# Synthesis, characterization and behavior of thermal degradation kinetics of copolymer-III derived from p-nitrophenol, 4,4'-methylene dianiline and formaldehyde

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Abstract : Copolymer resin (p-NP-4,4'-MDA-F-III) has been synthesized by using the monomers i.e. p-nitrophenol and 4,4'-methylene dianiline using the linkage of formaldehyde in 4 : 1 : 5 molar proportion by condensation polymerization reaction in presence of acid catalyst. The structure of newly synthesized copolymer has been elaborated and confirmed on the basis of elemental analysis and various spectral techniques i.e. UV-Visible, FT-IR and $^1$H NMR spectroscopy. Thermal analysis was carried out for studying the thermal degradation behavior and kinetics of synthesized copolymer which shows three decomposition steps. Thermal degradation curve has been discussed with minute details for each decomposition step by applying Friedman, Chang, Sharp-Wentworth, Freeman-Carroll and Coat-Redfern equations to evaluate the kinetic parameters such as activation energy ($E_a$), order of reaction ($n$) and frequency factor (z).

Keywords : Synthesis, polycondensation, thermogravimetric analysis (TGA), activation energy, Freeman-Carroll, Coat-Redfern, Friedman.

## Introduction

Since the modern history of thermogravimetry, thermal degradation of polymers and study of its kinetics has been at the centre of thermal analysis[1,2]. Thermogravimetric analysis is the common method to study the decomposition pattern and kinetics of polymer degradation and can be carried out in inert as well as oxidative atmosphere[3]. Kinetic analysis may effectively assist in studying degradation mechanism as well as in predicting the thermal stability of polymers[4]. These goals are achieved only when using proper methods for kinetic evaluations. Most evaluations are performed by fitting kinetic data to variation reaction models, which provide kinetic parameters whose reliability depends on proper choice of reaction model[5]. In this study, certain generalizations are made by applying TGA data to five different thermal degradation kinetic techniques.

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]. Michael PEP et al. have reported the thermal degradation of 8-hydroxyquinoline-guanidine-formaldehyde terpolymer[7]. Kinetics of thermal degradation studies of some new terpolymer derived from 2,4-dihydroxypropiophenone, oxamide and formaldehyde has been studied by Tarase et al.[8]. Thermoanalytical study and kinetics of 8-hydroxyquinoline 5-sulphonic acid – oxamideformaldehyde terpolymer resins has been studied by Singru et al.[9]. Detailed study has been done by Paik and Kar[10] 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.

Braun et al. have reported free radical terpolymerization of three nonpolymerizable monomers[11-13]. Rzaev et al. have investigated several terpolymerization systems[14-16]. Zakir has also discussed the radical

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terpolymerization of maleic anhydride, *trans*-stilbene and acrylonitrile as accepter-donar-accepter monomer system[17]. Shah *et al.* reported the terpolymerization system synthesized from salicylic acid-resorcinol-formaldehyde[18] and 8-hydroxyquinoline-catechol-formaldehyde[19].

In the present article, synthesis, characterization, thermal degradation behavior and kinetics by TGA under nonisothermal conditions of *p*-NP-4,4'-MDA-F-III has been studied. Activation energy, pre-exponential factor and order of reaction have been determined using Friedman, Chang, Sharp-Wentworth, Freeman-Carroll and Coat-Redfern methods. The computed results are discussed and elaborated. 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 and formaldehyde (37%) were purchased from S. D. Fine Chemicals, India. 4,4'-Methylene dianiline was purchased from Acros Chemicals, Belgium. Solvents like *N*,*N*-dimethylformamide, dimethylsulphoxide, tetrahydrofuran, acetone and diethyl ether were procured from Merck, India.

### Synthesis :

*p*-NP-4,4'-MDA-F-III copolymer has been synthesized by condensation polymerization reaction by using the molar proportion 4 : 1 : 5 of reacting monomers i.e. *p*-nitrophenol (5.56 g, 0.4 mol) and 4,4'-methylene dianiline (1.98 g, 0.1 mol) with formaldehyde (18.75 ml, 0.5 mol) in presence of 2 *M* HCl as a catalyst at 130 °C in an oil bath for about 3 h of continuous heating with occasional shaking (Fig. 1). The temperature of electrically heated oil bath was controlled with the help of a dimmerstat. The resinous dark reddish 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 NaOH/water with constant stirring and filtered. The resulting polymer sample was washed several times with boiling water and dried in a desiccator at room temperature. Further dried polymeric sample extracted with diethyl ether to remove the excess *p*-nitrophenol-formaldehyde dimers, which might be present along with the *p*-NP-4,4'-ODA-F-III terpolymer. Finally the product was passed through 300-mesh size sieve and kept in a vacuum over silica gel[20].

