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Research Article

Thermal Degradation Studies of Terpolymer Derived from 2-Aminothiophenol, Hexamethylenediamine, and Formaldehyde

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Terpolymer (2-ATPHMDAF-I) has been synthesized by the condensation of 2-aminothiophenol and hexamethylenediamine with formaldehyde in the presence of 2 M hydrochloric acid as a catalyst with 1 : 1 : 2 molar proportion of reacting monomers. The structure of newly synthesized terpolymer has been elucidated and confirmed on the basis of elemental analysis and various spectral techniques, that is, UV-visible, FT-IR, and ^{1}H-NMR spectroscopy. Number average molecular weight ($\overline{\text{Mn}}$) has been determined by conductometric titration in nonaqueous medium. The viscosity measurements in dimethyl sulfoxide (DMSO) have been carried out to ascertain the characteristic functions and constants. 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), order of reaction (n), and frequency factor (z) were calculated by Friedman, Chang, Sharp-Wentworth and Freeman-Carroll methods. Activation energy calculated by Friedman and Chang methods are in close agreement with each other while the results obtained from Freeman-Carroll and Sharp-Wentworth's methods are found to be in a similar order.

1. Introduction

Study of thermal 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. Since the modern history of thermogravimetry, thermal degradation of polymers and the study of their kinetics have been at the center of thermal analysis. 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 has become a subject of recent interest, being an important property which primarily decides thermal stability and processability. A wide variety of thermally stable polymers have been synthesized and studied their thermogravimetric property and finds many applications such as ion-exchangers [1–5], semiconductors [6], high dielectric constant for energy storage capacitors [7], packaging, adhesives and coatings in electrical sensors, activators, catalysts and thermally stable materials [8–10]. 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 [11].

The thermal stability of terpolymers has been extensively studied by employing the method of thermogravimetric analysis (TGA) by several authors [12–21]. 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]. Thermal and metal ion bonding properties of terpolymer resin synthesized from resorcinol-thiourea-formaldehyde have been reported by Karunakaran et al. [14]. The thermal degradation kinetics of some new terpolymers

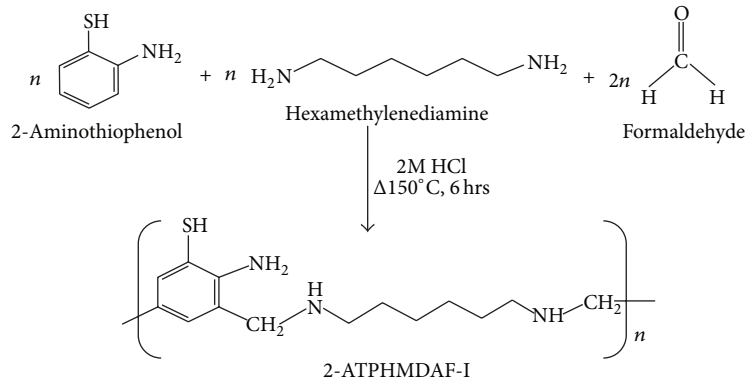

Figure 1: Chemical reaction of 2-ATPHMDAF-I terpolymer.

derived from 2,4-dihydroxypropiophenone, oxamide, and formaldehyde have been studied by Tarase et al. [15]. Non-isothermal decomposition and kinetic analysis of copolymer derived from 2,4-dihydroxybenzoic acid, melamine, and formaldehyde have been reported by Butoliya et al. [16]. Michael et al. carried out thermal degradation of terpolymers synthesized from salicylic acid/8-hydroxyquinoline and guanidine with formaldehyde [17, 18]. Thermogravimetric analysis of terpolymer resins derived from 2,4-dihydroxyacetophenone, dithiooxamide, and formaldehyde by Rahangdale et al. [19], 8-hydroxyquinoline, dithiooxamide, and formaldehyde by Katkamwar et al. [20], and 8-hydroxyquinoline-5-sulphonic acid, catechol, and formaldehyde by Mandavgade et al. [21] has been studied in detail. 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 being negligible.

In our earlier communications [3, 12, 13, 15–17, 19, 20, 22], various studies on synthesis, characterization, and thermogravimetric analysis of some new polymeric resins have been reported. Hence, in the present investigation, it has been planned to study the nonisothermal thermogravimetric analysis of terpolymer derived from 2-aminothiophenol, hexamethylenediamine, and formaldehyde which has not been reported so far in literature.

2. Materials and Methods

2.1. Starting Materials. 2-Aminothiophenol and hexamethylenediamine used in the present investigation of analytical grade purity were purchased from Acros Chemicals, Belgium, and Aldrich, USA, respectively. 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.

2.2. Synthesis. 2-ATPHMDAF-I terpolymer was prepared by condensing 2-aminothiophenol and hexamethylenediamine with formaldehyde in the presence of 2 M hydrochloric acid as a catalyst in 1 : 1 : 2 molar proportions at temperature 150°C in an oil bath for about 6 hrs. The yellowish white colored solid product was obtained. The product obtained was extracted with diethyl ether to remove the excess of 2-aminothiophenol-formaldehyde copolymer which might be present along with 2-ATPHMDAF-I terpolymer. The chemical reaction of above synthesis has been depicted in Figure 1.

