

Synthesis and Non-Isothermal Degradation Studies of Biphenol and Hexamethylenediamine

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Abstract: Polycondensation reaction was employed to synthesize the new 2,2'-BPHMDAF terpolymer from the monomers namely 2,2'-Biphenol (2,2'-BP), Hexamethylenediamine (HMDA) with Formaldehyde (F) in presence of 2M HCl as a catalyst using 1:1:2 molar ratios at temperature 150 °C. The terpolymer after purification was characterized by elemental analysis and spectral studies such as UV-Visible, FT-IR and ¹H-NMR spectra which were used to elucidate and confirmed the most probable structure of synthesized terpolymer. The synthesized terpolymer was then further characterized by different physicochemical techniques viz. Number average molecular weight determines by Non-aqueous Conductometric titration and Intrinsic viscosity by Ubbelohde Viscometer. The thermogravimetric study of the prepared terpolymer has been carried out by non isothermal thermogravimetry technique in which sample is subjected to condition of continuous increase in temperature at linear rate. Thermal study of the terpolymer was carried out to determine their mode of decomposition and relative thermal stability by calculating activation energy, order of reaction and frequency factor. Freeman-Carroll method's activation energy was further used to determine the thermodynamic parameters such as entropy change, free energy change and apparent entropy change. 2,2'-BPHMDAF terpolymer was synthesized to determine its thermal stability and which were proved to be thermally stable by studying above methods.

Keywords: Condensation polymerization, spectral studies, physicochemical techniques, thermogravimetric analysis, Study of kinetic parameters

1. Introduction

Polymers have become an essential and ubiquitous part of our lives. Polymer uses are being developed in such diverse areas like conduction and storage of electricity, heat and light, molecular based information, storage and processing, molecular composites, unique separation membranes, revolutionary new forms of food processing and packaging, health, housing, transportation, etc. Manufacturers have also used the polymers in creation of a variety of products from adhesives and lubricants to implantable devices like orthopedic plates, artificial joints and heart valves, non plastic objects like silicone and paper, and became a large part of our everyday life and can be found in hundreds of different products.

The decomposition pattern and kinetics of polymer degradation can be studied by thermogravimetric analysis and which can be carried out in inert as well as oxidative atmosphere [1]. A wide variety of thermally stable polymers have been synthesized and the sequence of their thermal stabilities has been predicted from their TG data. Kinetic analysis may effectively assist in studying degradation mechanism as well as in predicting the thermal stability of polymers [2]. 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 [3].

2. Literature Survey

Thermal degradation studies of p-nitrophenol based copolymer was done by Kalbende et al [4] and Friedman, Chang, Sharp-Wentworth, Freeman-Carroll and Coat-Redfern methods have been implemented in order to compute the kinetic parameters. Urade et al [5] carried out

structural and thermokinetic parameters of terpolymeric resin derived from p-hydroxyacetophenone, bis (2-amino- 1, 3, 4 -thiadiazole) and glycerol.

Thermoanalytical studies and kinetics of newly synthesized copolymer derived from p-hydroxybenzoic acid and semicarbazide with formaldehyde were carried out by Nandekar, Dontulwar and Gurnule [6]. Thermogravimetric and spectroscopic analysis of 8-hydroxyquinoline 5-sulphonic acid-melamine-formaldehyde polymer resin-IV was studied by Singru [7]. Butoliya et al [8] studied the non-isothermal decomposition and kinetic analysis of 2,4-dihydroxybenzoic acid-melamine-formaldehyde copolymer. Non-isothermal kinetic study of p-cresol-dithioxamide-formaldehyde terpolymer was done by Gurnule and Katkamwar [9]. Tarase et al carried out kinetics of thermal degradation studies of terpolymers derived from 2,4-dihydroxypropiophenone, oxamide and formaldehyde [10]. Acid catalyzed terpolymer resin 2,2'- biphenol-ethylenediamine-formaldehyde has been synthesized by Bobde et al and studied its physico-chemical and thermal degradation behaviour [11].