### Analytical and physicochemical studies :

Copolymers were subject to elemental analysis for carbon, hydrogen and nitrogen on Perkin-Elmer 2400 Elemental Analyzer. UV-Visible spectra were recorded
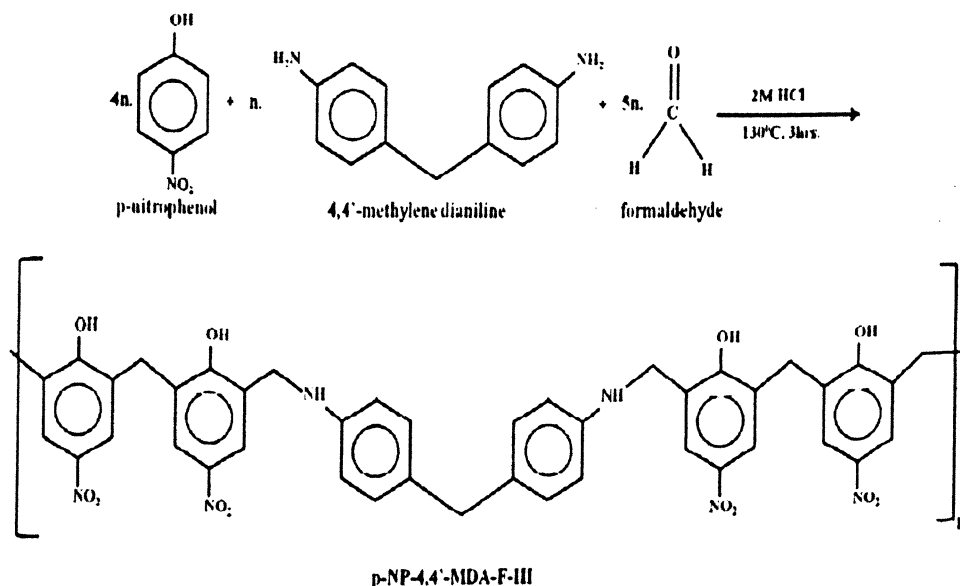


Fig. 1. Chemical reaction of *p*-NP-4,4'-MDA-F-III copolymer.

in dimethylsulphoxide on Shimadzu UV-Visible double beam spectrophotometer in the range of 200–850 nm. Infrared spectrum was recorded in nujol mull on Perkin-Elmer-spectrum RX-I spectrophotometer in the range of 4000–500 cm$^{-1}$. $^1$H NMR studies were performed in dim-ethyl-sulphoxide 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 Instrumenta-tion Facility (SAIF), Punjab University, Chandigarh.

*Thermal studies* :

The 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 tem-perature range 100–650 °C. TGA was carried out at SICART, Anand, 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[21]. Heating is performed under strictly controlled conditions and can reveal changes in structure and other important properties of the material being stud-ied. Kinetic parameters have been determined using Fried-man[21,22], Chang[23], Sharp-Wentworth[24], Freeman-Carroll[25] and Coat-Redfern[26] techniques as follows :

*Friedman technique* :

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

where $\alpha$ 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 ob-tained.

*Chang technique* :

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

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 pro-vide the $(-E_a/R)$ and $\ln(z)$ values, respectively.

*Sharp-Wentworth technique* :

$$\log\frac{dc/dt}{1-c} = \log\left(\frac{A}{\beta}\right) - \frac{E_\alpha}{2.303R}\cdot\frac{1}{T} \quad (3)$$

where, $dc/dt$ = rate of change of fraction of weight with change in temperature, $\beta$ is linear heating rate, $dT/dt$; *c* is the fraction of polymer decomposed at time *t*.

Thus, a linear plot of $\log\log\frac{dc/dt}{1-c}$ versus $\frac{1}{T}$ is obtained whose slope gives the value of $E_a$ and *A* may be evaluated from the intercept. The linear relationship con-firmed that the assumed order is correct.

*Freeman-Carroll technique* :

$$\frac{\Delta\log(dw/dt)}{\Delta\log Wr} = \left(-\frac{E_\alpha}{2.303R}\right)\cdot\frac{\Delta\left(\frac{1}{T}\right)}{\Delta\log Wr} + n \quad (4)$$

where $dw/dt$ = rate of change of weight with time.

$Wr = Wc - W$

*Wc* is the weight loss at the completion of reaction or at a definite time *t*; *W* is the total weight loss upto time *t*; $E_a$ is energy of activation; *R* is gas constant; *T* is tempera-ture and *n* is the order of reaction.

