machine parts, because of their high thermal stability, chemical and heat resistance [2]. Thermal study of the resin 8-hydroxyquinoline 5-sulphonic acid and oxamide with formaldehyde was carried out to determine the mode of decomposition and relative thermal stability. [3]. Aswar *et al* [4] have reported the sequences of thermal stability of polymeric chelates 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 [4]. Kapse *et al* studied the structural and thermokinetics of the terpolymer resin derived from p-hydroxyacetophenone-quinhydrone–melamine, The activation energies, entropy and free energy of degradation were determined by Freeman-Carroll and Sharp-Wentworth methods, the order of degradation reaction was determined for this resin [5]. Azarudeen et al adopted an ecofriendly technique to synthesize a terpolymer from Anthranilic acid Thiourea and Formaldehyde, thermal analysis was carried out and the thermal data showed that the terpolymer was thermally stable and the order of the decomposition reaction was

1932

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nearly one [6]. The thermogravimetric analysis of copolymer resin 2, 2'-dihydroxybiphenyl, dithiooxamide and formaldehyde was carried out by non-isothermal thermo gravimetric analysis technique [7]. Masram *et al* [8] reported kinetic study of thermal degradation of resin derived from salicylaldehyde, ethylenediamine and formaldehyde . Karunakaran et al [9] evaluated thermo kinetic parameters of the terpolymer resin derived from Resorcinol-thiourea-formaldehyde by using different methods and it was found that activation energy was nearly equal for all the methods.

In present work thermo kinetic parameters were determined by using following methods. [10-13].

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

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

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

B) **Sharp-Wentworth method (SW):** Following expression is used to evaluate the kinetic parameters,

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

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

## MATERIALS AND METHODS

**Chemicals**
All chemicals were of AR grade and chemically pure grade, p-toluene sulfonicacid, m-cresol and formaldehyde was procured from Sd fine, India. Triple distilled water was used for the entire experimental procedure.

**Synthesis of p-toluenesulfonic acid, m-cresol and formaldehyde terpolymeric resin (PTSMF-II)**
PTSMF-II was prepared by condensing p-toluenesulfonic acid (0.05 mol) m-cresol (0.1 mol), and formaldehyde (0.2M) in 250 ml round bottom flask fitted with water condenser, in presence of 1M HCL (200ml), reaction mixture was refluxed on oil bath for 5 hrs at 105-110°C with occasional shaking, the temperature of electrically heated oil bath was controlled with the help of dimmer stat. The precipitate was immediately removed from the flask as soon as the reaction period was over. Pinkish colored product was obtained. The resinous product so obtained was repeatedly washed with hot water to remove unreacted monomers. It was purified by dissolving in 8% sodium hydroxide solution, filtered and re-precipitated by 1:1 HCl with constant and rapid stirring to avoid lump formation. The precipitate so obtained was filtered off. The product was further washed several times with hot water and dried. The air dried product was then extracted with diethyl ether and then with petroleum ether to remove m-cresol-formaldehyde copolymer which might be present along with PTSMF-1I terpolymeric resin. The product was dried, and then grinded to fine powder. The detailed analytical data of terpolymer PTSMF-II is tabulated in Table 1.

**Table1.Analytical data of resin**

| Parameters/conditions | specifications |
|---|---|
| Terpolymeric resin | PTSMF-II |
| p-Toluenesulfonic acid | 0.05M |
| m-Cresol | 0.1M |
| Formaldehyde | 0.2M |
| Temperature | 105-110°C |
| Time | 5 hrs |
| yield | 75% |

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## RESULTS AND DISCUSSION

**Elemental analysis and molecular weight determination**
 The terpolymer resin was analyzed for carbon, hydrogen and sulphur contents. The elemental analysis was carried out at National Institute of Pharmaceutical Education and Research (NIPER) Punjab University, Chandigarh India. The number average molecular weight (Mn) of terpolymer was determined by non-aqueous conduct metric titration in DMF using 0.1M KOH in absolute alcohol as titrant. From the graphs of specific conductance against miliequivalents of base, first and last break were noted from which degree of polymerization (DP) and the number average molecular weight (Mn) was calculated for terpolymer resin using following equations [14-15].

$$DP = \frac{(Total\ miliequivalents\ of\ the\ base\ required\ for\ last\ break)}{(miliequivalents\ of\ the\ base\ required\ for\ first\ break)}$$