2.3. Characterization of Terpolymer. Newly synthesized and purified terpolymer was subjected to elemental analysis for carbon, hydrogen, nitrogen, and sulphur on Elementar Vario EL-III Elemental Analyzer and ultraviolet-visible spectra of terpolymer in dimethyl sulfoxide (DMSO) solvent recorded on Varian Carry 5000 UV-Vis spectrophotometer in the range from 200 to 800 nm at Sophisticated Test and Instrumentation Center Cochin, University of Science and Technology, Cochin. ^{1}H-NMR study was performed in DMSO as solvent on Bruker Advance-II 400 NMR spectrophotometer. Infrared spectrum was recorded in nujol mull on Perkin Elmer Spectrum RX-I spectrophotometer in the range from 4000 to 400 cm^{-1} at Sophisticated Analytical Instrumentation Facility (SAIF), Punjab University, Chandigarh. The nonisothermal thermogravimetric analysis of newly prepared terpolymer has been carried out using Perkin Elmer Diamond 3-II thermogravimetric analyzer, in air atmosphere with a heating rate of 10°C min^{-1} in the temperature range from 40 to 1000°C at Vishveshwarya National Institute of Technology (VNIT), Nagpur.

2.4. Analytical and Physicochemical Studies. The number average molecular weight ($\overline{\text{Mn}}$) was determined by conductometric titration in nonaqueous medium such as dimethyl sulfoxide (DMSO) using ethanolic KOH as a titrant. Conductometric titration in nonaqueous media has been proved to be a simple yet effective method used by earlier research workers [13, 23, 24] for the determination of number average molecular weight of phenol-formaldehyde resins [25].

The intrinsic viscosity of newly synthesized terpolymer has been evaluated using Ubbelohde viscometer [26, 27] fabricated in our research laboratory at different concentrations ranging from 0.3 to 0.05% of terpolymer in DMSO at 30°C.

Table 1: Elemental analysis data of 2-ATPHMDAF-I terpolymer.

Terpolymer	Carbon (%)		Hydrogen (%)		Nitrogen (%)		Sulphur (%)		Yield (%)
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	
2-ATPHMDAF-I	63.15	63.40	8.43	8.68	15.74	15.85	11.87	12.08	80.55

Intrinsic viscosity $[\eta]$ was calculated from relevant plots of Huggins equation (1) [28] and Kraemer's equation (2) [29]. Consider

$$\frac{\eta_{sp}}{C} = [\eta] + K_1[\eta]^2 \cdot C \quad (1)$$

$$\ln \frac{\eta_{rel}}{C} = [\eta] + K_2[\eta]^2 \cdot C, \quad (2)$$

where η_r is the relative viscosity, $[\eta] = \lim_{C \to 0}(\eta_{sp}/C)$, K_1 is Huggins' constant, and K_2 is Kraemer's constant.

2.5. Thermal Studies

2.5.1. 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 Friedman [30], Chang [31], Sharp-Wentworth [32], and Freeman-Carroll [33] methods as follows.

Friedman's technique is as follows:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(z) + n\ln(1-\alpha) - \frac{E_a}{RT}, \quad (3)$$

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.

Chang's technique is as follows:

$$\ln \frac{(d\alpha/dt)}{(1-\alpha)^n} = \ln(z) - \frac{E_a}{RT}. \quad (4)$$

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.

Sharp-Wentworth's technique is as follows:

$$\log \frac{dc/dt}{1-c} = \log\left(\frac{A}{\beta}\right) - \frac{E_a}{2.303R} \cdot \frac{1}{T}, \quad (5)$$

where dc/dt is the 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.

Freeman-Carroll's technique is as follows:

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} = \left(-\frac{E_a}{2.303R}\right) \cdot \frac{\Delta(1/T)}{\Delta \log W_r} + n, \quad (6)$$

where dw/dt is the rate of change of weight with time, $W_r = W_c - W$, W_c is the weight loss at the completion of reaction; W is the total weight loss up to time, E_a is the energy of activation, and n is the order of reaction.

The $\Delta\log(dw/dt)$ and $\Delta \log W_r$ values were 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.

3. Results and Discussion

3.1. Elemental Analysis. The results of elemental analysis are shown in Table 1 used to assign empirical formula and empirical weight for 2-ATPHMDAF-I terpolymer. Composition of terpolymer was assigned on the basis of elemental analysis and was found to be in good agreement with that of calculated values.

The number average molecular weight ($\overline{\text{Mn}}$) of this terpolymer has been determined by conductometric titration method in nonaqueous medium using standard potassium hydroxide (0.05 M) in absolute ethanol as a titrant. The specific conductance was plotted against milliequivalents of ethanolic KOH required for neutralization of 100 g of each terpolymer. There are several breaks before the complete neutralization of all phenolic thiol groups. The first break in the plot was the smallest break and it is assumed that this corresponds to a stage in titration when an average of one phenolic thiol group of each chain was neutralized. From the plot, the first and final breaks were noted. The average degree of polymerization ($\overline{\text{Dp}}$) and hence the number average molecular weight ($\overline{\text{Mn}}$) of terpolymer have been determined using the following formula:

$$\left(\overline{\text{Dp}}\right) = \frac{\text{Total milliequivalents of base required for complete neutralisation}}{\text{Milliequivalents of base required for smallest interval}},$$

$$\left(\overline{\text{Mn}}\right) = \left(\overline{\text{Dp}}\right) \times \text{Repeat unit weight}. \quad (7)$$

It is observed that the molecular weight of terpolymer increases with the increase in hexamethylenediamine content. This observation is in agreement with the trend observed by earlier researchers [17]. Conductometric titration curve of terpolymer was shown in Figure 2 and the results are presented in Table 2.