The development of new and improved polymers and their application in novel areas have led to infinite new products. Polymers differ in characteristics because of their unique structural complexities. Therefore, in this article, we have attempted to investigate the thermostability and several important kinetic parameters of terpolymer obtained by acid catalyzed polycondensation reaction of 2,2'-biphenol, hexamethylenediamine and formaldehyde to study the novelty of new thermally stable terpolymer.

3. Experimental

Materials and methods

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2,2'-Biphenol was purchased from Acros Organics Chemicals, Belgium, Hexamethylenediamine was procured from Aldrich, USA are of analytical grade purity and Formaldehyde (37 %) was purchased from S. D. Fine Chemicals, India. All the solvents used like N, N-dimethylformamide, dimethylsulphoxide, tetrahydrofuran, acetone and diethyl ether were procured from Merck, India.

Synthesis

2,2'-BPHMDAF terpolymer was synthesized by polycondensation of 2,2'-biphenol and hexamethylenediamine using the linkage of formaldehyde with the molar ratios of 1:1:2 in presence of 2M HCl (200 ml) as a catalyst. The mixture was heated at 150 °C in an oil bath for ten hours with frequent shaking [12-14]. The temperature of electrically heated oil bath was controlled with the help of dimmerstat. The solid pale pink colored product obtained was immediately removed from the flask as soon as the reaction period was over. The yield of this terpolymer was found to be 78.13 %. Figure 1 represents

proposed reaction and synthetic details are reported in Table 1 for the formation of 2,2'-BPHMDAF terpolymer as follows.

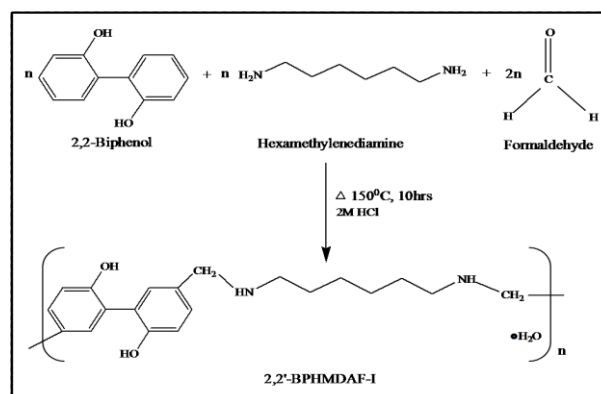


Figure 1: Proposed reaction for 2,2'-BPHMDAF terpolymer

Table 1: Synthesis details of 2, 2'-BPHMDAF terpolymer

Terpolymer	Reactants			Molar ratio	Catalyst 2M HCl (ml)	Reflux Temp. °C	Yield (%)	Time (hrs)
	2,2'-Biphenol (2,2'-BP) (mol)	Hexamethylene -diamine (HMDA) (mol)	Formaldehyde (F) (mol)					
2,2'-BPHMDAF	0.1	0.1	0.2	1:1:2	200	150	78.13	10

Characterization of terpolymer

Terpolymer was subjected to elemental analysis for carbon, hydrogen and nitrogen on Elementar Vario EL-III Elemental Analyzer and UV-VIS spectra of terpolymer in DMSO solvent recorded by Varian carry 5000 UV-VIS spectrophotometer at STIC, Cochin University of Science and Technology, Cochin. FT-IR spectra was recorded on Perkin Elmer Spectrum RX-1 spectrophotometer in the range of 4000 to 400 cm^{-1} and $^1\text{H-NMR}$ study has been carried out using Bruker Avance - II, 400 NMR spectrometer with DMSO- d_6 as a solvent were carried out at Sophisticated Analytical Instrumentation Facility (SAIF) Punjab University, Chandigarh.

The number average molecular weight (\overline{Mn}) has been determined by conductometric titration method in

$$\overline{DP} = \frac{\text{Total milliequivalents of base required for complete neutralisation}}{\text{Milliequivalents of base required for smallest interval}}$$

$$\overline{Mn} = \overline{DP} \times \text{weight of repeat unit (monomer)}$$

The intrinsic viscosity $[\eta]$ was determined by the corresponding linear plots using Ubbelohde viscometer [17-19] fabricated in our research laboratory at different concentrations ranging from 0.3 to 0.05 % of terpolymer in DMSO at 27 °C. Intrinsic viscosity $[\eta]$ was calculated from relevant plots of Huggin's equation and Kraemer's equation. Huggin's [20] and Kraemer's [21] constants were determined by (1) and (2).