**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 PTSMF-II resin is given in following table 2.

**Table 2.Elemental analysis and molecular weight determination data of PTSMF-II resin**

| Resin | %C | | %H | | %S | | DP | Molecular weight $(M_n)$ | Molecular Formula of repeat unit | Molecular Weight of repeat unit |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cal | Found | Cal | Found | Cal | Found | | | | |
| PTSMF-II | 68.49 | 68.50 | 5.9 | 6.2 | 7.3 | 7.35 | 22 | 9636 | $C_{25}H_{26}SO_5$ | 438 |

**UV-VIS spectra of PTSMF-II resin:-**
UV-VIS spectra of terpolymer resin in DMSO solvent recorded by UV-VIS Double Beam Spectrophotometer Schimadzu, Model No-1701 fitted with automatic pen chart recorder at Department of Pharmacy; RTM Nagpur University, Nagpur.The spectrum is shown in the figure. UV-Vis spectrum of PTSMF-II was scanned from 190-700 nm. A peak at 213nm was assigned to n-□σ * transition is due to –$SO_3H$ group. A peak at 259.5 nm was assigned to π-π*due to aromatic ring. The n-π*transition at 284.5 nm, this is due to S=O group present in -$SO_3H$ group.
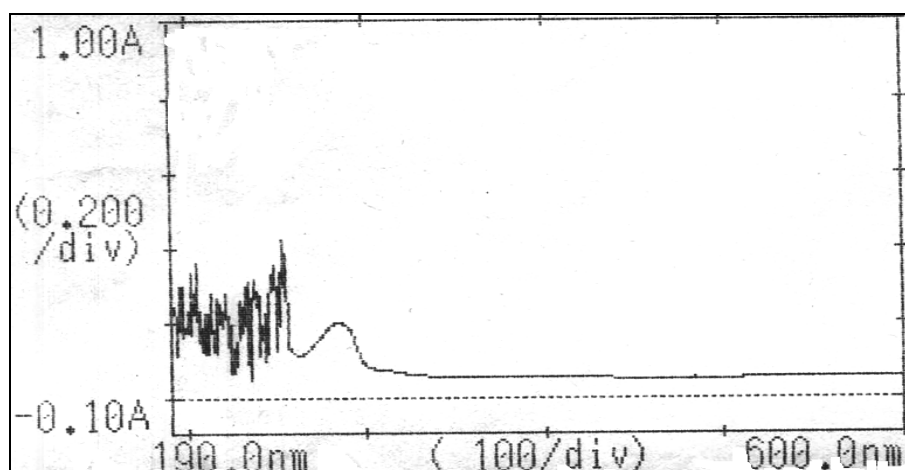


**Figure-1 UV-VIS spectrum of PTSMF-II resin**

**IR spectra of resin PTSMF-II**
IR spectra of synthesized terpolymeric resin was recorded at Department of pharmacy, RTM Nagpur University, Nagpur using FT-IR spectrophotometer Shimadzu model No-8101A. FT-IR spectral data are given in following Table3.
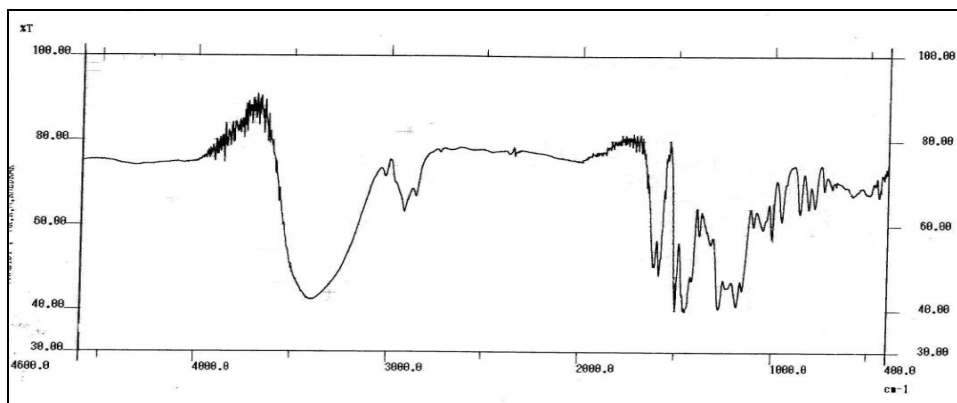
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**Figure-2  FT-IR spectrum of PTSMF - II**