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

*Coat-Redfern equation* :

$$\ln\left[\frac{q(\alpha)}{T^2}\right] = \ln\left\{\frac{AR}{qE_a}\left[1-\frac{2RT}{E_a}\right]\right\} - \frac{E_a}{RT} \quad (5)$$

where, *q* and *A* is the heating rate (°C/min) and fre-quency factor respectively.

$g(\alpha)$ is equal to $-\ln(1-\alpha)$ for $n=1$ and $([1-(1-\alpha)^n]/(1-n)$ for $n\neq 1$.

Thus a plot of either $\ln[(1-(1-\alpha)^{1-n})/(T^2(1-n))]$

**Table 1.** Elemental analysis data of *p*-NP-4,4′-MDA-F-III

| Copolymer | Monomer empirical formula | Empirical formula weight | Elemental analysis (%) : Calcd. (Expt.) | | |
| --- | --- | --- | --- | --- | --- |
| | | | C | H | N |
| *p*-NP-4,4′-MDA-F-III | $C_{42}H_{34}N_6O_{12}$ | 814 | 61.91 | 4.17 | 10.31 |
| | | | (60.00) | (4.03) | (10.24) |

vs ($1/T$) or ln [−ln ($1 - \alpha$)/$T^2$] vs ($1/T$) should result in straight line of slope [$-E_a/R$] for correct value of $n$, since it may be shown that for most values of $E_a$ and for the temperature range over which reaction generally occurs the expression ln [($AR/qE_a$) ($1 - (2RT/E_a)$)] is constant.
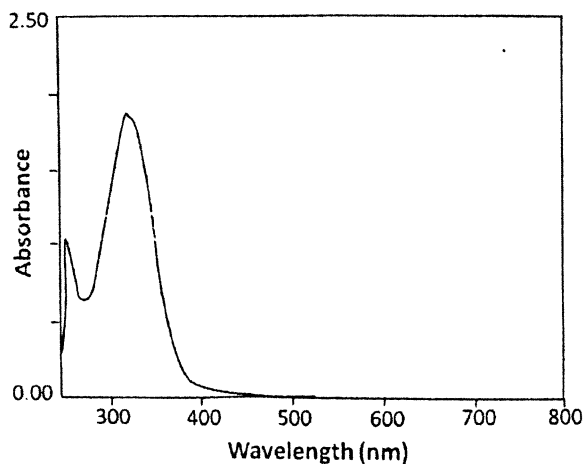
### Results and discussion

*Characterization :*

*Elemental analysis :*

The yield of *p*-NP-4,4′-MDA-F-III copolymer is found to be 76%. Composition of copolymer obtained on the basis of elemental analysis data and was found to be in good correlation with that of calculated values as shown in Table 1.

*UV-Visible (in DMSO-d₆ in the range 200–850 nm) :*

UV-Visible spectrum of *p*-NP-4,4′-MDA-F-III copolymer sample in pure DMSO was recorded in the wavelength region 200–850 nm which is shown in Fig. 2. The spectrum displayed two characteristic bands at wavelengths 250 and 330 nm. The former and less intense band may be due to $n{\rightarrow}\pi^*$ transitions observed at 250 nm indicate the presence of biphenyl methane moiety. Hypsochromic shift observed in biphenyl may be due to introduction of $-CH_2$ group between two phenyl groups which destroys

the conjugation.

Later and more intense band observed at 330 nm may be accounted for $\pi{\rightarrow}\pi^*$ transition might be due to chromophoric ($-NO_2$) group. The auxochromic substituents ($-OH$) interacting with $\pi$ electron of the benzene ring. This interaction stabilizes $\pi^*$ state and thus lowers the energy as a result bathochromic shift is caused. The auxochromic influence is more pronounced when an electron donating and electron attracting groups are *para* 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.
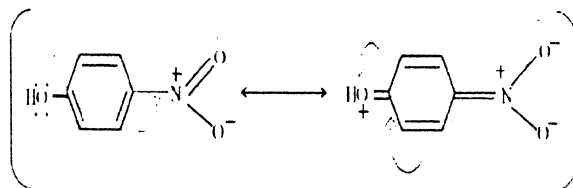


*FT-IR spectra :*

The FTIR-spectrum of *p*-NP-4,4′-MDA-F-III copolymer is represented in Fig. 3 and the data is reported in Table 2. Broad band appeared at 3451.1 cm⁻¹, which may be assigned to the stretching vibration of the phenolic $-OH$ group exhibiting intermolecular hydrogen bonding[27]. The presence of a weak peak at 2924.4 cm⁻¹ des-



