



SYNTHESIS AND THERMAL DEGRADATION STUDIES OF P-TOLUDINE, ETHYLENEDIAMINE, AND FORMALDEHYDE COPOLYMER RESIN

Chetana G. Kohad and Wasudeo B. Gurnule*

*Department of Chemistry, Kamla Nehru Mahavidyalaya, Sakkardara, Nagpur- 440024, Maharashtra, India

Email: wbgurnule@gmail.com and che_khot@rediffmail.com

ABSTRACT

A copolymer resin involving *p*-toluidine and ethylenediamine with formaldehyde (p-TEDF) was synthesized by the condensation of *p*-toluidine and ethylenediamine with formaldehyde in the presence of 2M hydrochloric acid as a catalyst with 1:1:2 molar proportions of reacting monomers. The structure of newly synthesized copolymer has been elucidated and confirmed on the basis of Elemental analysis and various spectral techniques, that is, UV-visible, FT-IR, and $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ spectroscopy. Number average molecular weight (M_n) has been determined by conductometric titration in non-aqueous medium. The studies have been further extended to nonisothermal thermogravimetric analysis for determination of their mode of decomposition and relative thermal stability. Activation energy (E_a) and order of reaction, (n) were calculated by Sharp-Wentworth and Freeman-Carroll methods. Activation energy calculated by Sharp-Wentworth and Freeman-Carroll methods are in close agreement with each other. Thermodynamic parameters such as free energy change (ΔF), entropy change (ΔS), apparent entropy change (S^*), and frequency factor (Z) have also been evaluated based on the data of Freeman-Carroll method. SEM was used to establish the surface morphology and nature of the copolymer.

Keywords: Synthesis, condensation, thermogravimetric analysis, activation energy, spectra.

INTRODUCTION

The synthesis of copolymer has stimulated an enhanced interest in recent years due to their wide applications. Since last few decades many scientist are working to develop new and easier techniques for synthesis and characterization of copolymer due to its versatile applications in domestic as well as in industrial sector. copolymer found very useful applications as adhesive, high temperature flame resistance, melting temperature control, fibers, coating materials, semiconductor, catalyst, ion exchange resin, flexibility impact modifier for engineering plastic, heat sealing film in car interior, pipelines, electrical resistance textiles, bullet-proof vests biomaterials, light guide panel laptop computers and pharmaceutical uses [1-4]. The polymeric material is often not a single component and hence simple chemical analysis will rarely provide all information required. Characterization of new copolymer resins requires several physicochemical techniques and spectral studies [5]. Thermogravimetric analysis comprises a group of techniques in which a physical property of substance is measured as a function of temperature when the substance is subjected to a controlled temperature program. Thermally stable terpolymers have recently become boon to polymer chemist due to their superior and high performance utility. Many researchers tried to improve the thermal stability at elevated temperature by changing the monomer composition in polymer synthesis. The thermal degradation study of terpolymer being an important property which primarily decides thermal stability and processability. A wide variety of thermally stable polymers has been synthesized and studied their thermogravimetric

property and finds many applications. Phenolic resins are known for their wide applications in various areas because of their thermal stability, easy availability, cost effectiveness, and some of their excellent properties [6, 7].

The thermal stability of terpolymers has been extensively studied by employing the method of thermogravimetric analysis (TGA) by several authors. Thermogravimetric analysis of terpolymer resins derived from 2,4-dihydroxyacetophenone, dithiooxamide, and formaldehyde by Rahangdale et al. [8], 8-hydroxyquinoline, dithiooxamide, and formaldehyde by Katkamwar et al. [9]. The thermal degradation kinetics of some new terpolymers derived from 2,4-dihydroxypropiophenone, oxamide, and formaldehyde have been studied by Tarase et al. [10]. and 8-hydroxyquinoline-5-sulphonic acid, catechol, and formaldehyde by Mandavgade et al. [11]. Thermoanalytical and kinetic studies of terpolymer resins derived from 8-hydroxyquinoline-5-sulphonic acid/p-cresol, oxamide/melamine with formaldehyde have been reported by Singru et al. [12, 13]. Nonisothermal decomposition and kinetic analysis of copolymer derived from 2,4-dihydroxybenzoic acid, melamine, and formaldehyde have been reported by Butoliya et al. [14]. Thermal and metal ion bonding properties of terpolymer resin synthesized from resorcinol-thiourea-formaldehyde have been reported by Karunakaran et al. [15]. Michael et al. carried out thermal degradation of terpolymers synthesized from salicylic acid, 8-hydroxyquinoline and guanidine with formaldehyde [16, 17] has been studied in detail.

