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Synthesis, Characterization and Non-isothermal Thermogravimetric Analysis of Cross-linked Phenol Based Copolymer Resins

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ABSTRACT

Copolymer resins (*p*-NP-TETA-F-I, II and III) have been synthesized by using three monomers namely *p*-Nitrophenol, Triethylenetetramine and Formaldehyde by condensation polymerization reaction in basic medium using varied molar proportion of reacting monomers. The copolymer resins were characterized by elemental analysis and spectroscopic methods such as UV-Visible, FT-IR and ¹H-NMR spectra which were used to confine the most probable structure of synthesized copolymers. Thermal degradation curve was examined with minute detail in order to determine their mode of decomposition. Kinetics of nonisothermal degradation was studied for each degradation step by thermogravimetric analysis (TGA). Friedman, Chang, Sharp-Wentworth and Freeman-Carroll methods have been employed in order to compute the order of reaction (*n*), thermal activation energy (*E_a*) and frequency factor (*z*).

Keywords: Condensation, Characterization, Activation energy, Friedman, Sharp-Wentworth, thermogravimetry.

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INTRODUCTION

Synthetic polymeric materials are replacing metals and other natural products in different areas with their versatile applications and as a result of this more and more new polymeric materials with exceptional physical, chemical and engineering properties are developed. A great deal of attention has been focused on phenolic copolymers are well known as matrix or binding resins for various applications. The main advantages of phenolics are their easy availability and some of their excellent properties [1]. Polymeric materials have found many applications in organic chemistry [2-4], macromolecular chemistry [5], material science [6], and as an ion-exchanger [7].

Rath et al [8] were synthesized terpolymers by condensing 2, 4-dinitrophenyl hydrazone of 4-hydroxyacetophenone with substituted benzoic acids/phenols and formaldehyde in presence of NaOH or HCl as catalyst. Tamami et al [9] have derived polyureas from 4-aryl-2, 6-bis-(4-amino-phenyl) pyridines and diisocyanates and studied its thermal stability. Salicylic acid-guanidine-formaldehyde (SGF) copolymer was characterized on the basis of elemental analysis and UV-visible, FT-IR and ¹H-NMR spectral studies. Also, Freeman-Carroll and Sharp-Wentworth methods were used to calculate the activation energy and thermal stability [10]. Jadhav et al [11] studied the thermal degradation of terpolymer resins derived from 2, 2'-dihydroxybiphenyl, urea and formaldehyde. Thermal degradation curve of salicylic acid-diaminonaphthalene-formaldehyde (SDNF) has been discussed in order to determine their mode of decomposition, order of reaction, activation energy, frequency factor, free energy change, entropy change and apparent energy change [12].

Kinetics of thermal degradation of some newly synthesized copolymers has been studied by other researchers in our laboratory [13-19]. A detailed study has been done by Pradip Paik and Kamal K. Kar [20] on kinetics of thermal degradation and estimation of lifetime for polypropylene particles and its effect on particle size, involving the use of single as well as multiple heating rate techniques.

Copolymers are either branched or non-branched macromolecules, which are synthesized by repetition of given monomers using either divergent or convergent strategies [21-24]. Well known process such as condensation polymerization has been used extensively [25, 26]. The reaction is characterized by very high yields, mild and simple reaction conditions, water tolerance, ease of product isolation and without any side reactions. Due to immense interest of our laboratory researchers in developing new copolymers [27-29], attempt has been made in exploring efficient cross linked condensation polymerization.

The present article highlights and summarizes the synthesis and characterization of phenolic cross linked copolymers (*p*-NP-TETA-F-I, II and III) by condensation terpolymerization reaction of *p*-nitrophenol and triethylenetetramine using linkage of formaldehyde. Thermal degradation behavior was studied by TGA under nonisothermal conditions. Activation energy, pre-exponential factor and order of reaction were determined using Friedman, Chang, Sharp-Wentworth and Freeman-Carroll methods. Methods for the estimation of kinetic parameters from thermogravimetric studies are

generally based on the assumption that the Arrhenius equation is valid with thermal and diffusion barriers that are negligible.

EXPERIMENTAL

Materials

All the chemicals used were of analytical grade purity. *p*-Nitrophenol, triethylenetetramine and formaldehyde (37%) were purchased from S. D. Fine Chemicals, India. Solvents like N, N-dimethylformamide, dimethyl sulphoxide, tetrahydrofuran, diethyl ether used in this study were purchased from Merck.

Synthesis

The synthesis of phenol-formaldehyde resins are based on Lederer-Manasse reaction. The hydroxymethyl derivatives of phenol formed by this reaction are linked to each other by methyl linkages with the elimination of water molecule between the methylol group of one molecule and the ortho or para hydrogen of another molecule. In presence of acid or base as a catalyst and with the excess of formaldehyde, three dimensional crosslinked polymers are formed. It is possible to insert another kind of molecule in this structure e.g. primary or secondary amine by mannich reaction so that a terpolymer can be synthesized [30].

p-NP-TETA-F-I copolymer was synthesized by condensation of *p*-nitrophenol (5.56 gm, 0.4 mol) and triethylenetetraamine (1.5 ml, 0.1 mol) with formaldehyde (18.75 ml, 0.5 mol) in presence of 2M NaOH as a catalyst. Reaction was carried out in round-bottom flask fitted with water condenser and heated at 160^o C in an oil bath for about 10 hrs of continuous heating with occasional shaking (Figure 1). The temperature of electrically heated oil bath was controlled with the help of a dimmerstat. The resinous brown colored solid product was immediately removed, filtered and repeatedly washed with cold-distilled water, dried in air and powdered with the help of an agated mortar and pestle. It was purified by dissolving in 1:1 (v/v) concentrated HCl/water with constant stirring and filtered. The resulting polymer sample was washed several times with boiling water to remove unreacted monomers and dried in a desiccator at room temperature. Further dried polymeric sample extracted with diethyl ether to remove the excess dimmers formed during the reaction. Finally the copolymer was passed through 300-mesh size sieve and kept in a vacuum over silica gel [31, 32]. Similar procedure has been applied for the synthesis of other two copolymers viz. *p*-NP-TETA-F-II and *p*-NP-TETA-F-III for the molar proportion of 8:1:9 and 12:1:13 respectively (Table1).

Analytical and physicochemical studies

Copolymers were subject to elemental analysis for carbon, hydrogen and nitrogen on Perkin Elmer 2400 Elemental Analyser. UV-visible spectra were recorded in dimethylsulphoxide on Shimadzu UV-Visible double beam spectrophotometer in the range of 200-850 nm. Infrared spectra of all copolymers were recorded in nujol mull on Perkin-Elmer-spectrum RX-I spectrophotometer in the range of 4000-500 cm⁻¹. ¹H-NMR studies were performed in dimethylsulphoxide as solvent on Bruker Advance-II 400 MHz proton

NMR spectrophotometer. All the analytical and spectral studies for newly synthesized copolymers were carried out at Sophisticated Analytical Instrumentation Facility (SAIF), Punjab University, Chandigarh.