The intrinsic viscosity $[\eta]$ was determined by the corresponding linear plots (Figure 3). Huggins and Kraemer's

Table 2: Molecular weight determination and viscometric data of 2-ATPHMDAF-I terpolymer.

Terpolymer	Empirical formula of repeat unit	Empirical weight of repeat unit	Average degree of polymerization ($\overline{Dp}$)	Average molecular weight ($\overline{Mn}$)	Intrinsic viscosity [η] dL g^{-1}	Huggins constant (K_1)	Kraemer's constant (K_2)	$K_1 + K_2$
2-ATPHMDAF-I	$C_{14}H_{23}N_3S_1$	265	32	8480	0.82	0.286	0.272	0.558

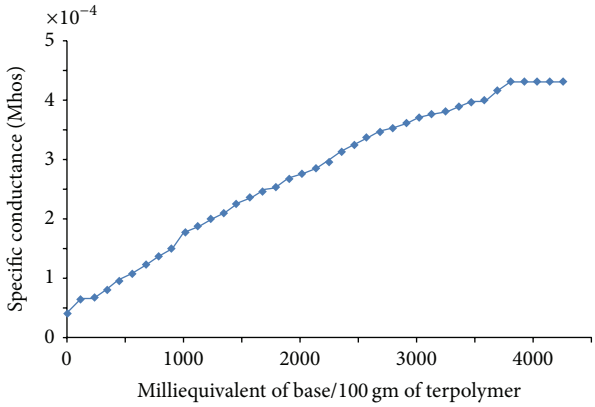

Figure 2: Conductometric titration curve of 2-ATPHMDAF-I terpolymer.

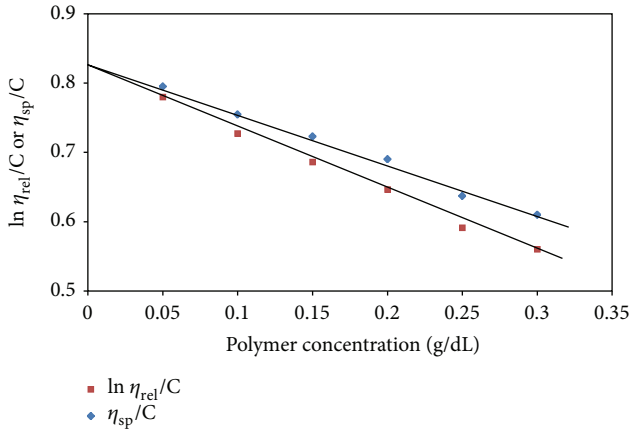

Figure 3: Viscometric plot of 2-ATPHMDAF-I terpolymer.

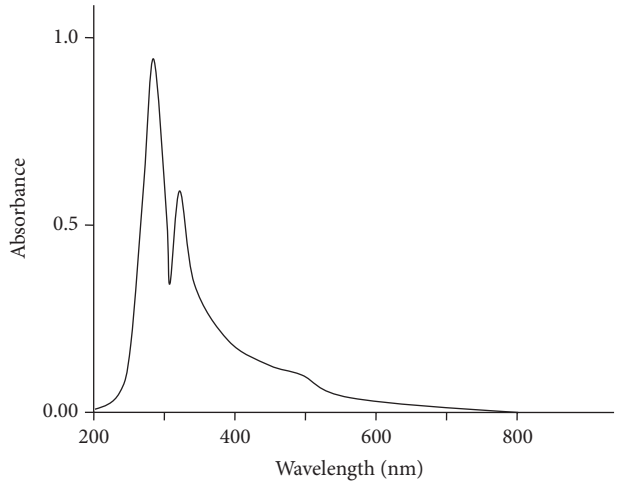

Figure 4: UV-visible spectrum of 2-ATPHMDAF-I terpolymer.

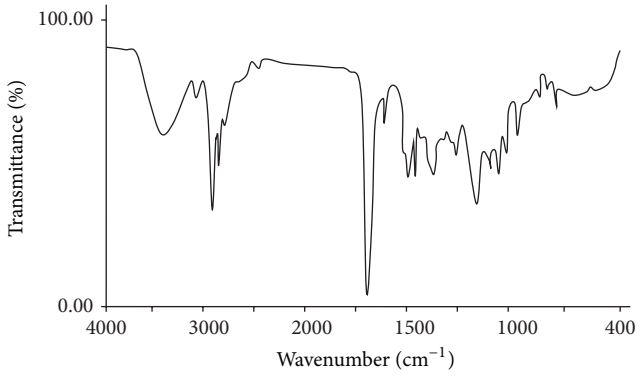

Figure 5: FT-IR spectrum of 2-ATPHMDAF-I terpolymer.

constants were determined by (1) and (2). According to the above relations, the plots of η_{sp}/C and $\ln \eta_{rel}/C$ against C were linear with slopes of K_1 and K_2, respectively. By extrapolating linear plot to zero concentration, intercepts on the viscosity function axis give [η] value in both plots. The calculated values of the constants K_1 and K_2 (Table 2) in most cases satisfy the relation $K_1 + K_2 = 0.5$ favorably. It was observed that terpolymer having higher ($\overline{Mn}$) shows higher value of [η].