The present study deals with the synthesis and physicochemical characterization and thenonothermal thermogravimetric analysis of copolymer derived from p-toluidine, ethylenediamine, and formaldehyde which has not been reported so far in literature.

MATERIALS AND METHODS

Starting Materials

p-Toulidine and ethylenediamine used in the present investigation of analytical grade purity were purchased from Sigma Aldrich Chemicals. Formaldehyde (37%) was purchased from S.D. Fine Chemicals, India. All the used solvents like N,N-dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, acetone, and diethyl ether were procured from Merck, India.

Synthesis of Copolymer

p-TEDF copolymer was prepared by condensing p-toulidine and ethylenediamine with formaldehyde in the presence of 2M Hydrochloric acid as a catalyst in 1:1:2 molar proportions at temperature 126°C in an oil bath with occasional shaking, to ensure thorough mixing. for about 5hrs. The brown coloured resinous product was obtained. The product obtained was washed with hot distilled water and methanol to remove the excess of p-toulidine-formaldehyde copolymer which might be present along with p-TEDF copolymer. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether. The brown colour resinous product was immediately removed from the flask as soon as reaction period was over and then purified. The reaction and suggested structure of p-TEDF is shown in Fig. 1

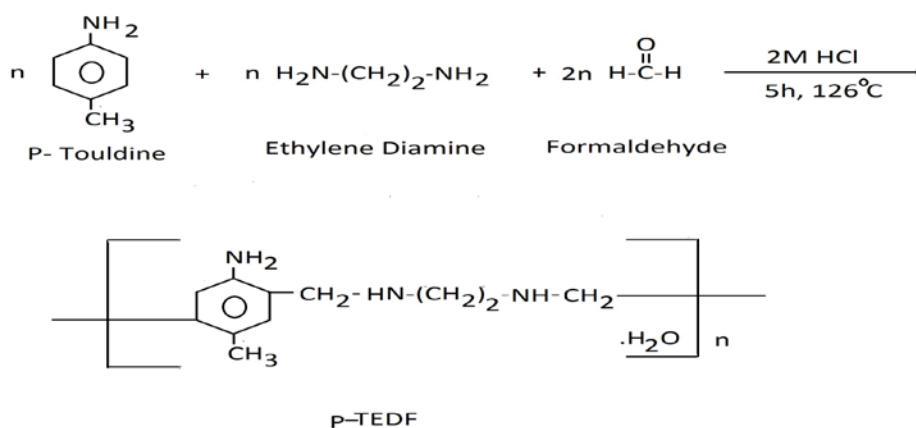


Figure 1: Chemical reaction of p-TEDF copolymer.

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 p-TEDF thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desiccator over silica gel.

Characterization of Copolymer

Newly synthesized and purified copolymer was subjected to elemental analysis for carbon, hydrogen, nitrogen, on Perkin Elmer 2400 Elemental Analyzer instrument and ultraviolet-visible spectra of copolymer in dimethyl sulfoxide (DMSO) solvent recorded on Varian Carry 5000 UV-Vis spectrophotometer in the range from 200 to 800nm. An infra-red spectrum of copolymer resin was recorded on Perkin-Elmer-983 spectrophotometer in KBr pellets in the range from of 4000 - 400 cm^{-1} Spectrophotometer $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ study was performed in DMSO as solvent on Bruker Advance-II 400 NMR spectrophotometer at Sophisticated Test and Instrumentation Centre Cochin, University of Science and Technology, Cochin. The nonisothermal thermogravimetric analysis of newly prepared copolymer has been carried out

using Perkin Elmer Diamond 3-II thermogravimetric analyzer, in air atmosphere with a heating rate of $10^\circ\text{C min}^{-1}$ using 5 - 6 mg of samples in platinum crucible from temperature of 40°C to 800°C and thermograms are recorded for p-TEDF sample at STIC, Cochin. SEM was used to establish the surface morphology and nature of the copolymer.

Analytical and Physicochemical Studies

The number average molecular weight (M_n) was determined by conductometric titration in non aqueous medium such as dimethylsulphoxide (DMSO) using ethanolic KOH as a titrant. The specific conductance was plotted against milliequivalents of ethanolic KOH required for neutralization of 100 gm of terpolymer. There are several breaks before the complete neutralization of all phenolic hydroxyl groups. The first break in the plot was the smallest break and assumed that this corresponds to a stage in titration when an average one phenolic hydroxyl group of each chain was neutralized.