**Table 3. FT-IR spectral data**

| IR (wave number in cm^{-1}) | Nature of fragment assigned |
|---|---|
| 3019 | O–H str. |
| 2918 | -$CH_2$- str. |
| 1618.5 | aromatic C=C str. |
| 1448 , and 781.3 | bend, wag ,rock. vibr. of methylene (-$CH_2$-) bridges |
| 1320 and 1155 | S=O antisymmetric and symmetric str. |
| 1226 | C-O- str. of Phenolic   group |
| 820 | 1,23,5 tetra substi. benzene ring |
| 605.7 and731 | C-S str. |

The broad band at 3401 cm$^{-1}$ is due to the O–H stretching [14]. The absorption at 2939 cm$^{-1}$ was assigned to-$CH_2$-stretch, shows the bridges of $CH_2$ composite [15-16]. The peak at 1618.5 cm$^{-1}$    corresponds to aromatic C=C stretching. The presence of 1226 cm$^{-1}$ was due to the C-O stretching of phenolic group [10]. The inflections around 1448 cm-$^{1}$, and 781.3 cm$^{-1}$ suggest the presence of bending, wagging, rocking vibrations of methylene (-$CH_2$-) bridges in polymeric chains [17-19]. The band present at 820 cm$^{-1}$ is assigned to 1,23,5 tetra substituted benzene ring [20].Weak band   appears at 605.7 cm$^{-1}$ and 731 cm$^{-1}$ which corresponds to C-S str. [16]. Another peak at 1414 cm$^{-1}$ is also related to stretching of $SO_3$ group.  1320 cm$^{-1}$and 1155 cm$^{-1}$ region corresponds to S=O antisymetric and symmetric stretching in p-toluenesulphonic acid [17]. According to data obtain in physicochemical methods; the tentative structure of terpolymeric resin was assigned as shown in fig. 3.
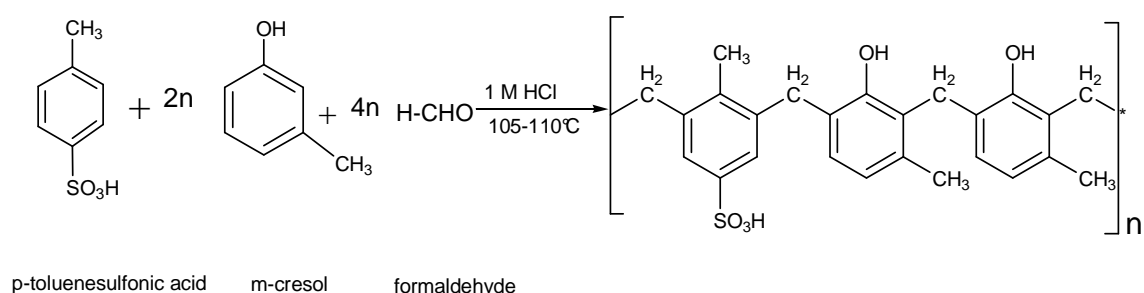


**Figure-3 Reaction Scheme-synthesis of PTSMF - II**

**Thermo gravimetric analysis:**
The thermogram of PTSMF-II terpolymer resin as shown in fig. 4 was recorded at Dept. of Material Science, VNIT Nagpur using Perkin Elmer Diamond TGA/DTA analyzer in argon environment.  The polymeric sample was allowed to heat up to 1015$^0$C. The thermo gram reveals that initial weight loss up to 130$^0$C due to loss of water. The decomposition of resin between 393-498$^0$C was studied. Freeman-Carroll Method and Sharp-Wentworth plots are

