Research Article

Preparation, Characterization, and Thermal Degradation Studies of *p*-Nitrophenol-Based Copolymer

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Polycondensation reaction was employed to synthesize a new copolymer resin (p-NP-4,4$'$-MDA-F) from p-nitrophenol (p-NP) and 4,4$'$-methylene dianiline (4,4$'$-MDA) with formaldehyde (F) in presence of 2 M hydrochloric acid as a catalyst at 130±1°C. The resin was characterized by elemental analysis and spectral studies such as UV-visible, FT-IR, and ^{1}H-NMR spectra which were used to confine the most probable structure of synthesized copolymer. Thermal degradation pattern and kinetics have been investigated by thermogravimetric analysis. Thermal degradation curve have been studied with minute detail for each degradation step. Friedman, Chang, Sharp-Wentworth, Freeman-Carroll, and Coat-Redfern methods have been implemented in order to compute the kinetic parameters, that is, thermal activation energy (E_a), order of reaction (n), and frequency factor (z).

1. Introduction

Due to global applications of polymeric materials polymer science and technology have been developing rapidly and attracted much attention towards the polymer scientists. Polymers have been found to be very useful applications as adhesive, high-temperature flame-resistant fibers, coating materials, semiconductors, catalysts, and ion-exchange resins [1–6]. Varieties of researches regarding the thermal studies of polymers are emerging out to investigate their renewed applications for the betterment of mankind. Area of polymer reaction kinetics is enhanced by applying various model fitting kinetic equations in order to study its kinetic and thermodynamic aspects [7].

Much attention has been focused to synthesize the terpolymers by applying various synthetic techniques to examine its advanced applications. In the recent past, appreciable progress has been made in many ternary systems such as acrylonitrile-methylmethacrylate-methacrylic acid [8],

methylmethacrylate-styrene-butadiene [9], acrylonitrile-methyl acrylate-itaconic acid [10], styrene-acrylonitrile-methyl acrylate [11], butadiene-acrylonitrile-chlorocyclo-vinylketone [12], maleic anhydride terpolymers [13], 2,4-dihydroxyacetophenone-dithiooxamide-formaldehyde [14], and 8-hydroxyquinoline-guanidine-formaldehyde [15]. Shah et al. have reported the chelating ability of resin synthesized by a microwave irradiation technique involving salicylic acid and formaldehyde with resorcinol [16]. Patel and Manavalan [17] have prepared the terpolymer of salicylic acid/p-hydroxybenzoic acid and thiourea with trioxane in presence of acid catalyst with different molar proportion of monomers. Jadhav et al. have reported the synthesis, characterization, and thermal degradation kinetics of copolymers derived from 2,2$'$-dihydroxybiphenyl- formaldehyde [18] copolymer and 2,2$'$-dihydroxybiphenyl, urea, and formaldehyde [19] terpolymer. Paik and Kar [20] studied the kinetics of thermal degradation and estimation of lifetime for polypropylene particles and its effect on
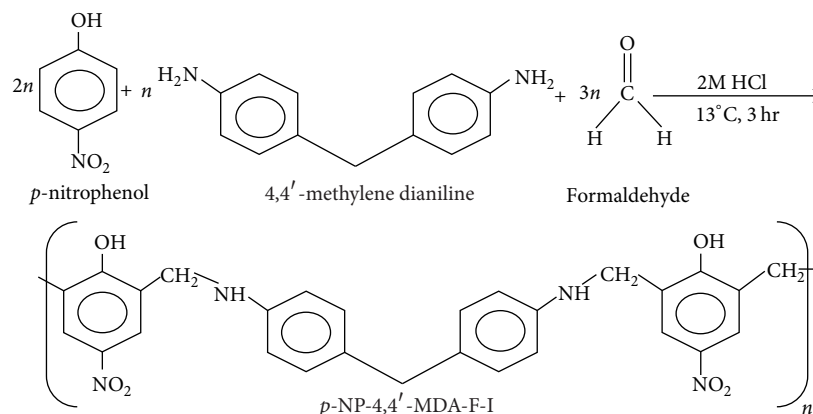
Figure 1: Chemical reaction of p-NP-4,4$'$-MDA-F copolymer.

particle size, involving the use of single, and multiple heating rate techniques.