From the plot the first and final breaks were noted. The average degree of polymerization (DP) and hence the number average molecular weight (M_n) of the terpolymer has been determined using the formula. This observation is in agreement with the trend observed by earlier workers [18].

$$\overline{DP} = \frac{\text{Total milliequivalents of base required for complete neutralization}}{\text{Mill equivalents of base required for smallest interval}}$$

$$\overline{M_n} = \overline{DP} \times \text{Molecular weight of repeating unit}$$

Theoretical Consideration

Thermogram was interpreted and analyzed to obtain information about the % weight loss at different temperatures which gives information about sample composition, product formed after heating, and kinetic parameters. Kinetics parameters have been determined using Sharp-Wentworth [19] and Freeman-Carroll [20] methods as follows.

Sharp -Wentworth method:

Using the equation derived by Sharp and Wentworth,

$$\log \left[\frac{dc/dT}{(1-c)} \right] = \log (A/\beta) - [E_a/2.303R] \cdot 1/T \dots\dots\dots(1)$$

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 (E_a) from its slope. Where β is the conversion at time t , R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature. The plots 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

$$[\Delta \log (dw / dt)] / \Delta \log W_r = (-E / 2.303R) \cdot \Delta (1/ T) / \Delta \log W_r + n \text{-----(1)}$$

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

$$W_r = W_c - W$$

W_c = weight loss at completion of reaction.

W = fraction of weight loss at time t.

E_a = 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 (E_a) and intercept on Y-axis as order of reaction (n). The change in entropy (S), frequency factor (z), apparent entropy (S*) can also becalculated by further calculations.[21, 22]

(i) Entopy Change:

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

Where, K = 1.3806 x 10⁻¹⁶ erg/deg/mole, R = 1.987 Cal/deg/mole

$$h = 6.625 \times 10^{-27} \text{ erg sec. , } \phi = 0.166$$

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

(ii) Free Energy Change:

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

Where, ΔH = Enthalpy Change = activation energy

T = Temperature in K

S = Entropy change from (i) used.

(iii) Frequency Factor:

$$B_n = \text{Log } Z E_a / \phi R \text{-----(4)}$$

$$B_1 = \log [\ln 1 / 1 - \alpha] - \log P (x) \text{-----(5)}$$

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:

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

Z = from relation (4)

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

RESULTS AND DISCUSSION

The newly synthesized purified p-TEDF copolymer resin was found to be brown in colour. The copolymer is soluble in solvents such as DMF, DMSO and THF, pyridine, concentrated H₂SO₄. No precipitation and degradation occurs of resin in all the solvents, while insoluble in almost all other organic solvents. The melting point of the copolymer was determined by using electrically heated melting point apparatus and is found to be of 394 K. This resin was analyzed for carbon, hydrogen and nitrogen content.

The results of elemental analysis are shown in Table1.used to assign empirical formula and empirical weight for p-TEDF copolymer. Composition of copolymer was assigned on the basis of elemental analysis and was found to be in good agreement with that of calculated values.

Table 1: Elemental analysis data of p-TEDF copolymer

Copolymer	% of C found (cal.)	% of H found (cal.)	% of N found (cal.)	Empirical Formula	Formula Weight
p-TEDF	63.37 (63.15)	8.84 (9.09)	20.32 (20.09)	C ₁₁ H ₁₉ N ₃ O	209

The number average molecular weight(M_n) of this copolymer has been determined by nonaqueous conductometric titration method in DMSO medium using standard potassium hydroxide (0.05M) in absolute ethanol as a titrant. A plot of specific conductance was plotted against milliequivalents of ethanolic

KOH required for neutralization of 100g of each copolymer. The number average molecular weight (M_n)of copolymercould be obtained by multiplying the average degree of polymerization(DP) by formula weight of repeating unit. It is observed that the molecular weight of terpolymer increases with the increase

in ethylenediamine content. This observation is in agreement with the trend observed by earlier researchers [23]. Conductometric titration curve

of terpolymer was shown in Figure 2 and the results are presented in Table 2.

Table 2 :Molecular weight determination of p-TEDF copolymer.