**Fig. 2.** UV-Visible spectra of *p*-NP-4,4′-MDA-F-III copolymer.
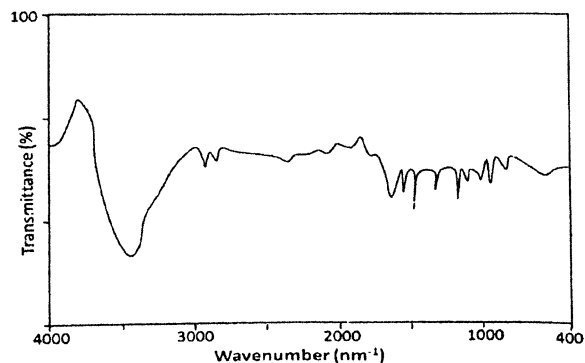


**Fig. 3.** FT-IR spectra of *p*-NP-4,4′-MDA-F-III copolymer.

**Table 2.** IR frequencies and $^1H$ NMR spectral data of *p*-NP-4,4'-MDA-F-III copolymer

| IR Wavenumber (cm$^{-1}$) | Assignment | $^1H$ NMR chemical shift ($\delta$) ppm of copolymer | Nature of protons assigned |
|---|---|---|---|
| 3451.0 b,st | -OH (phenolic) | 10.7 | 1H, s, -OH |
| 2924.4 sh,w | -NH- (amino) | 7.9 | 1H, s, tetrasubstituted, Ar-H |
| 2855.0 sh,w | -CH$_2$- stretching methylene bridge | 8.0 | 2H, s, *ortho* to -CH$_2$ in methylene dianiline moiety |
| 1650.0-1660.2 b,m | >C=C< in aromatics | 6.8-6.9 | 2H, d, *ortho* to >NH in methylene dianiline moiety |
| 1498.9 sh,st | Asymm. N=O str, b | 3.5 | 1H, s, CH$_2$-NH-Ar |
| 1338.3 sh,m | Symm. N=O str, b | 3.1 | 2H, s, Ar-CH$_2$-Ar in methylene dianiline moiety |
| 1286.7 b,st | C-N str. in amine, b | 2.5 | 2H, s, Ar-CH$_2$ NH- |
| 1217.2 sh,m | C-O str. in phenol, m | | |
| 850.7 sh,w ⎱ | Tetrasubstituted benzene ring | | |
| 965.4 sh,w ⎰ | | | |
| | Methylene bridge (-CH$_2$) modes | | |
| 1460.0 b,m ⎱ | Bending | | |
| 1345-1350 sh,m ⎬ | Wagging | | |
| 750-770 sh,w ⎰ | Rock | | |

sh - sharp; b - broad; st - strong; m - medium; w - weak.

cribes the -NH- in 4,4'-methylene dianiline moiety which might be present in copolymeric chain. A sharp and weak peak obtained at 2855.1 cm$^{-1}$ indicates the presence of stretching vibrations of methylene group (-CH$_2$-) in the copolymer chain[28]. A medium band displayed between 1650.0 -1660.2 cm$^{-1}$, may be due to stretching vibration of >C=C< in aromatics. Broad and strong bands displayed at 1498.8 cm$^{-1}$ for asymmetric and 1338.9 cm$^{-1}$ for symmetric vibrations, confirms the presence of nitro group in the polymer chain[28]. C-O stretch in phenol is represented at 1217.2 cm$^{-1}$. The presence of methylene bridges (-CH$_2$-) in the polymeric chain can be accounted by the presence of bands at 1460.4 cm$^{-1}$, 1345-1355 cm$^{-1}$ and 750-770 cm$^{-1}$ for bending, wagging and rocking vibrations respectively[29,30]. The presence of tetrasubstitution of aromatic ring is recognized from the weak band appearing at 850.7 and 965.4 cm$^{-1}$ [29].

*$^1H$ NMR spectra :*

$^1H$ NMR spectrum of *p*-NP-4,4'-MDA-F-III copolymer was scanned in solvent DMSO-$d_6$. Spectral data is given in Table 2 and spectrum is presented in Fig. 4. Spectra reveal different pattern of peaks, since each of

them possesses a set of protons having different proton environment.