In this paper, we present the synthesis and characterization of phenolic straight chain copolymer (p-NP-4,4$'$-MDA-F) by condensation terpolymerization reaction of p-nitrophenol and 4,4$'$-methylene dianiline using the linkage of formaldehyde. Thermal degradation behavior was studied by TGA under nonisothermal conditions. Certain generalizations are made regarding the kinetic parameters computed by using Friedman, Chang, Sharp-Wentworth, Freeman-Carroll, and Coat-Redfern method.

2. Experimental

2.1. Materials.
4,4$'$-Methylene dianiline is of analytical grade purity which is purchased from Acros Chemicals, Belgium. p-Nitrophenol and formaldehyde (37%) were purchased from S. D. Fine Chemicals, India. All the used solvents like N, N-dimethylformamide, dimethyl sulphoxide, tetrahydrofuran, acetone, and diethyl ether were procured from Merck, India.

2.2. Synthesis.
p-NP-4,4$'$-MDA-F copolymer was prepared by condensing p-nitrophenol (2.78 g, 0.2 mol) and 4,4$'$-methylene dianiline (1.98 g, 0.1 mol) with formaldehyde (11.25 mL, 0.3 mol) in presence of 2 M HCl as a catalyst in the molar proportion of 2 : 1 : 3 at 130°C in an oil bath for 3 hours. The temperature of electrically heated oil bath was controlled with the help of a dimmerstat. The dark reddish brown resinous 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. The product obtained was extracted with diethyl ether to remove excess of p-nitrophenol-formaldehyde copolymer which might be present along with p-NP-4,4$'$-MDA-F copolymer. Dried resin sample was dissolved in 8% NaOH and regenerated using 1 : 1 HCl/water (v/v) with constant stirring and filtered. This process was repeated twice. Resulting copolymer sample was washed with boiling water and dried in a vacuum at room temperature. Purified copolymer resin was finely ground to pass through 300 mesh size sieve

and kept in a vacuum over silica gel [21]. The Chemical reaction of above synthesis is given in Figure 1.

2.3. Spectral and Thermal 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 were 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 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. 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 temperature range 50–600°C. TGA was carried out at SICART, Gujrat.

2.4. 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. Kinetics parameters have been determined using Friedman [22, 23], Chang [24], Sharp-Wentworth [25], Freeman-Carroll [26], and Coat-Redfern [27] techniques as follows.

2.4.1. Friedman Technique.
We have

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

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 $\ln(1 - \alpha)$ versus $1/T$, n can be obtained. The plot of $\ln(d\alpha/dt)$ versus $1/T$ should be linear with the slope E_a/R, from which E_a can be obtained.

TABLE 1: Elemental analysis data of *p*-NP-4,4′-MDA-F.

Copolymer	Monomer empirical formula	Empirical formula weight	Elemental Analysis (%)					
			C		H		N	
			Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
p-NP-4,4′-MDA-F	$C_{28}H_{24}N_4O_6$	512	65.62	65.00	4.68	4.49	10.93	11.10

2.4.2. Chang Technique. We have

$$\ln \frac{(d\alpha/dt)}{(1-\alpha)^n} = \ln(z) - \frac{E_a}{RT}. \qquad (2)$$

A plot of $[\ln(d\alpha/dt)/(1-\alpha)^n]$ versus $1/T$ 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.

2.4.3. Sharp-Wentworth Technique. We have

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

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 $\log((dc/dt)/(1-c))$ versus $1/T$ is obtained whose slope gives the value of E_a and A may be evaluated from the intercept. The linear relationship confirmed that the assumed order is correct.

2.4.4. Freeman and Carroll Technique. We have

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} = \left(-\frac{E_a}{2.303\ R}\right) \cdot \frac{\Delta(1/T)}{\Delta \log W_r} + n, \qquad (4)$$

where, dw/dt is rate of change of weight with time. W_r is $W_c - W$; W_c is Weight loss at the completion of reaction; W is Total weight loss upto time. E_a is Energy of activation; n is order of reaction.