Copolymer	First stage of neutralization (Meq/100gm sample)	Final stage of neutralization (Meq/100gm sample)	Degree of polymerization (DP)	Empirical Weight (gm)	Number average molecular weight (Mn)
p-TEDF	160	1450	9.062	209	1893.988

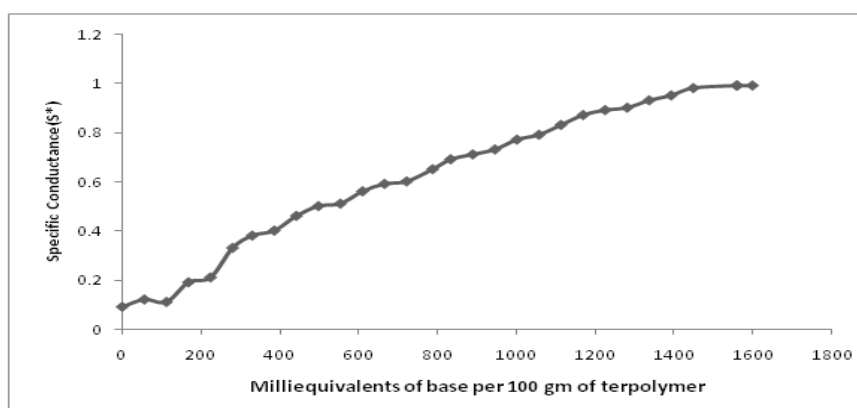


Fig 2: Conductometric titration curve p-TEDF copolymer.

FT-IR Spectra

The FT-IR spectrum of p-TEDF copolymer depicted in Figure 3. A broad and strong band appeared at 3384cm^{-1} which may be assigned due to the $>\text{NH}$ stretching (prim. amine) in aromatic ring. A medium and sharp band displayed at 2915cm^{-1} may be assigned due to the stretching vibration of aromatic C-H group. A broad weak band at 2856cm^{-1} indicates the presence of C-H stretching in aromatic alkyl (Ar-CH₃) group. A medium band appearing at

1614cm^{-1} indicates the presence of $>\text{C}=\text{C}<$ (aromatic) group. A sharp band appearing in the region of 1492cm^{-1} may be due to bending vibration of $>\text{NH}$ (sec. amine) group. Aromatic C-N stretch appeared in the region of 1236cm^{-1} which shows medium band. The bands obtained at 1346cm^{-1} suggest the presence of methylene bridges in the polymer chain. 1,2,4 substitution of aromatic ring is recognized from the bands appearing at 747 , 713 , and 830cm^{-1} respectively [24].

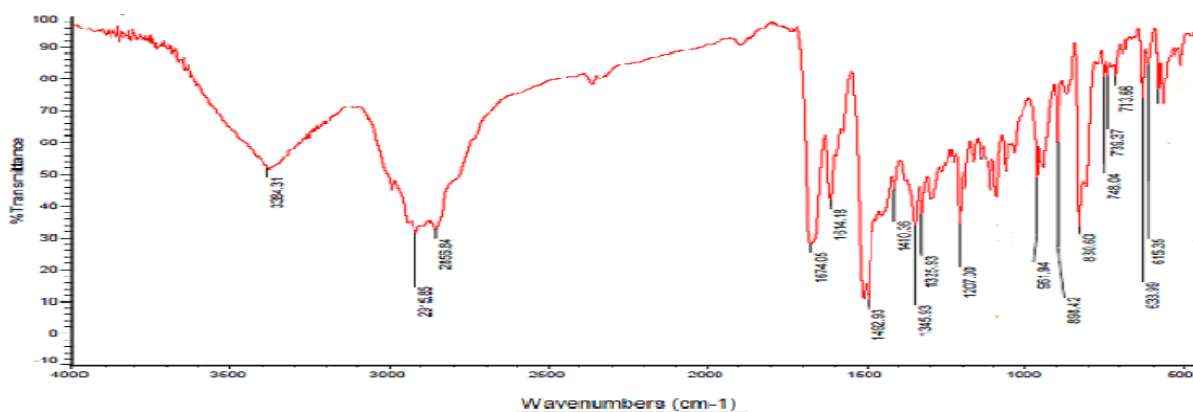


Figure 3: FT-IR spectrum of p-TEDF copolymer.