A significant downfield in chemical shift of proton of phenolic -OH group observed at $\delta$ 10.7 ppm is due to intermediate proton exchange reaction of phenolic -OH group[29]. Weak singlet is observed at $\delta$ 7.9 ppm is due to *meta* protons of phenol. In 4,4'-methylene dianiline moiety, the doublet observed in the region $\delta$ 6.8-6.9 and $\delta$ 8.0 ppm is attributed to protons *ortho* to -NH and protons *ortho* to -CH$_2$ respectively. A broad singlet observed at $\delta$ 3.5 ppm may be assigned to -CH$_2$-NH-Ar moiety. Methylenic protons of Ar-CH$_2$-NH and Ar-CH$_2$-Ar moiety may be recognized as signal appearing at $\delta$ 3.1 and $\delta$ 2.5 ppm respectively[31,32].

*Thermogravimetric analysis :*

*Thermogravimetry of p-NP-4,4'-MDA-F-III :*

Thermogravimetric analysis of *p*-NP-4,4'-MDA-F-III has been carried out at 10 °C min$^{-1}$ and the decomposition pattern of a representative polymer has been shown in Fig. 5.
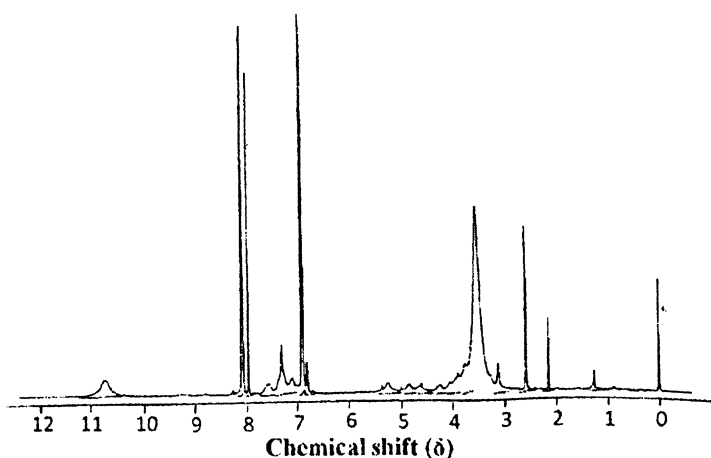
Thermogram of this copolymer depicted three step

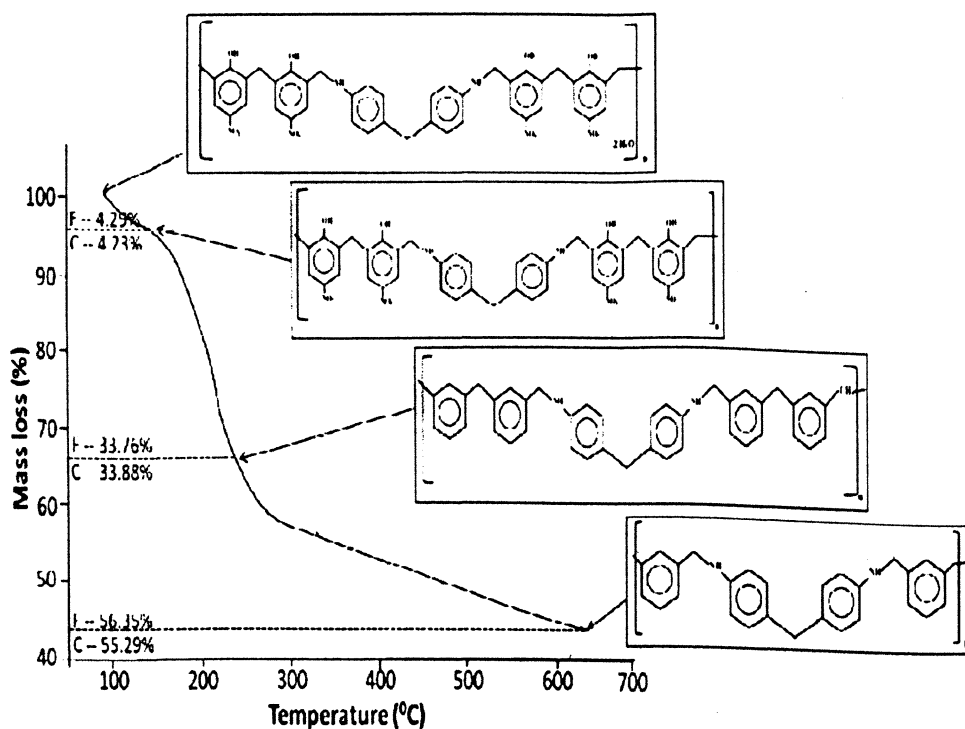Fig. 4. $^1$H NMR spectra of $p$-NP-4,4′-MDA-F-III copolymer.