3.2. UV-Visible Spectra. The UV-visible spectrum is depicted in Figure 4 for 2-ATPHMDAF-I terpolymer sample in pure DMSO recorded in the region from 200 to 800 nm. The spectrum exhibits two absorption maxima in the regions 280–300 and 300–330 nm. These observed positions for the absorption bands have different intensities. The more intense band is due to $\pi \rightarrow \pi^*$ allowed transition of conjugation in aromatic ring which is shifted from the basic value 269 nm to 280–300 nm and the medium band at 300–330 nm is due to $n \rightarrow \pi^*$ forbidden transition of –SH group.

The more intense band is due to the fact that bathochromic shift may be due to the combining effect of conjugation and the phenolic –SH and –NH_2 groups. Both bathochromic and hyperchromic effects of conjugation are shown by chromophore (aromatic ring) due to auxochromic substituents –SH and –NH_2 groups in terpolymer. This observation is in good agreement with the proposed most probable structure of above terpolymer.

3.3. FT-IR Spectra. The FT-IR spectrum of 2-ATPHMDAF-I terpolymer depicted in Figure 5 and spectral data are

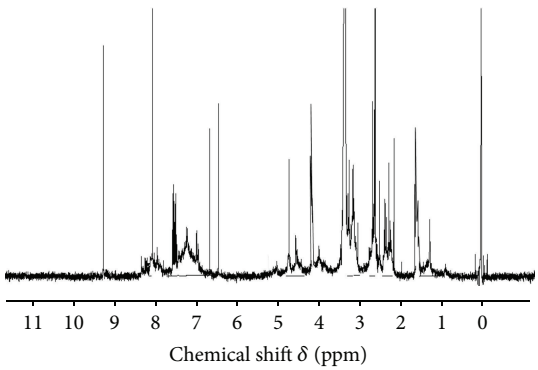

Figure 6: ^{1}H-NMR spectrum of 2-ATPHMDAF-I terpolymer.

Table 3: IR frequencies of 2-ATPHMDAF-I terpolymer.

Observed wavenumber (cm^{-1})	Assignments
3434 b, st	>NH stretching (sec. amine)
3024 m	>C–H stretching (aromatics)
2600 w	–SH (phenolic thiol)
1650–1700 sh	>NH bending (sec. amine)
1482 m	>C=C< (aromatic ring)
1236 m	C–N stretching (aromatic amine)
807 w 1013 m	Tetrasubstitution in benzene skeleton
	Methylene bridge
1467 m	$-CH_2$ bending
1345 b, m	$-CH_2$ wagging
729 m	$-CH_2$ rocking

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

Table 4: ^{1}H-NMR spectral data of 2-ATPHMDAF-I terpolymer.

^{1}H-NMR chemical shift (δ) ppm of terpolymer	Nature of protons assigned
8.05 s	Meta proton of Ar–H (aromatic –H)
7.2 s	Proton of Ar–SH (thiophenol)
6.7 s	Amino proton of $-CH_2-NH-CH_2-$ (NH-bridge)
6.5 s	Proton of Ar–NH_2 (phenolic –NH_2)
4.1 t	Methylene proton of $-NH-CH_2-CH_2-$ linkage
2.5 s	Methylene proton of Ar–CH_2–NH– linkage
1.5 q	Methylene proton of $-CH_2-CH_2-CH_2-$ linkage

tabulated in Table 3. A broad and strong band appeared at 3434 cm^{-1} which may be assigned due to the >NH stretching (sec. amine). A medium and sharp band displayed at 3024 cm^{-1} may be assigned due to the stretching vibration of aromatic C–H group. A weak band at 2600 cm^{-1} indicates the presence of a –SH (phenolic thiol) group. A sharp band appearing in the region of 1650–1700 cm^{-1} may be due to bending vibration of >NH (sec. amine) group. A medium band appearing at 1482 cm^{-1} indicates the presence of >C=C< (aromatic) group. Aromatic C–N stretch appeared in the region of 1236 cm^{-1} which shows medium band. The presence of tetrasubstituted benzene skeleton shows weak and medium peaks at 807 cm^{-1} and 1013 cm^{-1}. The methylenic bridge shows broad and medium peaks for bending, wagging, and rocking vibration appearing at 1467, 1345, and 729 cm^{-1}.

3.4. ^{1}H-NMR Spectra. ^{1}H-NMR spectral data are incorporated in Table 4 and spectrum is presented in Figure 6. 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 δ 8.05 ppm is due to metaproton of Ar–H. A singlet observed at δ 7.2 ppm is due to proton of Ar–SH (thiophenol). Amino proton of $-CH_2-NH-CH_2-$ linkage gives singlet that is observed at δ 6.7 ppm. Amino proton of aromatic amine gives singlet at δ 6.5 ppm. Methylenic proton of $-NH-CH_2-CH_2-$ linkage gives triplet at δ 4.1 ppm. Singlet is observed at δ 2.5 ppm due to methylenic proton of Ar–CH_2–NH– linkage. The quintet at δ 1.5 ppm may be attributed to methylenic proton of $-CH_2-CH_2-CH_2-$ linkage.