The $\Delta \log(dw/dt)$ and $\Delta \log W_r$ values are taken at regular intervals of $1/T$. In this case $(\Delta \log(dw/dt))/(\Delta \log W_r)$ versus $\Delta(1/T)/\Delta \log W_r$ gives a straight line. The slope and intercept are equal to $-(E_a/R)$ and n, respectively.

2.4.5. Coat Redfern Technique. We have

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

where, q and A are the heating rate (°C/min) and frequency 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 $\ln[(1-(1-\alpha)^{1-n})/(T^2(1-n))]$ versus $(1/T)$ or $\ln[-\ln(1-\alpha)/T^2]$ versus $(1/T)$ 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.

3. Results and Discussion

3.1. Spectral Studies of p-NP-4,4′-MDA-F Copolymer

3.1.1. Elemental Analysis. The yield of resin was found to be 80%. Composition of copolymer obtained on the basis of elemental analysis data and was found to be in good correlation to that of calculated values as follows (Table 1).

3.1.2. UV-Visible Spectra. UV-visible spectrum of *p*-NP-4,4′-MDA-F copolymer sample in pure DMSO was recorded in the wavelength region 200–850 nm which is shown in Figure 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 [28, 29] observed at 250 nm indicating 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) interact with π electron of the benzene ring. This interaction stabilizes π^* 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.
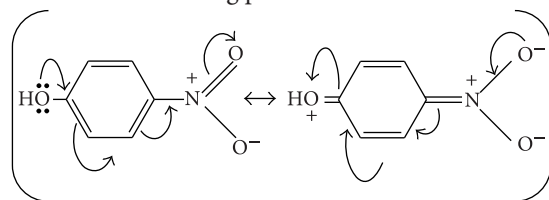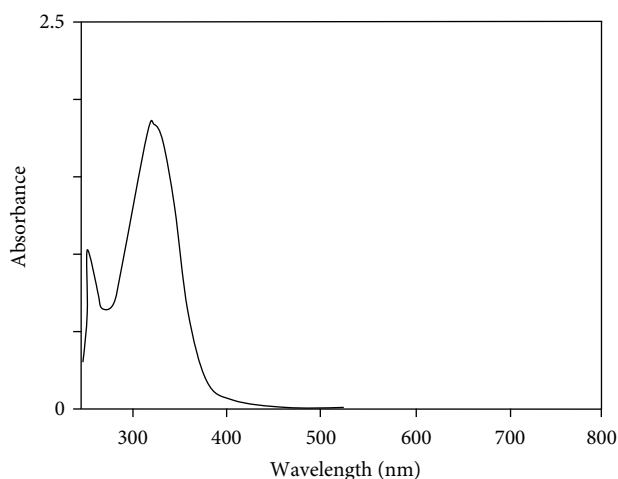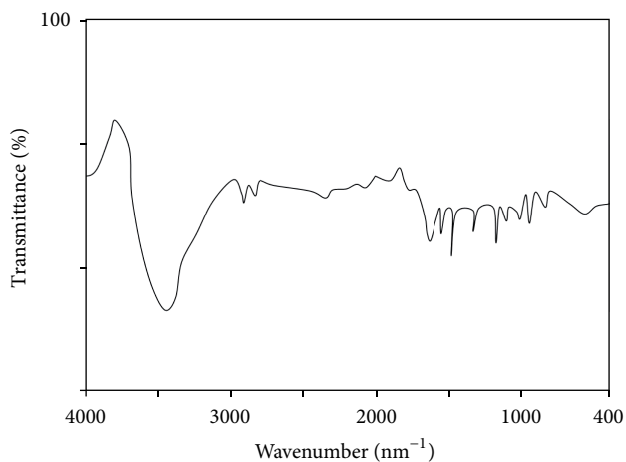

3.1.3. FT-IR Spectra. The FTIR-spectrum of *p*-NP-4,4′-MDA-F copolymer is represented in Figure 3 and the data is reported in Table 2. Broad band appeared at 3451.0 cm^{-1}, which may be assigned to the stretching vibration of the phenolic –OH groups exhibiting intermolecular hydrogen bonding [30, 31]. The presence of a weak peak at 2924.4 cm^{-1} describes the –NH– in 4,4′-methylene dianiline moiety which might be present in copolymeric chain [31]. A sharp and weak peak obtained at 2855.0 cm^{-1} indicates the presence of stretching vibrations of methylene group (–CH$_2$–) in the copolymer chain [30]. A medium band, displayed between

TABLE 2: IR frequencies and ^{1}H-NMR spectral data of p-NP-4,4′-MDA-F copolymer.