¹H-NMR Spectra

¹H-NMR Spectra of the p-TEDF copolymer resin was scanned in DMSO-d₆ solvent. The spectrum has been given in Fig. 4. The chemical shift (δ) ppm observed is assigned on the basis of data available in literature [25]. Spectrum reveals different patterns of peaks, since each of them possesses a set of protons having different proton environment. The significant singlet signal appearing at the region of 6.95 ppm is due to metaproton of Ar-H. Amino proton of -CH₂-NH-CH₂- linkage gives singlet that is

observed at 6.7 ppm. Triplet signal appeared in the region 7.171 (δ) ppm can be assigned to methyl proton of Ar-CH₃ group. proton of aromatic amine Ar-NH₂ gives singlet at 4.55 ppm. Methylenic proton of -NH-CH₂-CH₂- linkage gives triplet at 4.1 ppm. A medium singlet peak appeared at 3.66 (δ) ppm may be assigned to methyl protons of Ar-CH₂-N group and signal at 2.77 (δ) ppm may be due to methylene proton of Ar-CH₂. Intense signal appeared in the region 2.14 (δ) ppm may be due to Ar-CH₂-Ar.

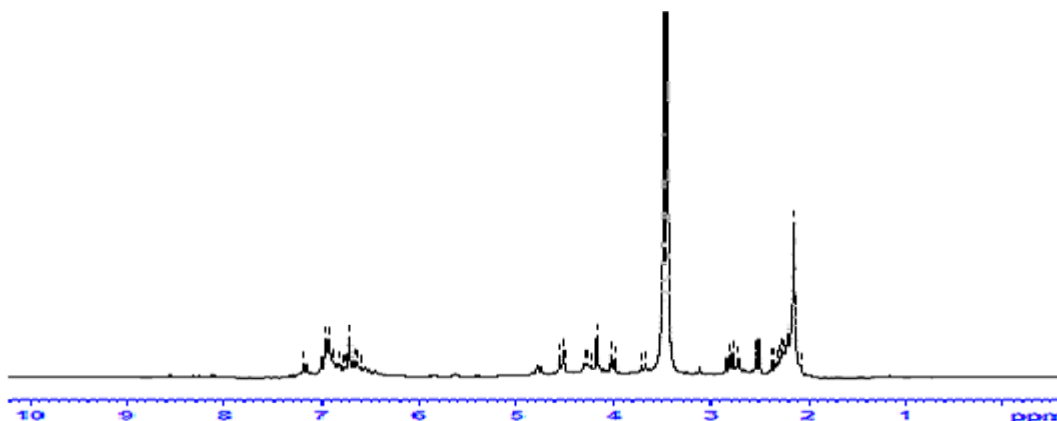


Figure 4: ¹H-NMR spectrum of p-TEDF copolymer

Scanning Electron Microscopy (SEM)

Surface analysis found great use in understanding the surface features of the materials. The SEM photographs obtained in different magnifications for the of p-TEDF copolymer resin are shown in Fig. 5. It indicates that the p-TEDF copolymer shows spherulites with deep corrugation [26]. 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 indicates that more or less the resin shows amorphous character with less close packed surface having deep pits. Thus SEM study shows that p-TEDF copolymer resin has crystalline and some amorphous characters. Thus it has the transition structure between crystalline and amorphous.

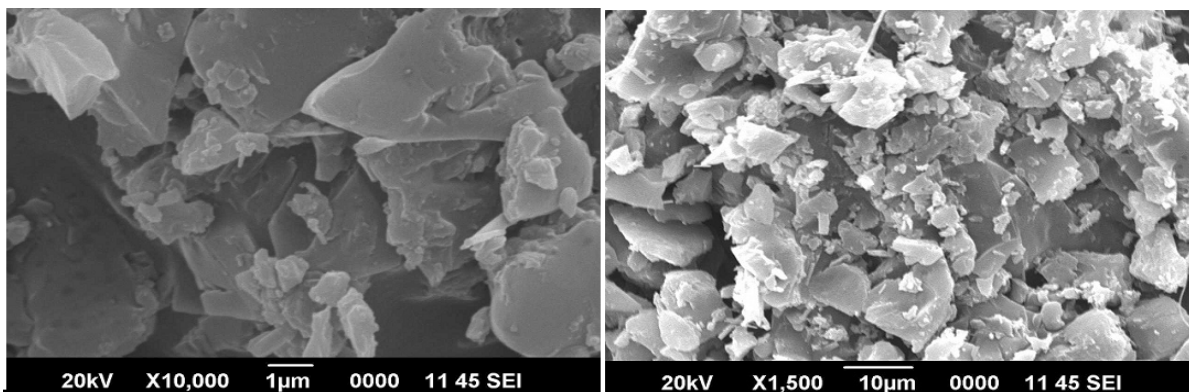


Figure 5: SEM micrograph of p-TEDF copolymer

Thermogravimetric Analysis

p-TEDF copolymer was subjected to thermogravimetric analysis and the data was used to assess the degradation pattern. Thermal

degradation behaviour of synthesized copolymer has been incorporated in Table 3. and decomposition pattern is shown in Figure 6. in temperature range from 40 to 800°C.