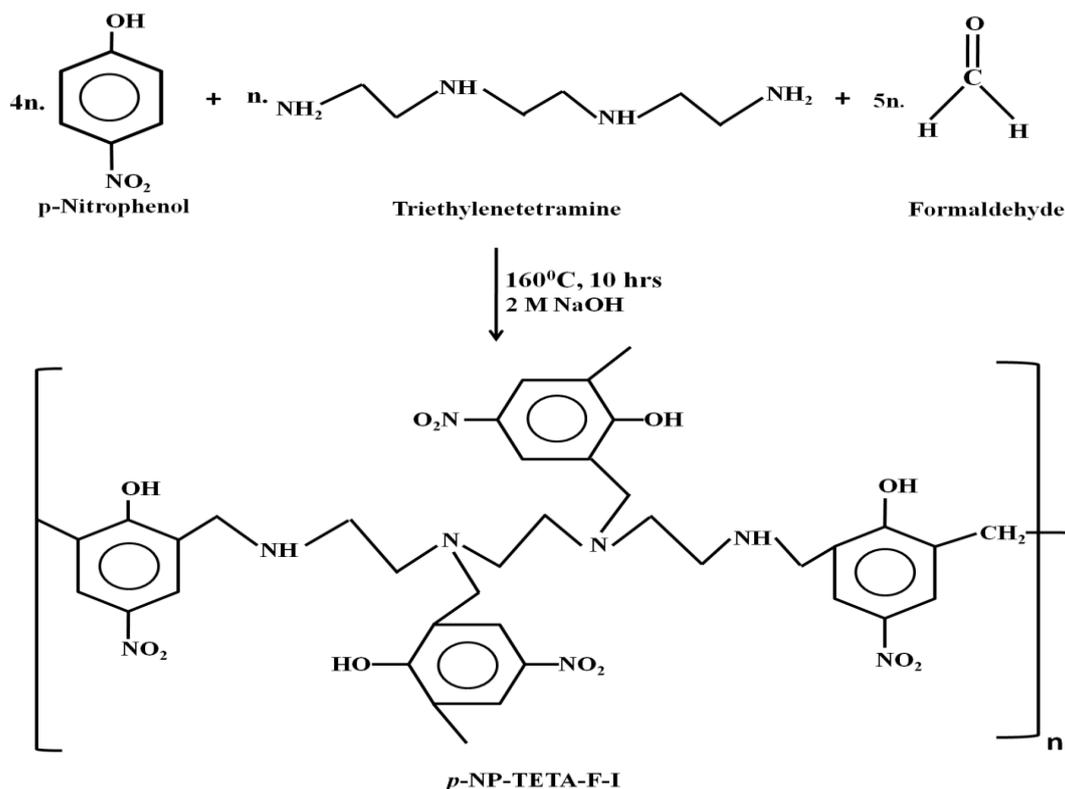


Figure 1. Chemical reaction of *p*-NP-TETA-F-I copolymer

Table I. Synthesis of PNPTETAF copolymers

Terpolymers	Reactants			Molar ratios	2M NaOH (ml)	Reflux Temp. °C
	<i>p</i> -nitrophenol (<i>p</i> -NP) (mol)	Triethylenetetramine (TETA) (mol)	Formaldehyde (F) (mol)			
<i>p</i> -NP-TETA-F-I	0.4	0.1	0.5	4:1:5	200	160 ± 2
<i>P</i> -NP-TETA-F-II	0.8	0.1	0.9	8:1:9	200	160 ± 2
<i>P</i> -NP-TETA-F-III	1.2	0.1	1.3	12:1:13	200	160 ± 2

Thermal studies

Non-isothermal thermogravimetric analysis of newly prepared copolymers has been carried out using Perkin Elmer, Pyris1 Thermogravimetric Analyzer, in air atmosphere with a heating rate 10 °C.min⁻¹ in the temperature range 50-600 °C. TGA was carried out at SICART, Gujarat.

Theoretical considerations

Thermogram expresses the dependence of change in mass on the temperature which gives information about sample composition, product formed after heating and kinetic parameters [33, 34]. Heating is performed under strictly controlled conditions and can reveal changes in structure and other important properties of the material being studied. In non-isothermal or dynamic TGA the sample is subjected to conditions increase in temperature at linear rate. Kinetic parameters have been determined using Friedman [35, 36], Chang [37], Freeman-Carroll [38] and Sharp-Wentworth [39] techniques which are given as under.

Friedman technique:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(z) + n\ln(1 - \alpha) - \frac{E_a}{RT} \quad (1)$$

Where α is the conversion at time t . R is the gas constant (8.314 J/mol/K), and T is the absolute temperature (K). From the slope of the linear plot of $\ln(1-\alpha)$ vs. $1/T$, n can be obtained. The plot of $\ln(d\alpha/dt)$ vs. $1/T$ should be linear with the slope E_a/R , from which E_a can be obtained.

Chang technique:

$$\ln\left(\frac{\frac{d\alpha}{dt}}{(1-\alpha)^n}\right) = \ln(z) - \frac{E_a}{RT} \quad (2)$$

A plot of $[\ln(d\alpha/dt)/(1-\alpha)^n]$ vs. $1/T$ will yield a straight line if the order of decomposition reaction, n is selected correctly. The slope and intercept of this line will provide the $(-E_a/R)$ and $\ln(z)$ values, respectively.

Freeman and Carroll technique:

$$\frac{\Delta \log(dw/dt)}{\Delta \log Wr} = \left(-\frac{E_a}{2.303 R}\right) \cdot \frac{\Delta\left(\frac{1}{T}\right)}{\Delta \log Wr} + n \quad (3)$$

Where

dw/dt = rate of change of weight with time; $Wr = Wc - W$; Wc = Weight loss at the completion of reaction; W = Total weight loss upto time t ; E_a = Energy of activation; n = order of reaction.

The $\Delta \log(dw/dt)$ and $\Delta \log Wr$ values are taken at regular intervals of $1/T$. In this case

$\frac{\Delta \log(dw/dt)}{\Delta \log Wr}$ vs $\frac{\Delta\left(\frac{1}{T}\right)}{\Delta \log Wr}$ gives a straight line. The slope and intercept are equal to $-(E_a/R)$ and n , respectively.

Sharp-Wentworth technique:

$$\log \frac{dc/dt}{1-c} = \log \left(\frac{A}{\beta} \right) - \frac{Ea}{2.303R} \cdot \frac{1}{T} \quad (4)$$

Where,

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

β is linear heating rate, dT/dt ; c is the fraction of polymer decomposed at time t .

Thus, a linear plot of $\log \frac{dc/dt}{1-c}$ versus $\frac{1}{T}$ is obtained whose slope gives the value of Ea and A may be evaluated from the intercept.