3.5. Thermogravimetric Analysis. 2-ATPHMDAF-I terpolymer was subjected to thermogravimetric analysis and the data was used to assess the degradation pattern. Thermal degradation behavior of synthesized terpolymer has been incorporated in Table 5 and decomposition pattern is shown in Figure 7 in temperature range from 40 to 1000°C.

Decomposition pattern of terpolymer thermogram shows four decomposition steps in which the loss of water molecule (6.12% expected and 6.36% calculated) has been observed in the first step up to 130°C. Second decomposition step starts from 130 to 230°C which represents the degradation of –SH and –NH_2 groups attached to aromatic nucleus (23.52% expected and 23.67% calculated). The third decomposition step starts from 230 to 320°C, corresponding to 59.66% mass loss of aromatic nucleus with two methylene groups against calculated 59.71%. The fourth decomposition step starts from 320 to 990°C which corresponds to loss of complete hexamethylenediamine moiety (98.67% expected and 100% calculated). Consequently, no residue may be assigned after complete degradation.

3.6. Kinetics of Thermal Decomposition by the Friedman, Chang, Sharp and Wentworth, and Freeman-Carroll Methods. The observed thermal stability of 2-ATPHMDAF-I 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 Friedman, Chang, 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 6. This kinetic analysis should be

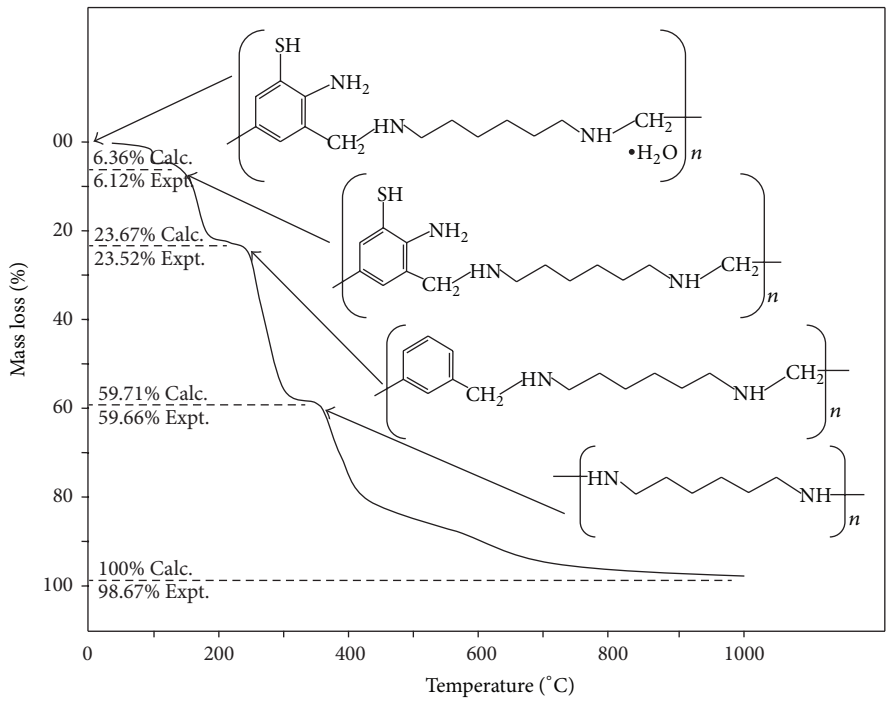

Figure 7: Decomposition pattern of 2-ATPHMDF-I terpolymer.

Table 5: Thermal degradation behavior of 2-ATPHMDAF-I terpolymer.

Terpolymer	Stages of decomposition	Temp. range (°C)	Species degraded	Wt. loss (%)	
				Expt.	Calc.
2-ATPHMDAF-I	First	40–130	One water molecule	6.12	6.36
	Second	130–230	One –SH and one $-NH_2$ group	23.52	23.67
	Third	230–320	Benzene ring along with side chain of hexamethylenediamine moiety	59.66	59.71
	Forth	320–990	Complete loss of hexamethylenediamine moiety	98.67	100

Table 6: Thermoanalytical data for each degradation step of 2-ATPHMDF-I terpolymer.

Methods	Decomposition steps								
	I			II			III		
	E_a	n	z	E_a	n	z	E_a	n	z
Friedman	32.11	1.14	5.34	42.01	1.05	12.23	28.67	1.15	12.01
Chang	31.93	1.0	5.38	43.90	1.0	12.44	28.34	1.0	12.03
Sharp-Wentworth	13.95	1.0	7.04	18.19	1.0	7.66	12.42	1.0	8.47
Freeman-Carroll	15.56	0.9	6.12	25.19	1.33	5.30	8.12	1.32	5.21

a starting point to obtain the useful information on the behavior of sample.

To obtain the relative thermal stability of terpolymer, the methods described by Friedman, Chang, 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 Friedman and Chang's methods and some different results are obtained in Sharp and Wentworth and Freeman-Carroll's methods as shown in Table 6.