1935

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shown in fig. 5a and fig. 5b respectively. The order of decomposition was found to be 1.12 as determined by FC method which was further confirmed by SW method. Thermo kinetic parameters are tabulated in table 4
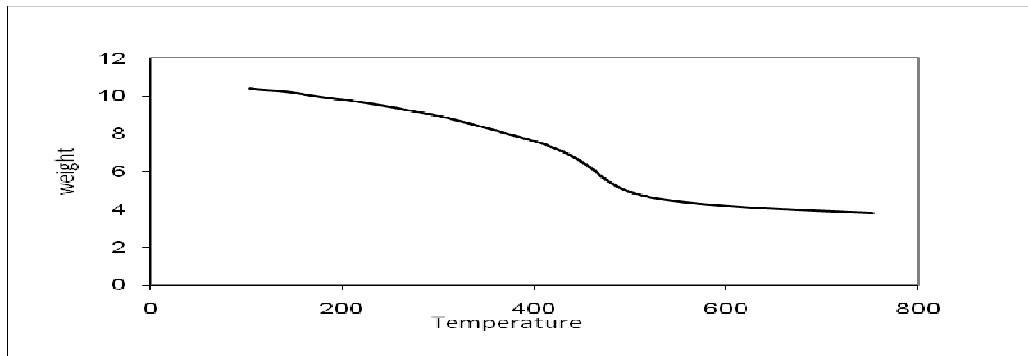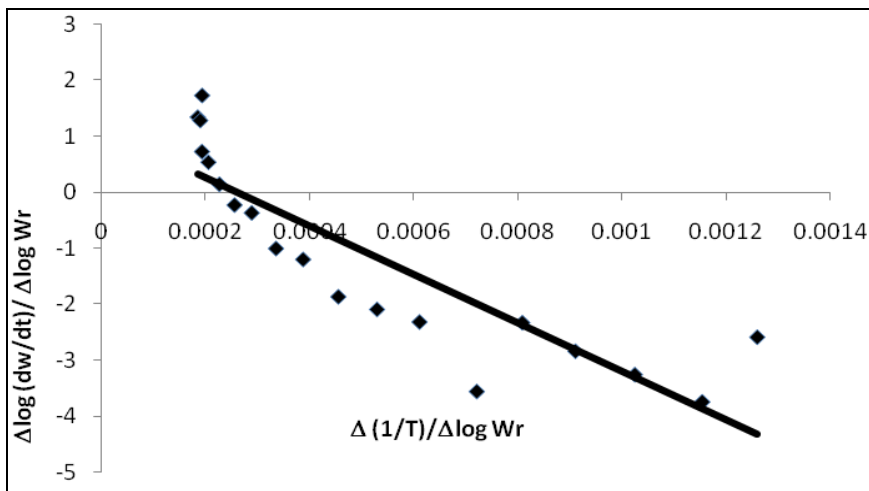


**Figure 4. Thermogram of PTSMF – II resin**
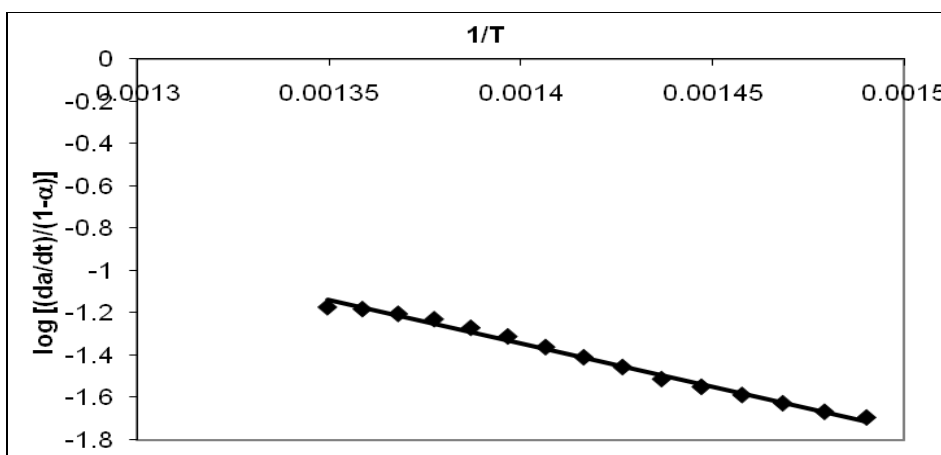


**Figure 5 (a) Freeman-Carroll plot of PTSMF-II**



**Figure 5(b) Sharp-Wentworth plot of PTSMF - II**

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**Table 4. Thermokinetic parameters of PTSMF-II terpolymeric resin**

| PTSMF-II terpolymeric resin | Ea (kJ) | A (min$^{-1}$) | $\Delta$S* (J/K) | $\Delta$G* (kJ) | Order (n) |
|---|---|---|---|---|---|
| FC method | 89.57 | 3.31x10$^5$ | -146.84 | 198.38 | |
| SW method | 78.17 | 2.35 x10$^5$ | -149.69 | 189.10 | 1.12≈1.0 |

*FC=Freeman-Carroll, SW= Sharp-Wentworth*

## CONCLUSION

The data of elemental analysis, UV–Vis spectra, FTIR spectra, nonaqueous conductometric titration supports to the above tentative structure of PTSMF-II terpolymer resin. The activation energies, entropy and free energy of first order degradation are determined by Freeman-Carroll and Sharp-Wentworth methods which are in good agreement. High value of frequency factor and entropy indicate the slow degradation of resin. The high value of energy of activation relative to thermal energy suggests that the PTSMF-II resin is thermally stable below 498$^0$C.

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