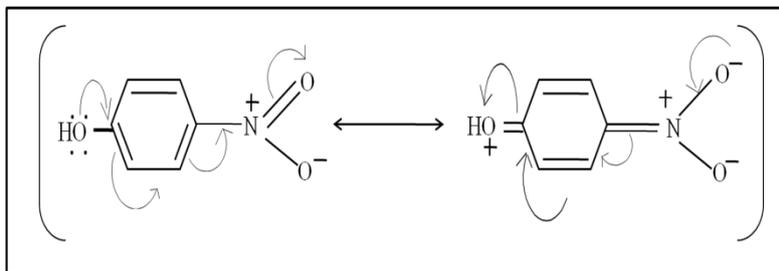
RESULT AND DISCUSSION

Characterization

p-NP-TETA-F-I: 78%

UV-Visible (in DMSO- d_6 in the range 200-850nm):

The UV-Visible spectra of all *p*-NP-TETA-F copolymer samples were recorded in the region 200-850 nm. The spectra displayed two characteristic absorption broad bands at 220nm and 330nm. The former less intense band observed at 220nm attributed to $n \rightarrow \pi^*$ may be due to chromophoric $-\text{NO}_2$ and auxochromic $-\text{OH}$ group and latter more intense band observed at 330nm accounted for $\pi \rightarrow \pi^*$ transition [40, 41] may be due to chromophoric $-\text{NO}_2$ group. The auxochromic substituents interacting with π electron of the benzene ring. This interaction stabilizes π^* state and thus lowers the energy. As a result a bathochromic shift is caused. The auxochromic influence is more pronounced when an electron donating and electron attracting groups are para position to each other. This is called complementary substitution. So a strong bathochromic shift is observed due to charge transfer absorption related to the contribution of following polar resonance structures.



The spectra shows that there is bathochromic effect (increase λ_{\max}) and hyperchromic effect (increase ϵ_{\max}) in the following sequence *p*-NP-TETA-F-I < *p*-NP-TETA-F-II < *p*-NP-TETA-F-III. This sequence is due to introduction of more and more aromatic rings which increases the conjugation length and auxochromic and chromophoric groups in the repeated unit of copolymer resin. This observation is in good agreement with the proposed structure of copolymer resins (Figure 2).

FT-IR: 3393.1 cm^{-1} (phenolic -OH str, b) [42, 43], 3063.7 cm^{-1} (>NH Str, st) [43], 2827.7 cm^{-1} (methylene-CH- str, st), 1662.2 cm^{-1} (>C=C< str in aromatics, m), 1590.8 cm^{-1} (Substituted aromatic ring C-C str, st), 1485.8 cm^{-1} (Asymm. N=O str, b), 1334.9 cm^{-1} (Symm. N=O str, b) [43], 1153.0 cm^{-1} (C-N str. in aliphatic amine, b), 1089.7 cm^{-1} (C-O str. in phenol, m); 837.8 cm^{-1} (tetrasubstituted benzene ring, m) (Figure 3).

$^1\text{H NMR}$ (400 MHz, DMSO- d_6): δ 8.1(s, 1H, -OH) [44, 45]; δ 7.7 (s, 2H, tetrasubstituted, Ar-H); δ 6.7-6.8 (s, 1H, $\text{CH}_2\text{-NH-CH}_2$); δ 4.6 (t, 2H, $\text{CH}_2\text{-CH}_2\text{-N}$) [44]; δ 3.8-3.9 (t, 2H, -NH- CH_2 - CH_2); δ 3.25 (s, 2H, -Ar- $\text{CH}_2\text{-N}$); δ 2.5 (s, 2H, -Ar- $\text{CH}_2\text{-NH}$) (Figure 4).

Elemental Analysis: Monomer empirical formula :($\text{C}_{35}\text{H}_{36}\text{N}_8\text{O}_{12}$);
Empirical formula weight: (760).

p-NP-TETA-F-II: 81%

UV-Visible (in DMSO- d_6 in the range 200-850nm):

The spectra of copolymer-II exhibit two absorption maxima in the region 220 and 330 nm (Figure 2).

FT-IR: 3383.7 cm^{-1} (phenolic -OH str, b), 3077.1 cm^{-1} (>NH Str, st), 2920.7 cm^{-1} (methylene -CH- str, m), 1656.8 cm^{-1} (>C=C< str in aromatics, m), 1591.4 cm^{-1} (Substituted aromatic ring C-C str, st), 1487.3 cm^{-1} (Asymm. N=O str, b), 1335.3 cm^{-1} (Symm. N=O str, b), 1153.5 cm^{-1} (C-N str. in aliphatic amine, b), 1095.8 cm^{-1} (C-O str. in phenol, m); 836.2 cm^{-1} (tetrasubstituted benzene ring, m) (Figure 3).

$^1\text{H NMR}$ (400 MHz, DMSO- d_6): δ 8.0 (s, 1H, -OH); δ 7.6 (s, 2H, tetrasubstituted, Ar-H); δ 6.7-6.8 (s, 1H, $\text{CH}_2\text{-NH-CH}_2$); δ 4.6-4.64 (t, 2H, $\text{CH}_2\text{-CH}_2\text{-N}$); δ 3.8-3.9 (t, 2H, -NH- CH_2 - CH_2); δ 3.25 (s, 2H, -Ar- $\text{CH}_2\text{-N}$); δ 2.5 (s, 2H, -Ar- $\text{CH}_2\text{-NH}$); δ 3.1 (s, 2H, -Ar- $\text{CH}_2\text{-Ar}$) (Figure 4).

Elemental Analysis: Monomer empirical formula :($\text{C}_{63}\text{H}_{56}\text{N}_{12}\text{O}_{24}$);
Empirical formula weight: (1364).

p-NP-TETA-F-III: 85%

UV-Visible (in DMSO- d_6 in the range 200-850nm):

The spectra of copolymer-III exhibit two absorption maxima in the region 220 and 330 nm (Figure 2).

FT-IR: 3397.9 cm^{-1} (phenolic -OH str, b), 3078.8 cm^{-1} (>NH Str, st), 2919.8 cm^{-1} (methylene -CH- str, m), 1655.6 cm^{-1} (>C=C< str in aromatics, m), 1590.9 cm^{-1} (Substituted aromatic ring C-C str, st), 1486.8 cm^{-1} (Asymm. N=O str, b), 1335.6 cm^{-1} (Symm. N=O str, b), 1154.6 cm^{-1} (C-N str. in aliphatic amine, b), 1095.9 cm^{-1} (C-O str. in phenol, m); 836.8 cm^{-1} (tetrasubstituted benzene ring, m) (Figure 3).

^1H NMR (400 MHz, DMSO- d_6): δ 8.0 (s, 1H, -OH); δ 7.7 (s, 2H, tetrasubstituted, Ar-H); δ 6.7-6.8 (s, 1H, $\text{CH}_2\text{-NH-CH}_2$) ; δ 4.6-4.7 (t, 2H, $\text{CH}_2\text{-CH}_2\text{-N}$); δ 3.8-4.1 (t, 2H, -NH- $\text{CH}_2\text{-CH}_2$ -); δ 3.24 (s, 2H, -Ar- $\text{CH}_2\text{-N}$); δ 2.4 (s, 2H, -Ar- $\text{CH}_2\text{-NH}$ -) δ 3.1 (s, 2H, -Ar- $\text{CH}_2\text{-Ar}$ -) (Figure 4).

Elemental Analysis: Monomer empirical formula :($\text{C}_{91}\text{H}_{76}\text{N}_{16}\text{O}_{36}$);

Empirical formula weight: (1968).

Above spectral data shows the formation of targeted copolymers i.e. *p*-NP-TETA-F-I, *p*-NP-TETA-F-II, *p*-NP-TETA-F-III which has been shown in the Figure 5.