Fairly comparable results of kinetic parameters, namely, E_a, n, and z, are obtained for each degradation step by Friedman and Chang method and may be due to analogy in mathematical model. Also, results 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

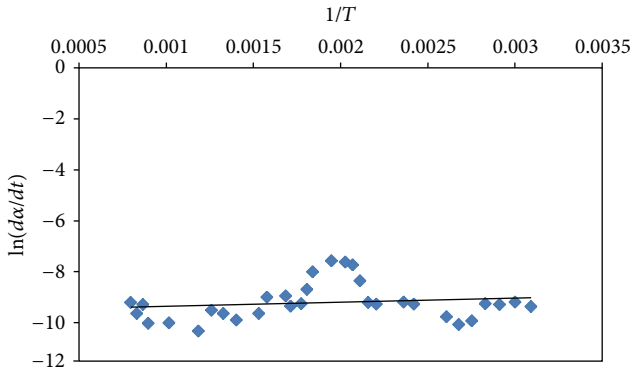

Figure 8: Friedman's plot of 2-ATPHMDAF-I terpolymer for energy of activation.

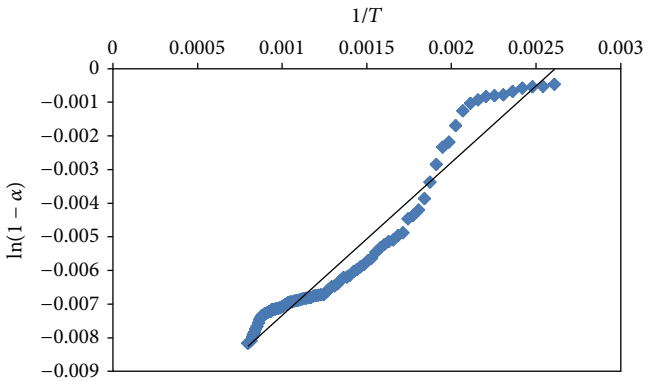

Figure 9: Friedman's plot of 2-ATPHMDAF-I terpolymer for order of reaction.

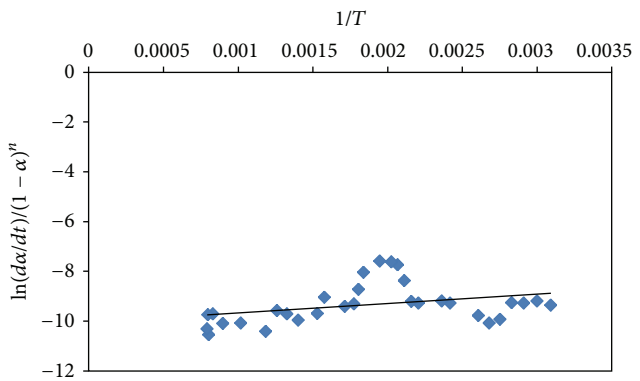

Figure 10: Chang's plot of 2-ATPHMDAF-I terpolymer.

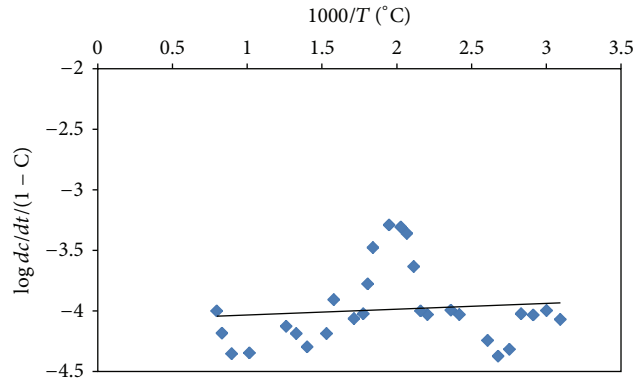

Figure 11: Sharp and Wentworth's plot of 2-ATPHMDAF-I terpolymer.

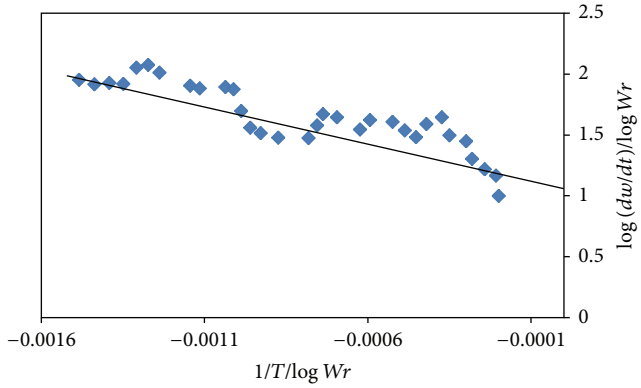

Figure 12: Freeman-Carroll's plot of 2-ATPHMDAF-I terpolymer for order of reaction.

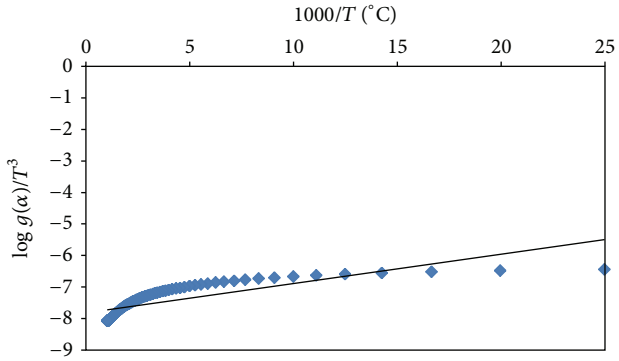

Figure 13: Freeman-Carroll's plot of 2-ATPHMDAF-I terpolymer for activation energy.