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

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

Where,

η_r is the relative viscosity,

$[\eta] = \lim_{C \rightarrow 0} (\eta_{sp}/C)$,

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. Conductometric titration in non-aqueous media has been proved to be a simple yet effective method used by earlier research workers [15, 16]. There are several breaks before the complete neutralization of all phenolic 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 group of each chain was neutralized. From the plot, the first and final breaks were degree of polymerization (\overline{Dp}) and hence the number average molecular weight (\overline{Mn}) of terpolymer has been determined using the following formula:

K_1 is Huggins' constant and K_2 is Kraemer's constant.

Thermal studies

Non-isothermal thermogravimetric analysis of newly prepared terpolymer has been carried out on Perkin Elmer Diamond 3-II thermogravimetric analyzer at heating rate of 10 °C per minute in air atmosphere in the temperature range 40-1000 °C at Vishweshwarya National Institute of Technology (VNIT), Nagpur. The thermogram is recorded for sample. With the help of thermogravimetric data, the thermal activation energy (E_a) and order of reaction (n) has been calculated.

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. To provide further evidence regarding the degradation system of analyzed compounds, we derived the TG curves by applying an analytical method proposed by Friedman [22], Chang [23] and Freeman-Carroll [24] techniques as follows:

Friedman Technique:

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

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 $\ln(1-\alpha)$ 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:

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

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-Carroll technique:

$$\frac{\Delta\log\left(\frac{dw}{dt}\right)}{\Delta\log W_r} = \left(-\frac{E_a}{2.303 R}\right) \cdot \frac{\Delta\left(\frac{1}{T}\right)}{\Delta\log W_r} + n \quad (5)$$

Where,

dw/dt = Rate of change of weight with time.

$W_r = W_c - W$

W_c 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 the energy of activation; R is gas constant; T is temperature and n is the 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 $\frac{\Delta\log\left(\frac{dw}{dt}\right)}{\Delta\log W_r}$ vs $\frac{\Delta\left(\frac{1}{T}\right)}{\Delta\log W_r}$ gives a straight line. The slope and intercept are equal to $-(E_a/R)$ and n , respectively.

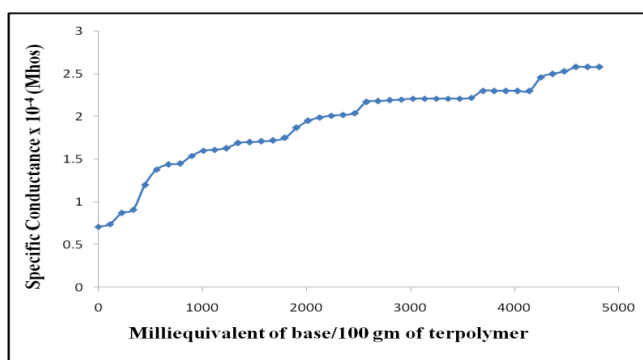
4. Results and Discussion

The percentage of C, H and N content during elemental analysis are shown in Table 2 used to assign empirical formula and empirical weight for 2,2'-BPHMDAF 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.

Table 2: Elemental analysis data of 2,2'-BPHMDAF terpolymer

Terpolymer	C (%)		H (%)		N (%)		Empirical formula of the repeating unit	Empirical formula weight
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.		
2,2'-BPHMDAF	73.25	73.62	7.59	7.98	8.21	8.59	$C_{20}H_{26}N_2O_2$	326

The results of conductometric titration method in nonaqueous medium have been presented in Table 3 and shown in Figure 2. From the plot, the first and last break was noted. The average degree of polymerization (\overline{Dp}) and hence the number average molecular mass (\overline{Mn}) of terpolymer has been determined using the above formula.

**Figure 2:** Conductometric titration curve of 2,2'-BPHMDAF terpolymer

Viscosity measurements were carried out using Ubbelohde viscometer. 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 $[\eta]$ value in both plots. The calculated values of the constants K_1 and K_2 in most cases satisfy the relation $K_1 + K_2 = 0.5$ favorably [25, 26]. It was observed that terpolymer having higher (\overline{Mn}) shows higher value of $[\eta]$. Viscometric data are tabulated in Table 3 and shown in figure 3.