Thermogravimetric analysis

Thermogravimetry of *p*-NP-TETA-F-I

Thermogravimetric analysis of *p*-NP-TETA-F-I has been carried out at $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and the decomposition pattern of a representative polymer has been shown in Figure 6. Thermogram of this copolymer depicted four step decomposition patterns in the temperature range $50\text{-}600\text{ }^\circ\text{C}$. First step is slow decomposition between $50\text{ to }130\text{ }^\circ\text{C}$ corresponds to 2.28% loss which may be attributed to loss of water molecule against calculated 2.31% present per repeat unit of the polymer. The second step of decomposition starts from $130\text{-}190\text{ }^\circ\text{C}$ which represents degradation of four (-OH) functional groups attached to the benzene skeleton (10.94% found and 11.05% calculated). Third step decomposition starts from $190\text{-}450\text{ }^\circ\text{C}$ corresponding to 34.64% loss of four (-NO₂) functional groups against calculated 34.70%. Fourth decomposition step starts from $450\text{-}600\text{ }^\circ\text{C}$ which shows the decomposition of two benzene skeleton with (-CH₂) group (57.75% found and 57.84% calculated) and consequently residue remained having the values (42.25% found and 42.16% calculated).

Thermogravimetry of *p*-NP-TETA-F-II

Thermogram of copolymer resin-II depicts four step decomposition in the temperature range $50\text{-}600\text{ }^\circ\text{C}$. First step is slow decomposition between $50\text{ to }120\text{ }^\circ\text{C}$ corresponds to 2.50 % loss which may be attributed to loss of two water molecules against calculated 2.57 % present per repeat unit of the polymer. The second step decomposition starts from $120\text{-}200\text{ }^\circ\text{C}$ which represents degradation of eight (-OH) functional groups attached to the benzene skeleton (12.19% found and 12.28 % calculated). Third step of decomposition starts from $200\text{-}480\text{ }^\circ\text{C}$ corresponding to 38.48% loss of eight (-NO₂) groups against calculated 38.57%. Fourth degradation step between $480\text{-}600\text{ }^\circ\text{C}$ represents the decomposition of two benzene skeleton with (-CH₂) group (51.31 % found and 51.42 % calculated) consequently residue remained may have the values (48.69% found and 48.58% calculated).

Thermogravimetry of *p*-NP-TETA-F-III

Thermogram of copolymer resin-III depicts four stepped decomposition reaction in the temperature range $50\text{-}600\text{ }^\circ\text{C}$. First step is slow decomposition between $50\text{-}125\text{ }^\circ\text{C}$ corresponds to 1.84 % loss which may be attributed to loss of two water molecules against calculated 1.79 % present per repeat unit of the polymer. The second step of decomposition

starts from 125-210 °C which represents degradation of twelve (-OH) functional groups attached to the benzene skeleton (12.09% found and 11.97% calculated). Third decomposition step starts from 210-520 °C corresponding to 39.62 % loss of twelve (-NO₂) functional groups against calculated 39.52 %. The fourth decomposition step starts from 520-600 °C corresponds to 48.61 % loss of two aromatic rings with (-CH₂-) group against calculated 48.50 %. Consequently residue remained may have the values (51.39 % found and 51.50 % calculated).

Kinetics of thermal decomposition by Friedman, Chang, Freeman-Carroll and Sharp-Wentworth techniques

By applying the thermogravimetric data to four thermal degradation kinetic techniques (viz. Friedman, Chang, Freeman-Carroll and Sharp-Wentworth), it shows four different degradation steps corresponding to loss of respective groups. The decomposition is due to breakdown of cross linked structure of copolymer due to which it takes much more time to attain the thermal equilibrium as well as degradation process occurs slowly.

The sequence of thermal stabilities was found to be *p*-NP-TETA-F-III > *p*-NP-TETA-F-II > *p*-NP-TETA-F-I. The sequence of thermal stabilities of polymers is predicted on the basis of initial decomposition temperature is in harmony with that predicted from activation energy values. From the above order it can be concluded that the higher thermal stability of *p*-NP-TETA-F-III may be due to the stronger intermolecular hydrogen bonding present in polymer structure because of water of crystallization which would be more difficult to break and hence more resistant to higher temperature [45] or it may be due to possibility of cross linked structure of copolymer which gives stability to polymer [46]. In general the water of hydration may be considered as crystal water. In case of all the three copolymers, the removal of water molecules is complete and is probably crystal water or moisture entrapped in the molecule.

Kinetic parameters for *p*-NP-TETA-F-I copolymer have been calculated using Friedman method (1) for each decomposition step. Activation energy (E_a) has been obtained from the plot between ln(dα/dt) vs. (1/T) (Figure 7) and order of reaction (n) from the plot between ln(1-α) vs (1/T) (Figure 8). Values of ln(z) are calculated at each temperature region from (1) with the help of E_a and n. The results from Friedman are shown in Table 2. The kinetic parameters show that E_a, n and ln(z) are different for different thermal decomposition reactions as the thermogram is divided into four different zones.

Figure 9 has shown Chang method (2) gives plots between [ln(dα/dt)/(1-α)ⁿ] vs. (1/T) for *p*-NP-TETA-F-I at the heating rate 10 °C.min⁻¹ which is used to calculate E_a and ln(z) of respective degradation reaction for best fitted value of n (from Friedman equation), which corresponds to correct reaction order for each respective thermal decomposition step. Varied values of activation energy and frequency factor are observed at each degradation step which indicates degradation of respective group.

Using the Freeman-Carroll technique (3) kinetic parameters has been calculated. Figure 10 has shown representative plot of $\frac{\Delta \ln(\frac{d\alpha}{dt})}{\Delta \ln(1-\alpha)}$ vs $\frac{\Delta(\frac{1}{T})}{\Delta \ln(1-\alpha)}$ for *p*-NP-TETA-F-I. The slope and intercept for each step are computed from (4), which is equal to (E_a/R) and n respectively.

Also, kinetic parameters for different thermal degradation zones have been calculated by Sharp-Wentworth method (4). E_a and $\ln(z)$ values are calculated from the plot between $\log \frac{dc/dt}{1-c}$ vs. $\frac{1}{T}$ with best fitted values of n for each respective degradation reaction (Figure 11). A plot of percentage mass loss vs temperature is shown in Figure 6 for a representative *p*-NP-TETA-F-I copolymer. From the TG curve, the thermoanalytical data and decomposition pattern has been determined for different stages as given in Table 2. Calculation of kinetic parameters by Friedman and Chang method leads to numerical results of the same magnitude may be due to analogy in the mathematical model. Also results obtained by Sharp-Wentworth and Freeman-Carroll method are in similar order with slight variations. But, results obtained for kinetic parameters by using Friedman, Chang, Sharp-Wentworth and Freeman-Carroll method for each respective degradation step of all the three copolymers are not in similar order as the degrading species at each particular step is same but the number of degrading species are different.

From the above discussion, it is therefore concluded that, for each technique the activation energy, order of reaction and frequency factor values depend on calculation technique used as well as degrading species at a particular stage. Low values of frequency factor revealed that decomposition reaction of copolymers can be classed as slow reaction and no other possible reason can be given [47]. Total calculations obtained from different kinetic methods demonstrated that the numerical value of kinetic parameters depends on the mathematical model used to analyze the experimental data as well as level of degradation at particular step [20].