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 terpolymer have been shown in Figures 8, 9, 10, 11, 12, and 13 to calculate energy of activation, order reaction, and frequency factor.

By using the above mentioned methods, fairly similar results are obtained in Friedman and Chang's methods and 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, 2-ATPHMDAF-I 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 Friedman, Chang, 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 [13, 34].

4. Conclusion

Synthesis of targeted terpolymer (2-ATPHMDAF-I) has been confirmed which is supported by the results obtained by elemental analysis and spectral data. From the elemental analysis, electronic, IR, and ^{1}H-NMR spectral studies, the proposed structure of the synthesized terpolymer is confirmed. The values of kinetic parameter calculated from the Friedman and Chang methods are in good agreement with each other and values obtained from the Sharp and Wentworth and Freeman-Carroll methods are also in similar order. Thermogram of targeted terpolymer shows four degradation steps and hexamethylenediamine molecule almost degrades completely up to 990°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.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

[1] W. B. Gurnule, P. K. Rahangdale, L. J. Paliwal, and R. B. Kharat, "Chelation ion-exchange properties of copolymer resin derived from 4-hydroxyacetophenone, oxamide, and formaldehyde," *Journal of Applied Polymer Science*, vol. 89, no. 3, pp. 787–790, 2003.

[2] V. D. Mane, N. J. Wahane, and W. B. Gurnule, "Copolymer resin. VII. 8-hydroxyquinoline-5-sulfonic acid-thiourea- formaldehyde copolymer resins and their ion-exchange properties," *Journal of Applied Polymer Science*, vol. 111, no. 6, pp. 3039–3049, 2009.

[3] M. V. Tarase, A. B. Zade, and W. B. Gurnule, "Resin I: synthesis, characterization, and ion-exchange properties of terpolymer resins derived from 2,4-dihydroxypropiophenone, biuret, and formaldehyde," *Journal of Applied Polymer Science*, vol. 108, no. 2, pp. 738–746, 2008.

[4] A. D. Kushwaha, A. B. Kalambe, V. V. Hiwase, and D. N. Urade, "Structural and antibacterial study of resin-II derived from p-nitrophenol, resorcinol and formaldehyde," *Journal of Chemical and Pharmaceutical Research*, vol. 4, no. 2, pp. 1111–1116, 2012.

[5] W. Hackenberger, R. Alberta, W. Paul, D. Jeong, and Q. Zhang, "High dielectric constant terpolymers for energy storage capacitors," in *Proceedings of the 25th Symposium for Passive Components*, pp. 239–243, Palm Springs, 2005.

[6] S. K. Kapse, V. V. Hiwase, and A. B. Kalambe, "Synthesis and semi conducting behaviour of the ter-polyligand derived from p-hydroxyacetophenone, quinhydrone and melamine," *Journal of Chemical and Pharmaceutical Research*, vol. 4, no. 3, pp. 1734–1739, 2012.

[7] D. N. Urade, V. V. Hiwase, and A. B. Kalambe, "Structural and thermokinetic parameters of terpolymeric resin derived from p-hydroxyacetophenone, bis (2-amino- 1, 3, 4 -thiadiazole) and glycerol," *Journal of Chemical and Pharmaceutical Research*, vol. 4, no. 1, pp. 732–740, 2012.

[8] S. Pashaei, S. Siddaramaiah, M. M. Avval, and A. A. Syed, "Thermal degradation kinetics of nylon6/gf/crysnano nanoclay nanocomposites by TGA," *Chemical Industry and Chemical Engineering Quarterly*, vol. 17, no. 2, pp. 141–151, 2011.

[9] A. Gardziella, L. A. Pilato, and A. Knop, *Phenolic Resins, Chemistry, Applications, Standardization, Safely and Ecology*, Springer, 2000.

[10] G. E. Zaikov, *Degradation and Stabilization of Polymers*, Theory and Practice, Nova Science Publishers, New Delhi, India, 1995.

[11] N. G. Grassie, *Scott Polymer Degradation and Stabilization*, Cambridge Press, Cambridge, Mass, USA, 1985.

[12] R. N. Singru, A. B. Zade, and W. B. Gurnule, "Thermoanalytical study and kinetics of new 8-hydroxyquinoline 5-sulphonic acid-oxamide-formaldehyde terpolymer resins," *E-Journal of Chemistry*, vol. 6, no. 1, pp. S171–S182, 2009.

[13] R. N. Singru, A. B. Zade, and W. B. Gurnule, "Synthesis, characterization, and thermal degradation studies of copolymer resin derived from p-cresol, melamine, and formaldehyde," *Journal of Applied Polymer Science*, vol. 109, no. 2, pp. 859–868, 2008.

[14] M. Karunakaran, C. T. Vijayakumar, C. Magesh, and T. Amudha, "Terpolymer resin-ii -thermal and metal ion binding properties of resorcinolthiourea- formaldehyde terpolymer resin," *International Journal of Engineering Science and Technology*, vol. 3, no. 1, pp. 162–176, 2011.