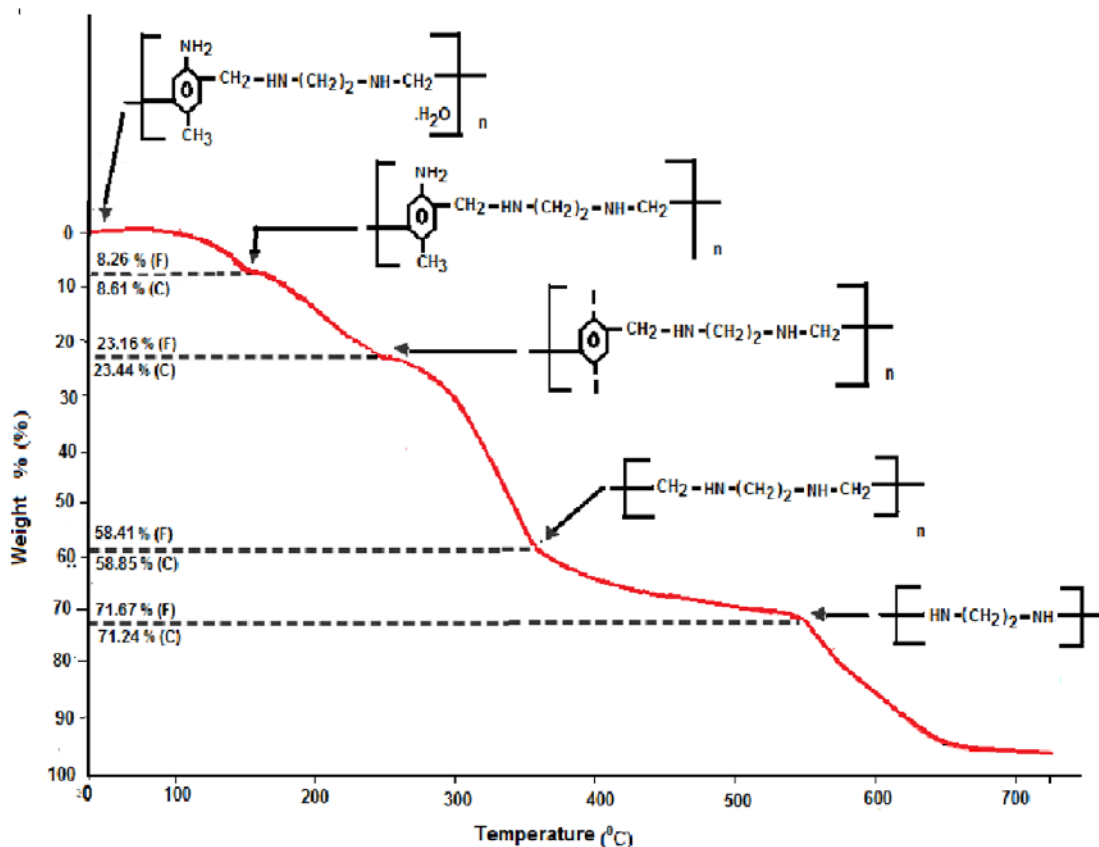


Figure 6: Decomposition pattern of p-TEDF copolymer.

Decomposition pattern of copolymer thermogram shows four decomposition steps in which the loss of water molecule (8.26% expected and 8.61% calculated) has been observed up to 150°C. first step decomposition step starts from 150 to 280°C which represents the degradation of $-\text{CH}_3$ and $-\text{NH}_2$ groups attached to aromatic nucleus (23.16% expected and 23.44% calculated). The Second decomposition step starts from 280 to 360°C, corresponding to 58.41% mass loss of aromatic nucleus against calculated 58.85%. The third decomposition step starts from 360 to 540°C which corresponds to loss of side chain of ethylene diamine. In fourth step 540-800°C complete ethylenediamine moiety (98.67% expected and 100% calculated). Consequently, no residue may be assigned after complete degradation.