Positive values of activation energy under the present investigation correspond to the energy of activation due to oxidation–reduction process of terpolymer in the higher temperature range [50]. In the mechanism of phenol-formaldehyde copolymer, the phenoxy radical is an important reaction intermediate in the high temperature oxidation of aromatic hydrocarbons; $C_6H_5O \rightarrow C_5H_5^- + CO$ is the dominant route by which the loss of aromaticity occurs in these systems. In the present investigation, partial loss of aromaticity occurs in the degradation process because at 600 °C remaining moiety with benzene skeleton possesses aromatic characters. Due to complex phenomena of polymer degradation process in nonisothermal thermogravimetry, the computed kinetic parameters are in fact only parameters of given mathematical equation which has the form of kinetic rate equation and which is used to fit the weight loss curves accompanying the thermal degradation of polymers in non-isothermal conditions. As a consequence these kinetic parameters are fictive from the point of view of chemical kinetics.

Thus, results obtained by using above mentioned kinetic techniques represent the versatility and great utility of thermal degradation kinetic equations in thermogravimetry and attempts are developing to implement the model free kinetic equations.

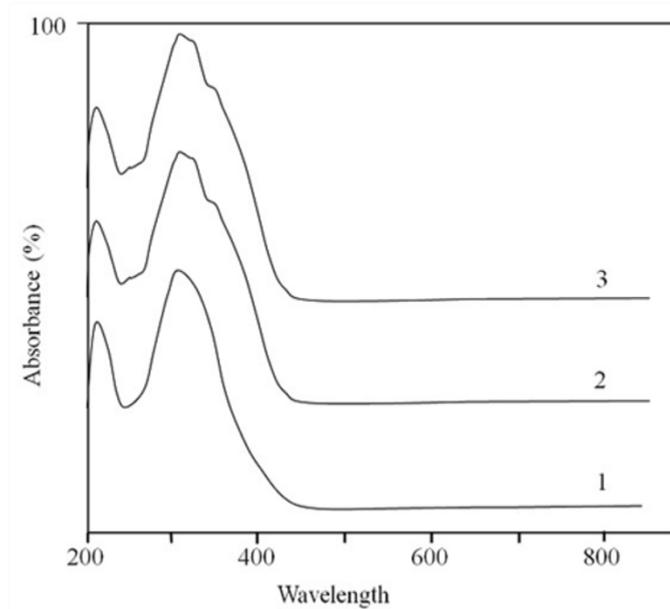


Figure 2. UV-visible spectra of (1) *p*-NP-TETA-F-I (2) *p*-NP-TETA-F-II (3) *p*-NP-TETA-F-III

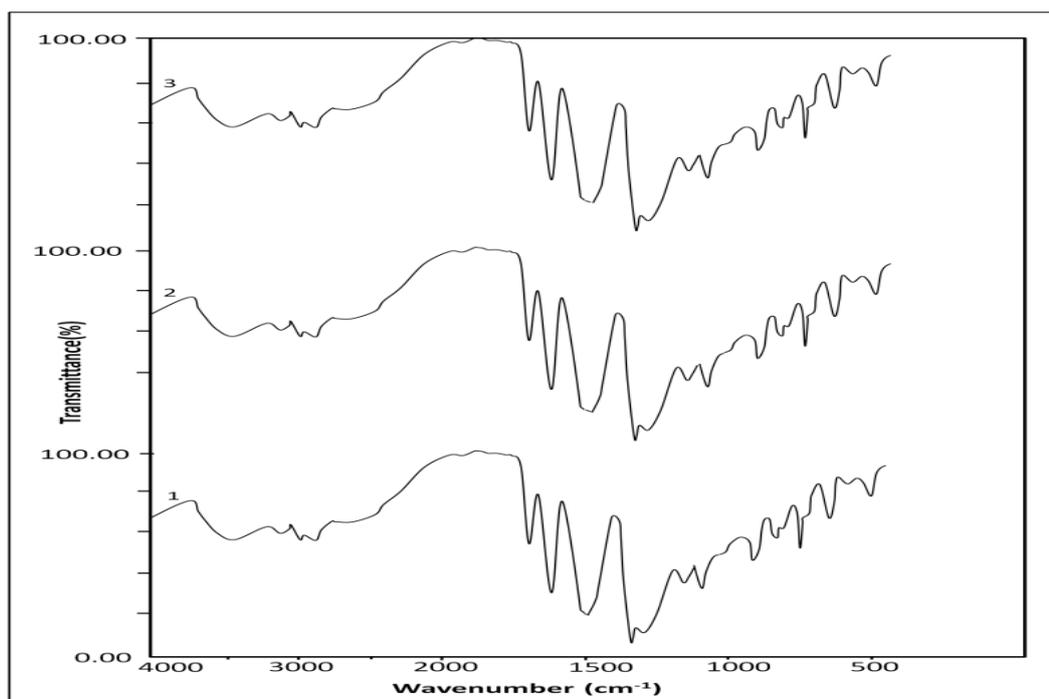


Figure 3. FT-IR spectra of (1) *p*-NP-TETA-F-I (2) *p*-NP-TETA-F-II (3) *p*-NP-TETA-F-III

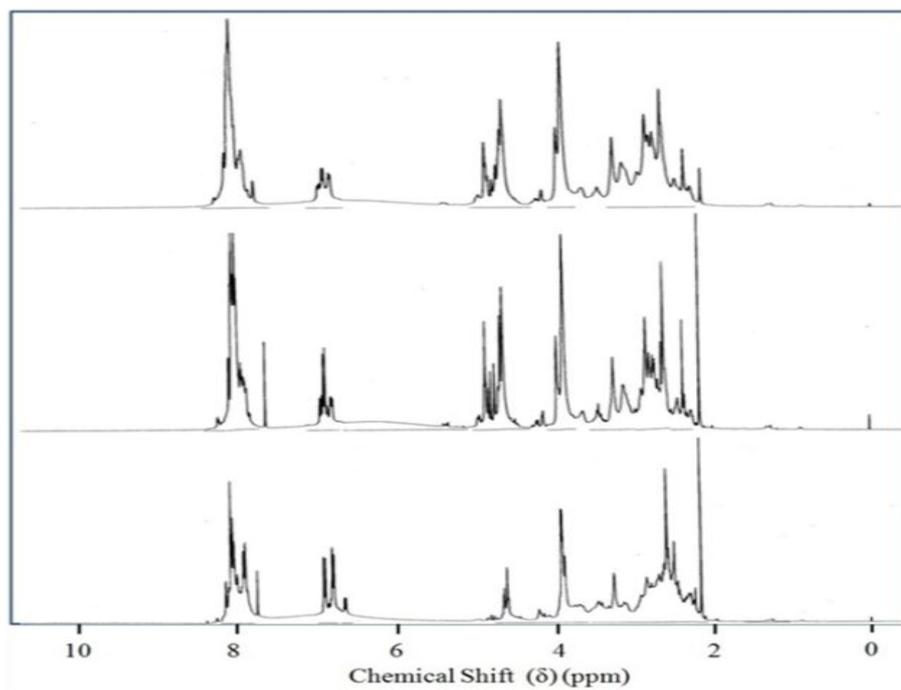


Figure 4. ^1H -NMR spectra of (1) *p*-NP-TETA-F-I (2) *p*-NP-TETA-F-II (3) *p*-NP-TETA-F-III