Fig. 5. Decomposition pattern of $p$-NP-4,4′-MDA-F-III copolymer.

decomposition steps in the temperature range 100–650 °C (Table 3). First step is slow decomposition between 100 to 130 °C corresponds to 4.29% loss which may be attributed to loss of two water molecules against calculated 4.23% present per repeat unit of the polymer[33]. The second step of decomposition starts from 130–330 °C which represents degradation of four (-OH) and four

(-NO$_2$) attached to the benzene skeleton (33.76% found and 33.88% calculated). Third step decomposition starts from 330–650 °C corresponding to 56.35% loss of two benzene ring with methylene group against calculated 55.29%. Consequently residue remained having the values (43.65% found and 44.71% calculated) and more temperature is required for complete decomposition.

**Table 3.** Thermal degradation behavior of *p*-NP-4,4'-MDA-F-III copolymer

| Decomposition steps | Half decomposition temp. (°C) | Temp. range (°C) | Wt. loss (%) : Found | Calcd. | Species degraded |
|---|---|---|---|---|---|
| 1 | | 100–130 | 4.29 | 4.23 | Two $H_2O$ molecules |
| 2 | 260 | 130–230 | 33.76 | 33.88 | Four (-OH) and four (-NO$_2$) groups |
| 3 | | 230–600 | 55.35 | 55.29 | Two benzene rings with two methylene groups |

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

The decomposition is due to pyrolysis of straight chain -linked structure of copolymer due to which it doesn't takes much more time to attain the thermal equilibrium as well as at 650 °C degradation process occurs upto final level leaving behind the remaining moiety. The thermal stability of *p*-NP-4,4'-MDA-F-III copolymer is concluded to be higher, 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[34] or it may be due to possibility of an almost linear structure of copolymer chain which gives stability to polymer chain[35].

In general the water of hydration may be considered as crystal water. In the present case of copolymer the removal of two water molecules is complete and is probably crystal water or moisture entrapped in the molecule. By applying the thermogravimetric data to five thermal degradation kinetic techniques (i.e. Friedman, Chang, Sharp-Wentworth, Freeman Carroll and Coat-Redfern), it shows three different degradation steps corresponding to loss of respective groups.

Kinetic parameters for *p*-NP-4,4'-MDA-F-III copolymer have been calculated using Friedman method (1). Activation energy ($E_a$) has been obtained from the plot between ln ($d\alpha/dt$) vs (1/T) (Fig. 6) and order of reaction (*n*) from the plot between ln (1 - $\alpha$) vs (1/T) (Fig. 7). Values of ln (*z*) are calculated at each temperature region from (1) with the help of $E_a$ and *n*. Fig. 8 has shown Chang method (2) gives plots between [ln ($d\alpha/dt$)/(1 - $\alpha$)$^n$] vs (1/T) for *p*-NP-4,4'-MDA-F-III 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*, which corresponds to correct reaction order for each re-
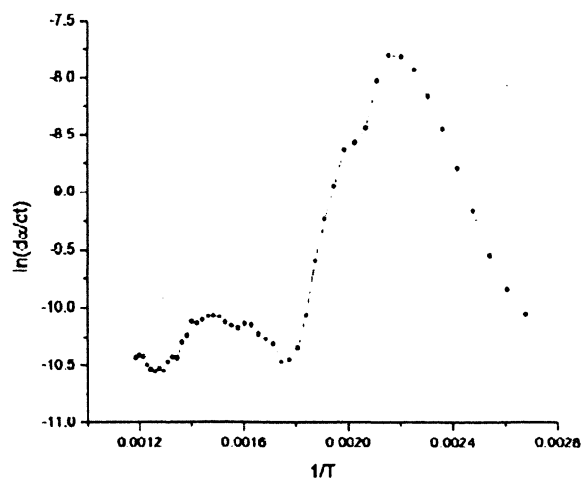


**Fig. 6.** Friedman plot of *p*-NP-4,4'-MDA-F-III copolymer for activation energy.
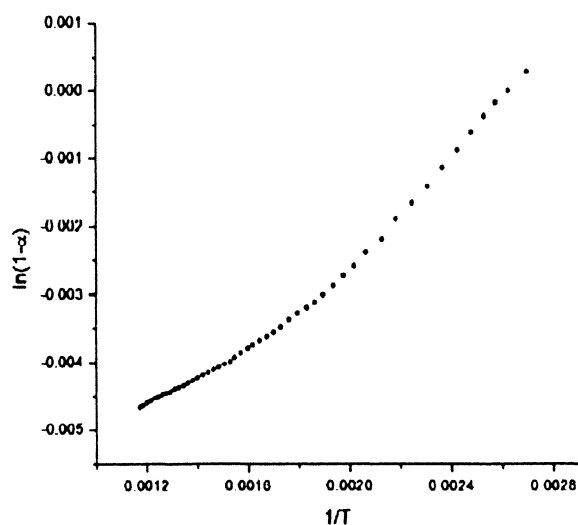


**Fig. 7.** Friedman plot of *p*-NP-4,4'-MDA-F-III copolymer for the order of reaction.

spective thermal decomposition step.