Kinetics of Thermal Decomposition by the, Sharp and Wentworth, and Freeman-Carroll Methods

The observed thermal stability of p-TEDF copolymer terpolymer may be due to the stronger intermolecular hydrogen bonding present in polymer which may be attributed due to the presence of water of crystallization resulting in the resistance to higher temperature. By applying the thermogravimetric data to four thermal degradation kinetic methods, that is, the Sharp and Wentworth, and Freeman-Carroll methods, it shows four different degradation steps corresponding to loss of respective groups. The thermoanalytical data has been determined for different stages as given in Table 3. This kinetic analysis should be a starting point to obtain the useful information on the behaviour of sample.

Table 3: Kinetic Parameters of p-TEDF copolymer resin

Copolymerp-TEDF							
Activation Energy (kJ/mol)		Half Decomposition Temp.T*K	Entropy Change ΔS (J)	Free Energy Change ΔF (kJ)	Frequency factor Z (S^{-1})	Apparent Entropy Change (S^*)	Order of reaction (n)
F.C	S.W						
16.83	18.11	610	-152.467	34.60	534	-22.97	0.7

To obtain the relative thermal stability of terpolymer p-TEDF, the methods described by Sharp and Wentworth, and Freeman-Carroll were adopted. From the results, it is concluded that the values of kinetic parameters show good agreement with each other in Sharp and Wentworth and Freeman-Carroll's methods as shown in Table 3.

Fairly comparable results of kinetic parameters, namely entropy change (ΔS), energy of activation (E_a), order of reaction (n), frequency factor (z), apparent entropy (S^*) are obtained for each degradation step obtained by Sharp and Wentworth and Freeman-Carroll methods are in good agreement with each other with slight variations between the results; it is concluded that the values of kinetic parameters depend on

kinetic methods used as well as degrading species at a particular step. Total calculations obtained from different kinetic methods demonstrated that the numerical value of kinetic parameters depends on the mathematical models used to analyze the experimental data and level of degradation. By using the above mentioned techniques, variations in the results are obtained which represents versatility and great utility of thermal degradation of mathematical kinetics equations in thermogravimetry. However, it is difficult to draw any unique conclusion regarding the decomposition mechanism.

From the thermogravimetric analysis, kinetic plots of the copolymer have been shown in Figures 7,8, and 9.

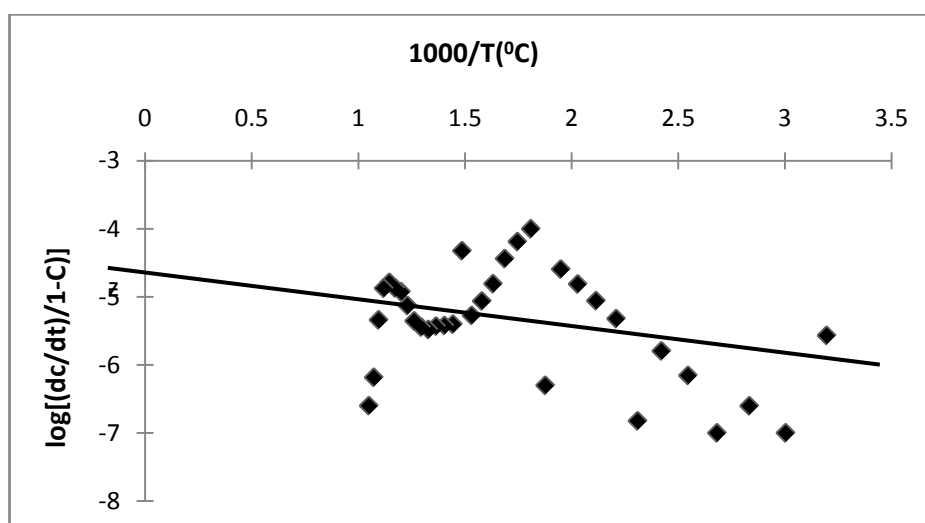


Figure 7: Sharp and Wentworth's plot of p-TEDF copolymer.