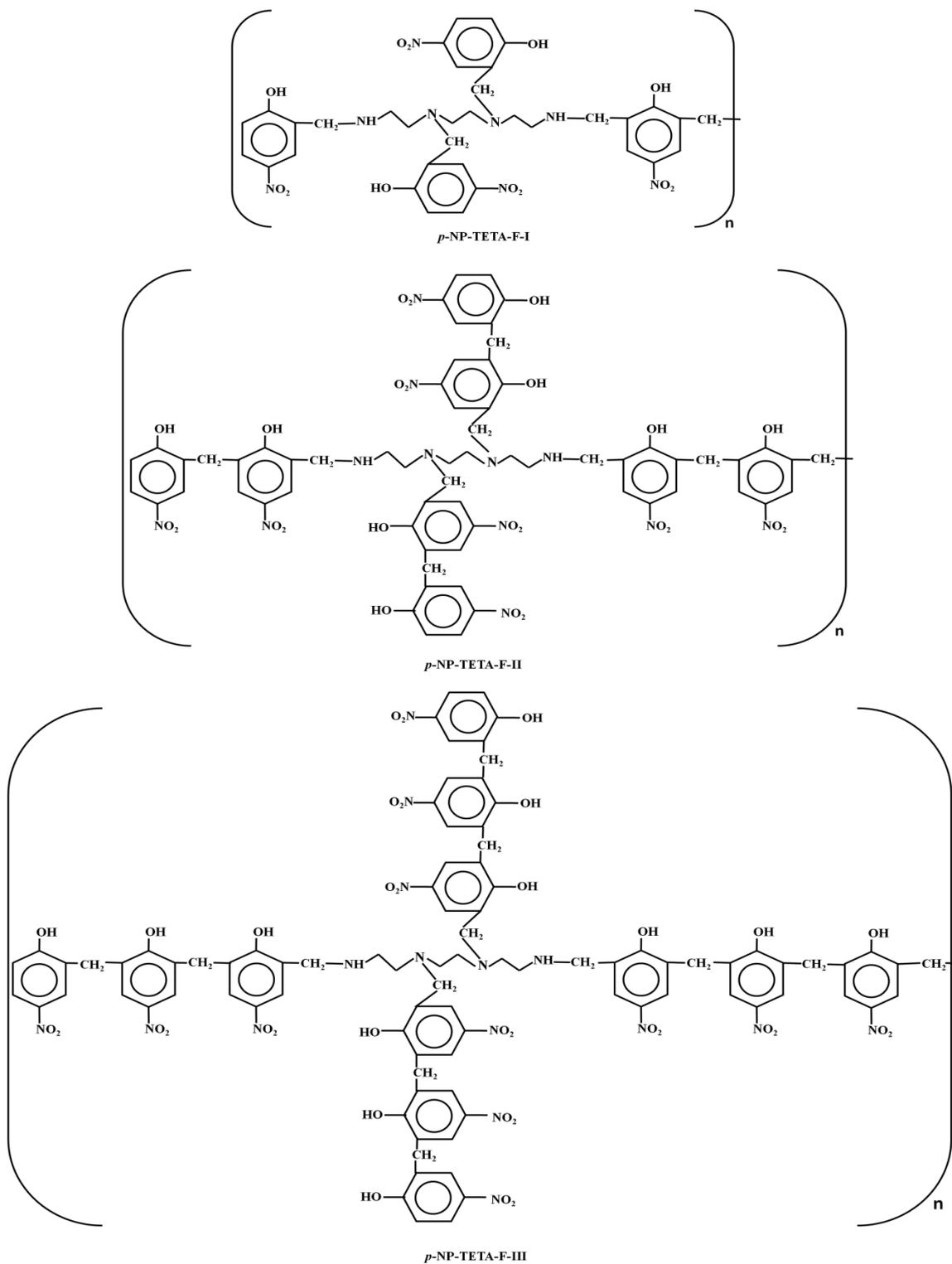


Figure 5. Suggested structures of copolymers

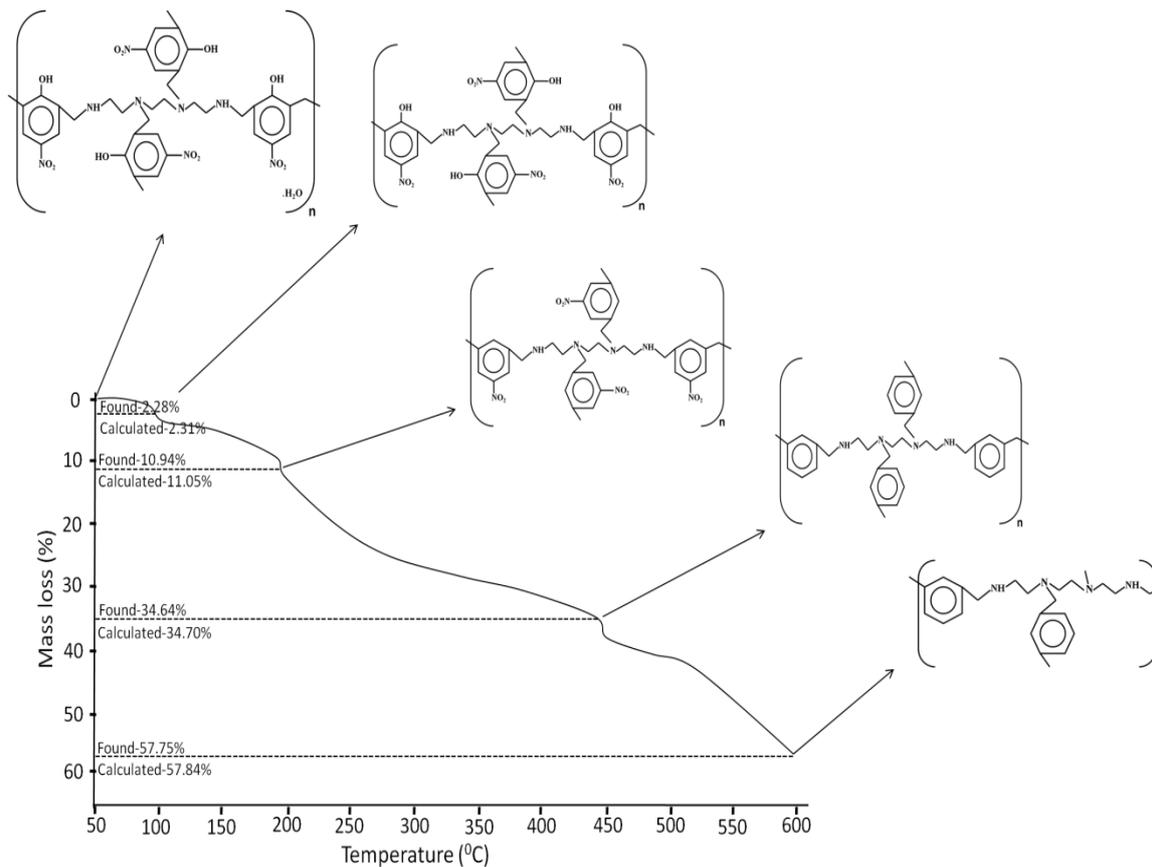


Figure 6. Decomposition pattern of *p*-NP-TETA-F-I copolymer

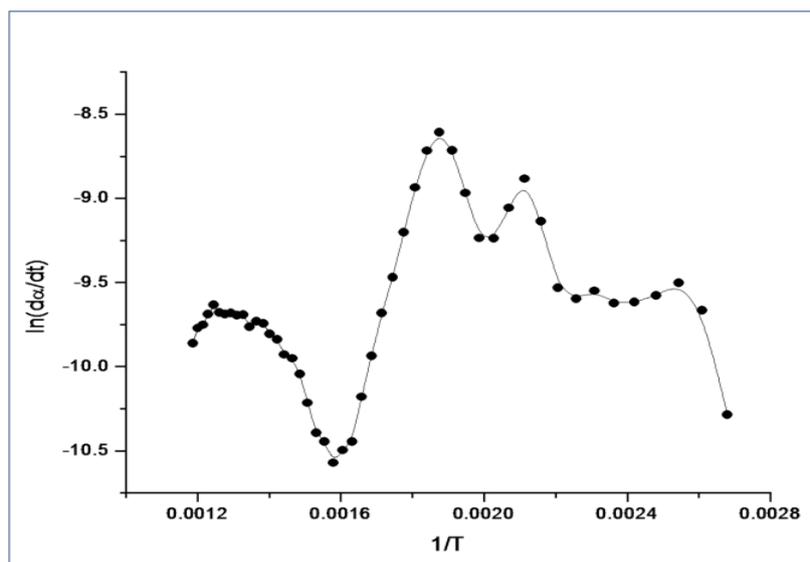


Figure 7. Friedman plot of *p*-NP-TETA-F-I copolymer for activation energy

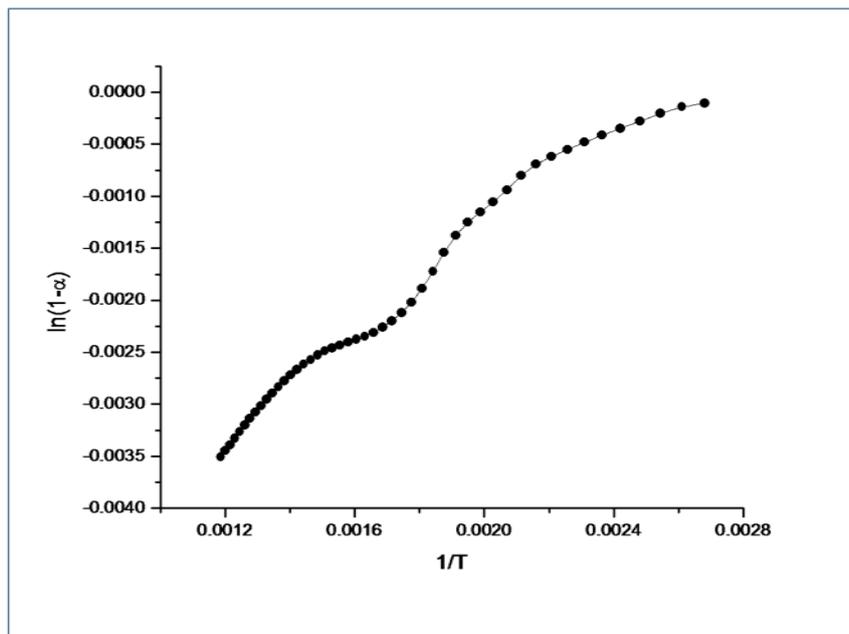


Figure 8. Friedman plot of *p*-NP-TETA-F-I copolymer for the order of reaction

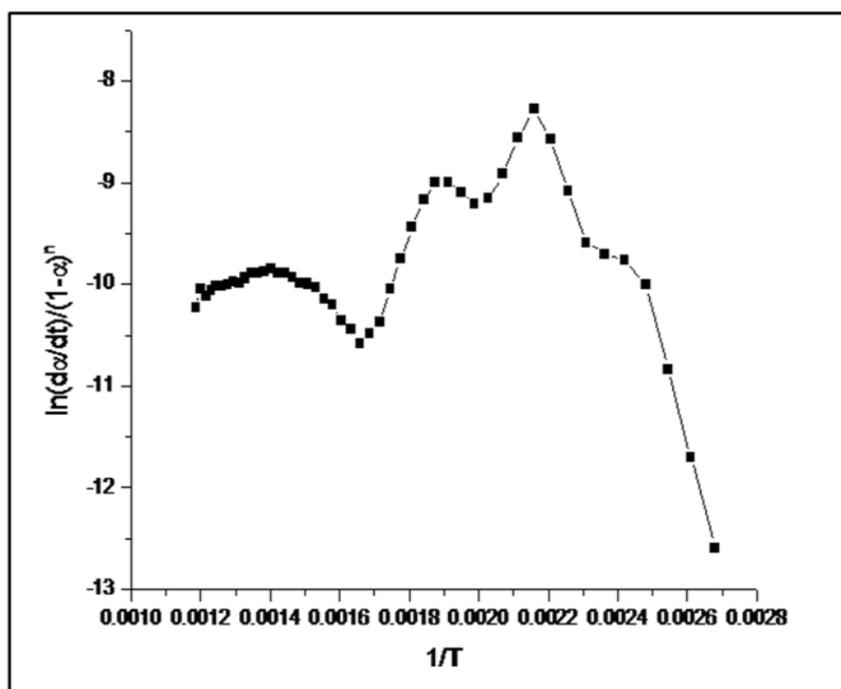


Figure 9. Chang plot of *p*-NP-TETA-F-I copolymer

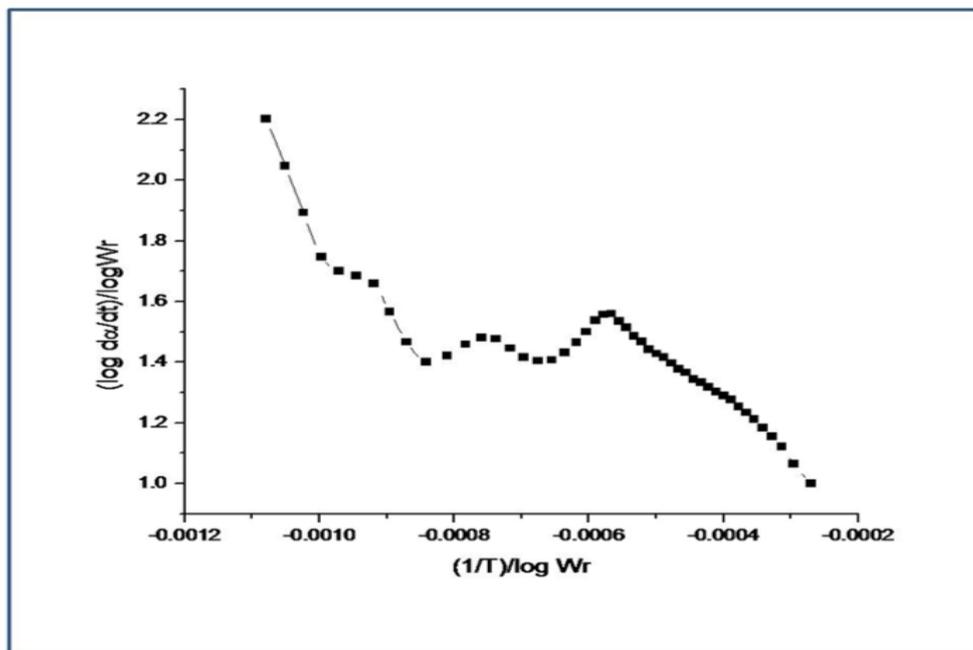


Figure 10. Freeman-Carroll plot of *p*-NP-TETA-F-I copolymer

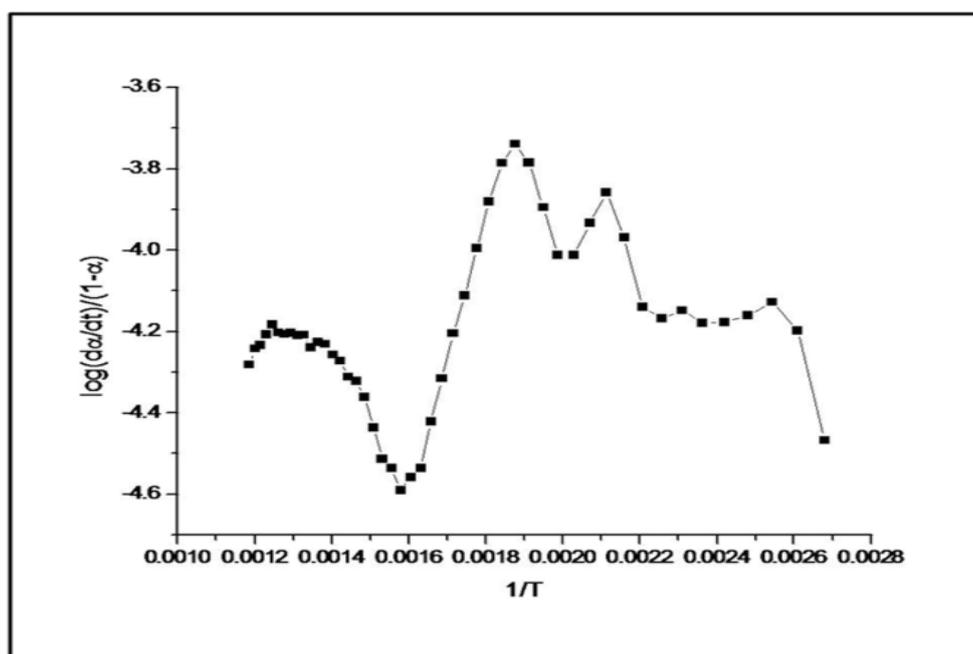


Figure 11. Sharp-Wentworth plot of *p*-NP-TETA-F-I copolymer



Table II. Thermoanalytical data and thermal degradation behavior of *p*-NPTETAF-I, II and III copolymers

Decomposition steps	Copolymers	Temp. Range (°C)	Wt. Loss (%)		Species Degraded	Friedman			Chang			Sharp-Wentworth			Freeman-Caroll		
			Found	Calc.		Ea	n	ln(z)	Ea	n	ln(z)	Ea	n	ln(z)	Ea	n	log z
1.	<i>p</i> -NP-TETA-F-I	50-130	2.15	2.19	One H ₂ O molecule	66.64	0.8	0.7	78.05	0.8	22.12	81.27	0.8	6.7	106	3.7	4.12