IR Wavenumber (cm^{-1})	Assignment	^{1}H-NMR chemical shift (δ) ppm of copolymer	Nature of protons assigned
3451.0 b, st	–OH (phenolic)	10.7	s, 1H, –OH
2924.4 sh, w	–NH– (amino)	7.9	s, 1H, tetrasubstituted, Ar–H
2855.0 sh, w	–CH$_2$– stretching methylene Bridge	8.0	s, 2H, ortho to –CH$_2$ in methylene dianiline moiety
1650.0–1660.2 b, m	>C=C< in aromatics	6.8–6.9	d, 2H, ortho to >NH in methylene dianiline moiety
1498.9 sh, st	Asymm. N=O str, b	3.5	s, 1H, CH$_2$–NH–Ar
1338.8 sh, m	Symm. N=O str, b	3.1	s, 2H, Ar–CH$_2$–Ar in methylene dianiline moiety
1286.7 b, st	C–N str. in amine, b	2.5	s, 2H, 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.

FIGURE 2: UV-Visible spectra of p-NP-4,4′-MDA-F copolymer.

FIGURE 3: FT-IR spectra of p-NP-4,4′-MDA-F copolymer.

1650.0–1660.2 cm^{-1}, may be due to stretching vibration of >C=C< in aromatics. Broad and strong bands displayed at 1498.9 cm^{-1} for asymmetric and 1338.8 cm^{-1} for symmetric vibrations confirm the presence of nitro group in the polymer chain [31]. 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 cm^{-1}, 1345–1350 cm^{-1}, and 750–770 cm^{-1} for bending, wagging, and rocking vibrations, respectively [32, 33]. The presence of tetrasubstitution of aromatic ring [31] is recognized from the weak band appearing at 850.7 and 965.4 cm^{-1}.

*3.1.4. ^{1}H- NMR Spectra.* ^{1}H-NMR spectral data is given in Table 2 and spectrum is presented in Figure 4. Spectra reveal different patterns 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 δ 10.7 ppm, is due to intermediate proton exchange reaction of phenolic –OH group [32, 34]. A weak singlet is observed at δ 7.9 ppm and is due to meta protons of phenol. In 4,4′-methylene dianiline moiety, the doublet observed in the region δ 6.8–6.9 and δ 8.0 ppm is attributed to protons ortho to –NH and protons ortho to–CH$_2$, respectively. A broad singlet observed at δ 3.5 ppm may be

TABLE 3: Thermal degradation behavior of p-NP-4,4$'$-MDA-F copolymer.

Decomposition steps	Temp. range (°C)	Wt. loss (%)		Half decomposition temperature (°C)	Species degraded
		Found	Calc.		
(1)	90–130	3.48	3.39		H$_2$O molecule
(2)	130–270	27.30	27.16	255	two (–OH) and two (–NO$_2$) groups
(3)	270–600	61.64	61.13		Two side benzene rings with methylene groups

TABLE 4: Thermoanalytical data for each degradation step of p-NP-4,4$'$-MDA-F copolymer.