[15] M. V. Tarase, A. B. Zade, and W. B. Gurnule, "Kinetics of thermal degradation studies of some new terpolymers derived from 2, 4-dihydroxypropiophenone, oxamide, and formaldehyde," *Journal of Applied Polymer Science*, vol. 116, no. 2, pp. 619–627, 2010.

[16] S. S. Butoliya, W. B. Gurnule, and A. B. Zade, "Study of non-isothermal decomposition and kinetic analysis of 2,4-dihydroxybenzoic acid-melamine-formaldehyde copolymer," *E-Journal of Chemistry*, vol. 7, no. 3, pp. 1101–1107, 2010.

[17] P. E. P. Michael, P. S. Lingala, H. D. Juneja, and L. J. Paliwal, "Synthetic, structural, and thermal degradation of a tercopolymer derived from salicylic acid, guanidine, and formaldehyde," *Journal of Applied Polymer Science*, vol. 92, no. 4, pp. 2278–2283, 2004.

[18] P. E. P. Michael, J. M. Barbe, H. D. Juneja, and L. J. Paliwal, "Synthesis, characterization and thermal degradation of 8-hydroxyquinoline-guanidine-formaldehyde terpolymer," *European Polymer Journal*, vol. 43, no. 12, pp. 4995–5000, 2007.

[19] S. S. Rahangdale, A. B. Zade, and W. B. Gurnule, "Thermal degradation studies of terpolymer derived from 2, 4-dihydroxyacetophenone, dithiooxamide and formaldehyde," *Ultra Scienceno*, vol. 19, pp. 213–218, 2007.

[20] S. S. Katkamwar, A. B. Zade, and W. B. Gurnule, *Ultra Science*, vol. 73, no. 2, pp. 103–108, 2007.

[21] S. K. Mandavgade, J. R. Dontulwar, and W. B. Gurnule, "Thermal degradation study of new polymer derived fr om 8-hydroxyquinoline 5-sulphonic acid and catechol," *Der Pharma Chemicano*, vol. 4, no. 4, pp. 1695–1703, 2012.

[22] M. V. Tarase, A. B. Zade, and W. B. Gurnule, "Kinetics of thermal degradation studies of some new terpolymers derived from 2, 4-dihydroxypropiophenone, oxamide, and formaldehyde," *Journal of Applied Polymer Science*, vol. 116, no. 2, pp. 619–627, 2010.

[23] R. N. Singru, W. B. Gurnule, V. A. Khati, A. B. Zade, and J. R. Dontulwar, "Eco-friendly application of p-cresol-melamine-formaldehyde polymer resin as an ion-exchanger and its electrical and thermal study," *Desalination*, vol. 263, no. 1-3, pp. 200–210, 2010.

[24] R. H. Gupta, A. B. Zade, and W. B. Gurnule, "Resin-IV: synthesis and characterization of terpolymers derived from 2-hydroxyacetophenone, melamine, and formaldehyde," *Journal of Applied Polymer Science*, vol. 109, no. 5, pp. 3315–3320, 2008.

[25] G. E. Dunn and R. C. Donald, "Infrared spectra of aqueous sodium benzoates and salicylates in the carboxyl-stretching region: chelation in aqueous sodium salicylates," *Canadian Journal of Chemistry*, vol. 47, no. 24, pp. 4577–4588, 1969.

[26] R. J. Young and P. A. Lovell, *Introduction To Polymers*, Nelson Thornes, 2nd edition, 1991.

[27] N. P. S. Chauhan, "Terpolymerization of p-acetylpyridine oxime, p-methylacetophenone and formaldehyde, and its thermal studies," *Journal of Thermal Analysis and Calorimetry*, vol. 110, no. 3, pp. 1377–1388, 2012.

[28] M. L. Huggins, "The viscosity of dilute solutions of long-chain molecules. IV. Dependence on concentration," *Journal of the American Chemical Society*, vol. 64, no. 11, pp. 2716–2718, 1942.

[29] E. O. Kraemer, "Molecular weights of celluloses and cellulose derivates," *Industrial & Engineering Chemistry Research*, vol. 30, no. 10, pp. 1200–1203, 1938.

[30] H. L. Freidman, "Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic," *Journal of Polymer Science C: Polymer Symposia*, vol. 6, no. 1, pp. 183–195, 1964.

[31] W. L. Chang, "Decomposition behavior of polyurethanes via mathematical simulation," *Journal of Applied Polymer Science*, vol. 53, no. 13, pp. 1759–1769, 1994.

[32] J. H. Sharp and S. A. Wentworth, "Kinetic analysis of thermogravimetric data," *Analytical Chemistry*, vol. 41, no. 14, pp. 2060–2062, 1969.

[33] E. S. Freeman and B. Carroll, "The application of thermoanalytical techniques to reaction kinetics. The thermogravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate," *The Journal of Physical Chemistry*, vol. 62, no. 4, pp. 394–397, 1958.

[34] J. J. Zsago, "Kinetic analysis of thermogravimetric data," *The Journal of Physical Chemistry*, vol. 72, no. 7, pp. 2406–2411, 1968.