Also kinetic parameters for different thermal degradation zones have been calculated by Sharp-Wentworth
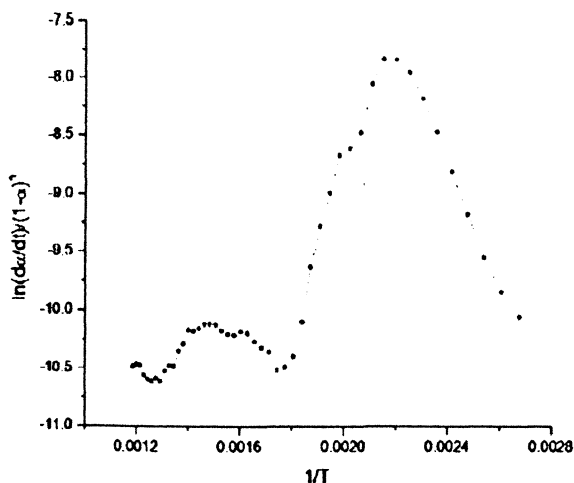
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Fig. 8. Chang plot of $p$-NP-4,4'-MDA-F-III copolymer.



Fig. 10. Freeman-Carroll plot of $p$-NP-4,4'-MDA-F-III copolymer.

method (3). $E_a$ and ln $(z)$ values are calculated from the plot between $\log \dfrac{dc/dt}{1-c}$ vs $\dfrac{1}{T}$ with best fitted values of $n$ for each respective degradation reaction (Fig. 9). Similarly using the Freeman-Carroll technique (4) kinetic parameters has been calculated. Fig. 10 has shown repre-

sentative plot of $\dfrac{\Delta \ln \left(\dfrac{d\alpha}{dt}\right)}{\Delta \ln (1-\alpha)}$ vs $\dfrac{\Delta \left(\dfrac{1}{T}\right)}{\Delta \ln (1-\alpha)}$ for $p$-

NP-4,4'-MDA-F-III. The slope and intercept for each step are computed from (4), which is equal to $(E_a/R)$ and $n$ respectively. Kinetic parameters have been evaluated by using Coat-Redfern (5) method by plotting ln $[(1 - (1 - \alpha)^{1-n})/(T^2(1 - n))]$ vs $(1/T)$ for $p$-NP-4,4'-MDA-F-III, which results in straight line of slope $[-E_a/R]$ for correct value of $n$ (Fig. 11). The results of kinetic param-
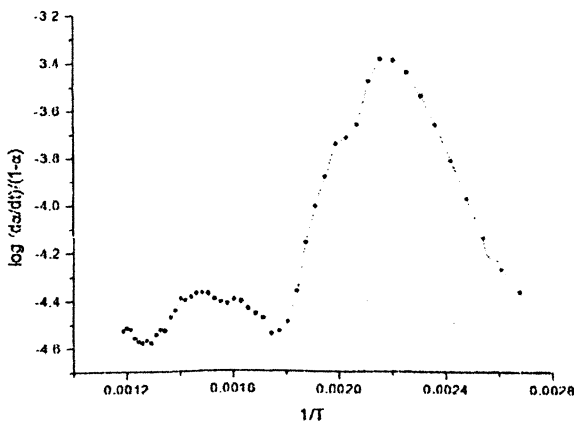