Kinetic equations	Decomposition steps								
	I			II			III		
	E_a	n	$\ln(z)$	E_a	n	$\ln(z)$	E_a	n	$\ln(z)$
Friedman	57.37	0.6	2.21	32.64	3.5	12.64	33.80	2.4	12.62
Chang	57.26	0.6	2.22	33.32	3.2	13.35	34.39	2.4	12.69
Sharp-Wentworth	24.92	1.0	9.15	8.71	1.0	4.92	14.66	1.0	5.47
Freeman-Carroll	25.39	0.3	9.08	7.80	1.4	4.20	14.21	1.4	5.15
Coat-Redfern	14.88	0.9	11.65	18.30	0.9	12.14	25.87	0.9	12.89
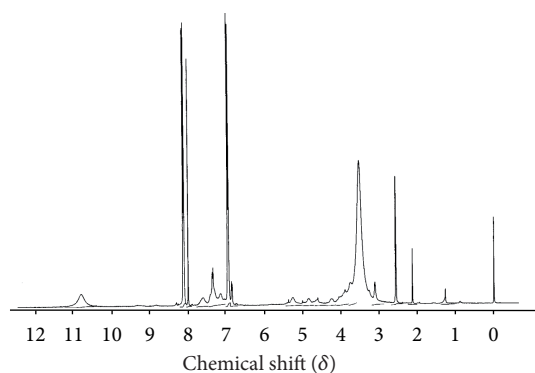
FIGURE 4: ^{1}H-NMR spectrum of p-NP-4,4$'$-MDA-F copolymer.

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 δ 3.1 and δ 2.5 ppm, respectively [31, 32].

3.1.5. Thermogravimetric Analysis.
Thermal degradation behavior and kinetic data of copolymer are recorded in Table 3 and thermogram is shown in Figure 5. The resin p-NP-4,4$'$-MDA-F exhibits three stages of decomposition. When temperature was raised to 130°C, it showed the weight loss about 3.48% and is corresponding to the moisture entrapped in molecule or water of crystallization associated with this copolymer [15, 35]. This is in agreement with the weight loss calculated theoretically which is about 3.39%. Second step is slow decomposition in temperature range 130–270°C, corresponding to 27.30% mass loss which may be attributed to loss of two hydroxyl and nitro groups against calculated value of 27.16% loss present per repeat unit of polymer. The third step of decomposition starts from temperature 270 to 600°C, corresponding to 61.64% loss of

degraded moiety (Figure 5) against calculated weight loss of 61.13%.

3.2. 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 does not takes much more time to attain the thermal equilibrium as well as at 600°C degradation process occurs upto final level leaving behind the remaining moiety. The thermal stability of p-NP-4,4$'$-MDA-F 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 [36] or it may be due to possibility of an almost linear structure of copolymer chain which gives stability to polymer chain [37].

In general, the water of hydration may be considered as crystal water. In the present case removal of one water molecule is complete and is probably crystal water or moisture entrapped in the molecule. By applying the thermogravimetric data to five thermal degradation kinetic techniques (viz. 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 copolymer have been calculated using Friedman method (1). Activation energy (E_a) has been obtained from the plot between $\ln(d\alpha/dt)$ versus $(1/T)$ (Figure 6) and order of reaction (n) from the plot between $\ln(1-\alpha)$ versus $(1/T)$ (Figure 7). Values of $\ln(z)$ are calculated at each temperature region from (1) with the help of E_a and n.