	<i>p</i> -NP-TETA-F-II	50-120	2.46	2.49	Two H ₂ O molecules	103.46	0.6	4.1	103.40	0.6	4.16	48.45	0.5	7.71	43.85	0.6	3.10
	<i>p</i> -NP-TETA-F-III	50-125	2.73	2.61	Three H ₂ O molecules	110.29	0.6	5.0	110.23	0.6	5.05	44.89	0.6	5.80	46.31	0.7	2.74
2.	<i>p</i> -NP-TETA-F-I	130-190	10.05	10.48	Four -OH groups	26.86	1.3	6.3	117.57	1.3	4.8	58.65	1.3	3.14	48.11	0.7	3.27
	<i>p</i> -NP-TETA-F-II	120-200	11.74	11.92	Eight -OH groups	38.58	1.4	4.7	38.25	1.4	4.81	19.17	1.4	0.84	19.51	0.6	3.59
	<i>p</i> -NP-TETA-F-III	125-210	11.51	11.73	Twelve -OH groups	32.07	1.2	10.20	31.81	1.2	5.7	34.95	1.2	0.16	17.39	0.8	1.68
3.	<i>p</i> -NP-TETA-F-I	190-450	32.74	32.92	Four -NO ₂ groups	37.28	2.6	12.93	33.60	2.6	12.70	7.40	2.6	5.37	3.924	1.3	1.00
	<i>p</i> -NP-TETA-F-II	200-480	37.05	37.44	Eight -NO ₂ groups	28.80	2.5	12.14	30.10	2.5	12.31	13.55	2.5	4.97	6.01	1.2	0.99
	<i>p</i> -NP-TETA-F-III	210-520	38.89	38.70	Twelve -NO ₂ groups	22.32	2.1	8.72	23.25	2.1	11.81	10.48	2.1	4.82	10.36	1.1	1.66
4.	<i>p</i> -NP-TETA-F-I	450-600	42.22	44.02	Two aromatic rings along with (-CH ₂ -)	9.71	3.8	10.35	29.27	3.8	11.99	46.07	3.8	7.52	41.16	0.4	3.12
	<i>p</i> -NP-TETA-F-II	480-600	42.68	43.75		28.87	4.1	11.56	32.46	4.1	11.92	28.31	4.1	15.14	44.91	0.3	2.97
	<i>p</i> -NP-TETA-F-III	520-600	42.61	43.15		20.33	3.4	6.9	56.14	3.4	14.65	50.55	3.4	5.70	50.14	0.2	3.17

Units of Ea and ln(z) are kJ/mole and min⁻¹ respectively.



CONCLUSION

Synthesis of targeted copolymers (*p*-NP-TETA-F-I, II and III) has been confirmed which is supported by the results obtained by the spectral analysis. The -CH₂- group as the linkage between phenol and amine shows the formation of condensation product. Thermogram obtained has shown four degradation stages indicating degradation of water molecule, four (-OH) and four (-NO₂) functional groups, two benzene rings along with their respective (-CH₂) groups. Results obtained from Friedman and Chang as well as Freeman-Carroll and Sharp-Wentworth methods show nearly similar values of kinetic parameters whereas comparison between Friedman-Chang and Sharp Wentworth-Freeman Carroll shows different observations. This indicates that the values of kinetic parameters are significantly controlled by level of degradation and calculation technique used to analyze the experimental data.

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