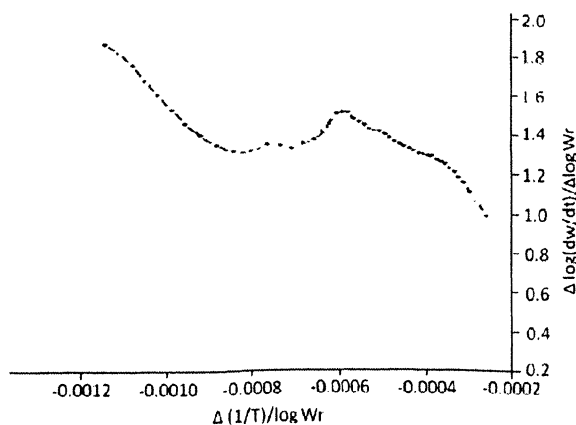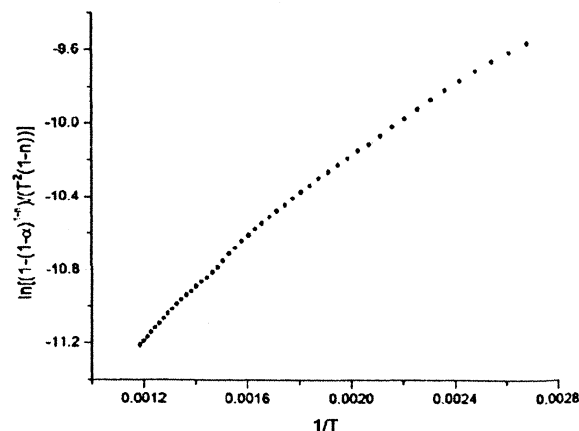Fig. 11. Coat-Redfern plot of $p$-NP-4,4'-MDA-F-III copolymer.

eters of above mentioned methods have been incorporated in Table 4.

A plot of percentage mass loss vs temperature is shown in Fig. 5 for a representative $p$-NP-4,4'-MDA-F-III copolymer. From the TG curves, 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 behavior of samples.

Fairly comparable results of kinetic parameters viz. $E_a$, $n$ and ln $(z)$ are obtained for each degradation step by Friedman and Chang may be due to analogy in mathematical model. Also results obtained by Sharp-Wentworth and Freeman-Carroll methods are in good agreement with each other with slight variations. But, Coat-Redfern method shows different observations.



Fig. 9. Sharp-Wentworth plot of $p$-NP-4,4'-MDA-F-III copolymer.

**Table 4.** Thermoanalytical data for each degradation step of p-NP-4,4'-MDA-F-III copolymer

| Decomposition steps | Friedman | | | Chang | | | Sharp-Wentworth | | | Freeman-Carroll | | | Coat-Redfern | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $E_a$ | $n$ | ln $(z)$ | $E_a$ | $N$ | ln $(z)$ | $E_a$ | $N$ | ln $(z)$ | $E_a$ | $n$ | $z$ | $E_a$ | $n$ | log $z$ |
| 1 | 85.47 | 0.8 | 5.8 | 85.35 | 0.8 | 5.17 | 31.12 | 1.0 | 3.18 | 36.65 | 0.3 | 3.06 | 14.88 | 0.98 | 11.65 |
| 2 | 16.85 | 1.5 | 15.3 | 15.88 | 1.5 | 15.69 | 17.37 | 1.0 | 17.7 | 17.78 | 0.6 | 18.36 | 18.52 | 0.98 | 12.12 |
| 3 | 22.86 | 1.6 | 11.77 | 25.31 | 1.6 | 11.97 | 14.79 | 1.0 | 5.26 | 15.98 | 0.9 | 21.15 | 24.45 | 0.98 | 12.69 |

Units of $E_a$ and ln $(z)$ are kJ/mol and s$^{-1}$ respectively.

From the above discussion, it is therefore concluded that for each technique, the values of kinetic parameters depend on calculation technique used as well as degrading species at a particular step. Total calculations obtained from different kinetic models demonstrated that the numerical value of kinetic parameters depends on the mathematical model used to analyze the experimental data and level of degradation[10]. Low values of frequency factor revealed that decomposition reaction of copolymer may be slow and no other possible reason can be given[35-37]. As the polymer degradation is a complex phenomena, 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 thermogravimetric data 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.

By using above mentioned techniques, variations in the result are obtained which represents versatility and great utility of thermal degradation mathematical kinetic equations in thermogravimetry. As model free kinetic approach eliminates the necessity of assumptions of mathematical functional form of rate law for calculating the kinetic parameters, so it is a trustworthy method to study the kinetics and attempts are developing to implement the model free kinetic equations[38].

*Conclusion* :

Synthesis of targeted copolymer (p-NP-4,4'-MDA-F-III) has been confirmed which is supported by the results obtained from elemental analysis and spectral data. Thermogram obtained has shown three degradation stages, first indicating the degradation of two water molecules, second shows four (-OH) and four (-NO$_2$) groups and third step represents removal of two benzene rings with two methylene (-CH$_2$) groups. Friedman and Chang meth-

ods show nearly similar values of kinetic parameters may be due to resemblance in mathematical model whereas results obtained from Sharp-Wentworth and Freeman-Carroll methods are in good correlation with each other. But, Coat-Redfern method shows different observations. From the results obtained, 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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