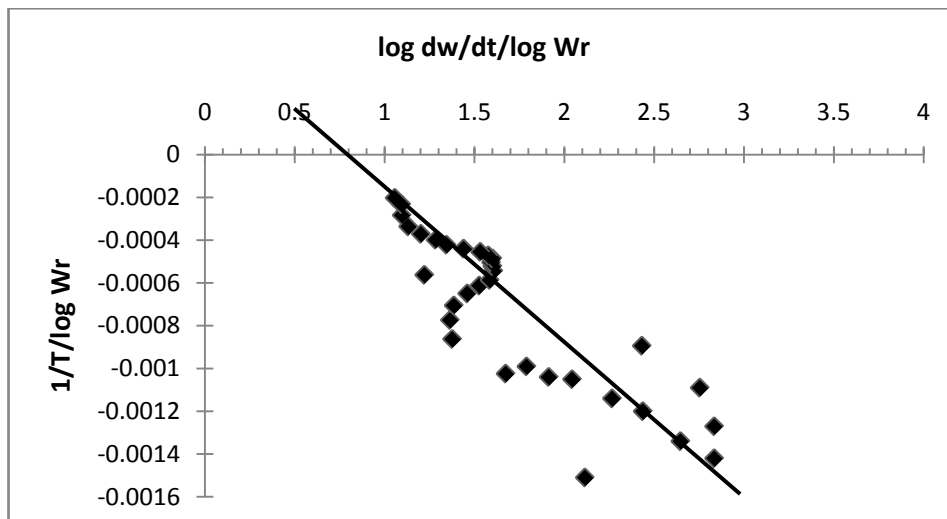


Figure 8: Freeman-Carroll's plot of p-TEDF copolymer for order of reaction.

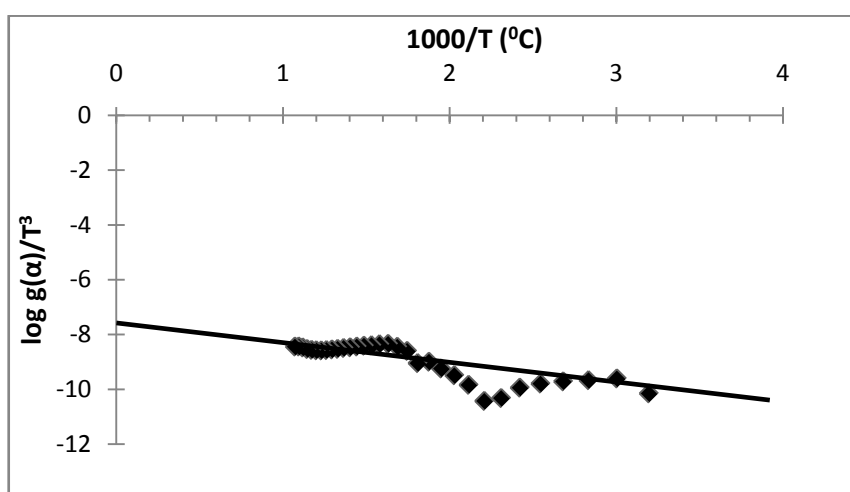


Figure 9: Freeman-Carroll's plot of p-TEDF copolymer for activation energy.

By using the above mentioned methods, slight variations are obtained in between Sharp and Wentworth and Freeman-Carroll method which are found to be in good agreement with each other. From the point of view of chemical kinetics, p-TEDF is thermally stable.

Low values of frequency factor revealed that decomposition reaction of terpolymer may be slow and no other possible reason can be given. However, in Freeman-Carroll, and Sharp and Wentworth's plots, all points did not fall on straight line, which indicates that the decomposition of terpolymer is not obeying first order of reaction perfectly [27, 28].

CONCLUSION

Synthesis of targeted copolymer (p-TEDF) has been confirmed which is supported by the results obtained by elemental analysis and spectral data. From the elemental analysis,

electronic, IR, and $^1\text{H-NMR}$ spectral studies, the proposed structure of the synthesized copolymer is confirmed. The values of kinetic parameter obtained from the Sharp and Wentworth and Freeman-Carroll methods are in good agreement with each other. Thermogram of copolymer resin shows four degradation steps and ethylenediamine molecule almost degrades completely up to 800°C . From the results obtained, the values of kinetic parameters are significantly controlled by the level of degradation and calculation methods used to analyze the experimental data. 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 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 p-toludine, ethylene diamine and formaldehyde copolymer can be classified as 'slow reaction'. The decomposition reaction was started at higher temperature, indicating a copolymer p-TEDF is thermally stable at higher temperature..

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