Figure 8 has shown that Chang method (2) gives plots between $[\ln(d\alpha/dt)/(1 - \alpha)^n]$ versus $(1/T)$ for p-NP-4,4$'$-MDA-F at the heating rate 10°C·min^{-1} which is used to
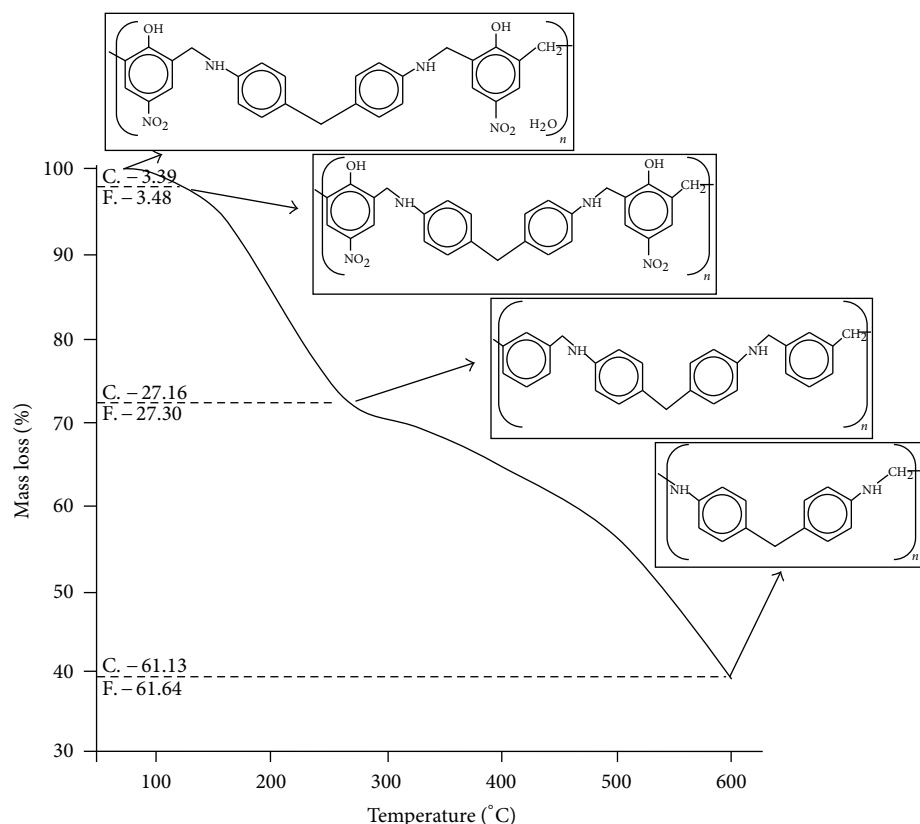
FIGURE 5: Decomposition pattern of p-NP-4,4$'$-MDA-F copolymer.
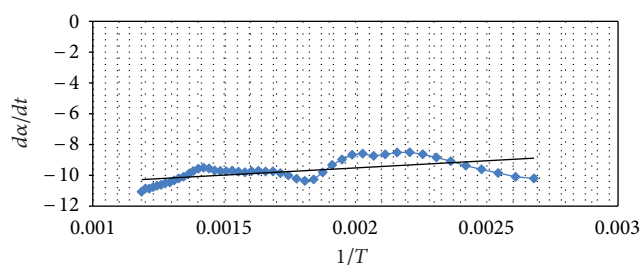
FIGURE 6: Friedman plot of p-NP-4,4$'$-MDA-F copolymer for activation energy.
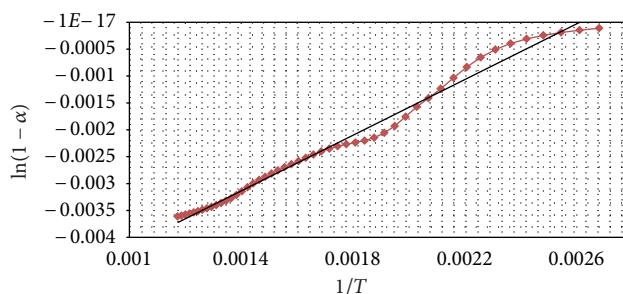
FIGURE 7: Friedman plot of p-NP-4,4$'$-MDA-F copolymer for the order of reaction.

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.
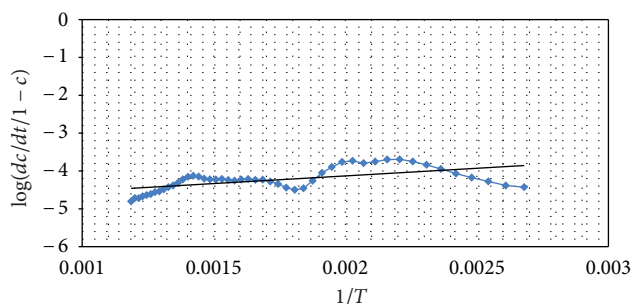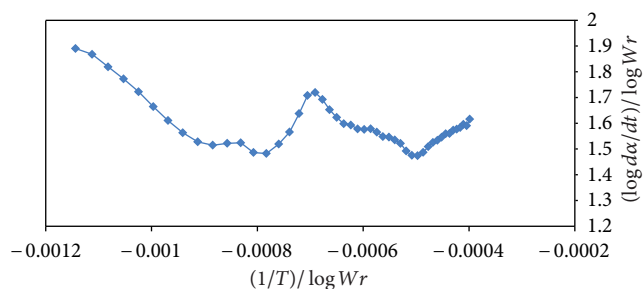
Also kinetic parameters for different thermal degradation zones have been calculated by Sharp-Wentworth method (3). E_a and ln (z) values are calculated from the plot between $\log(dc/dt)/(1-c)$ versus $1/T$ with best fitted values of n for each respective degradation reaction (Figure 9).

Similarly using the Freeman-Carroll technique (4) kinetic parameters has been calculated. Figure 10 has shown representative plot of $(\Delta \ln(d\alpha/dt))/(\Delta \ln(1-\alpha))$ versus $\Delta(1/T)/(\Delta \ln(1-\alpha))$ for p-NP-4,4$'$-MDA-F. 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 $\ln[(1-(1-\alpha)^{1-n})/(T^2(1-n))]$ versus $(1/T)$ for p-NP-4,4$'$-MDA-F, which results in straight line of slope $[-E_a/R]$ for correct value of n (Figure 11). The results of kinetic parameters of above-mentioned methods have been incorporated in Table 4.

A plot of percentage mass loss versus temperature is shown in Figure 5 for a representative p-NP-4,4$'$-MDA-F copolymer. From the TG curves, the thermoanalytical data and decomposition temperature have been determined for
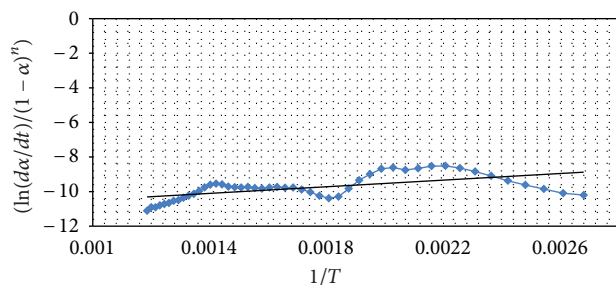
FIGURE 8: Chang plot of p-NP-4,4$'$-MDA-F copolymer.

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

FIGURE 9: Sharp-Wentworth plot of p-NP-4,4$'$-MDA-Fcopolymer.
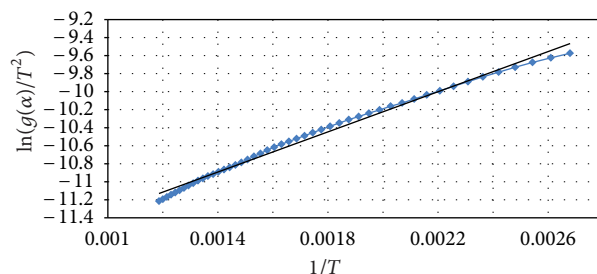
FIGURE 11: Coat-Redfern plot of p-NP-4,4$'$-MDA-F copolymer.

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 in the kinetic parameters, that is, E_a, n, and $\ln(z)$ that are obtained by Friedman and Chang may be due to analogy in mathematical model. Also fairly similar results with slight variations obtained by Sharp-Wentworth and Freeman-Carroll methods, but Coat-Redfern method, show different observations.

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 [20]. 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 nonisothermal conditions. Low values of frequency factor revealed that decomposition reaction of copolymer may be slow and no other possible reason can be given [38, 39]. As a consequence these kinetic parameters are fictive from the point of view of chemical kinetics.

By using above-mentioned techniques fairly similar results are obtained which represents versatility and great utility of thermal degradation mathematical equations in thermal studies and attempts are developing to implement the model free kinetic equations.

4. Conclusion

Synthesis of targeted copolymer (p-NP-4,4$'$-MDA-F) has been confirmed which is supported by the results obtained by the elemental analysis and spectral data. Thermogram has shown three degradation stages, first indicating degradation of water molecule, second shows removal of two (–OH) and (–NO$_2$) groups, and third step represents two side benzene rings with methylene groups. Friedman and Chang methods show nearly similar values of kinetic parameters may be due to resemblance in mathematical model, whereas results obtained from Freeman-Carroll and Sharp-Wentworth are in well agreement with each other, but Coat-Redfern method shows different observations. 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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