Table 3: Molecular weight determination and viscometric data of 2,2'-BPHMDAF terpolymer

Terpolymer	Average degree of polymerization (\overline{Dp})	Average molecular weight (\overline{Mn})	Intrinsic Viscosity $[\eta]$ dl g ⁻¹	Huggin's Constant (K_1)	Kraemer's Constant (K_2)	$K_1 + K_2$
2,2'-BPHMDAF	12.33	4020.66	0.51	0.254	0.269	0.523

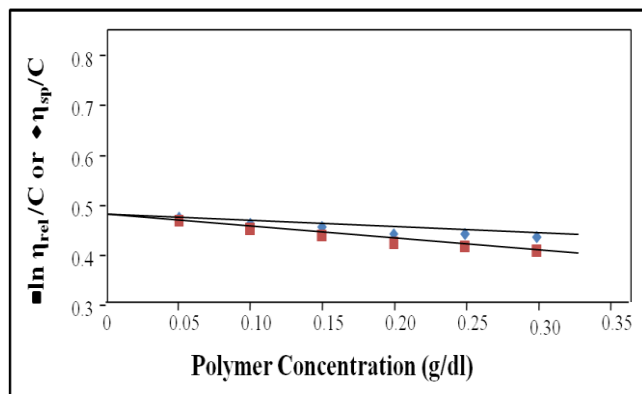


Figure 3: Viscometric plot of 2,2'-BPHMDAF terpolymer

UV-Visible spectra

Figure 4 represents the UV-Visible spectrum of 2,2'-BPHMDAF terpolymer and recorded in pure dimethylsulphoxide in the wavelength region 200-800 nm. This terpolymer shows that the curve has two characteristic absorption broad bands at 270 and 320 nm respectively. The more intense band observed at 270 nm accounted for $\pi \rightarrow \pi^*$, allowed transition of biphenyl ring, which attains coplanarity and shoulder merging (loss of fine structure). The later and less intense band may be due to $n \rightarrow \pi^*$ electronic transition indicates the presence of auxochromic -OH groups [27].

The auxochromic substituents (-OH groups) show the interaction with π electron of the benzene ring. This interaction stabilizes π^* state and thus lowers the energy, as a result bathochromic shift is caused and also responsible for hyperehromic shift in Σ_{max} . Phenolic hydroxyl group is electron releasing and shifts the wavelength of maximum absorption to higher side and increases the intensity of secondary absorption band.

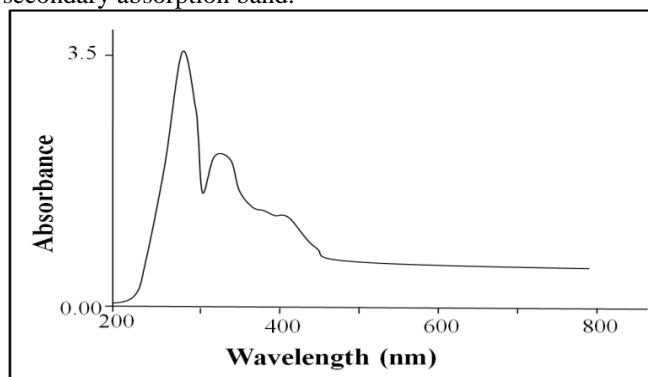


Figure 4: UV-Visible spectrum of 2,2'-BPHMDAF terpolymer

FT-IR spectra

IR-spectrum of terpolymer has been depicted in Figure 5. The broad and strong band appeared at 3273 cm^{-1} of the phenolic -OH groups exhibiting intermolecular hydrogen bonding [28-35]. The presence of a weak band at 3066 cm^{-1} describe the $>\text{NH}$ stretching of secondary amine [32]. The medium and strong band at 1605 cm^{-1} assigned for $>\text{NH}$ bending vibrations of secondary amine. The stretching vibration of $>\text{C}=\text{C}<$ in aromatics may be due to a medium and weak band, displayed at 1491 cm^{-1} . The C-N stretch in aliphatic amine may be accounted by the medium and weak band appeared at 1280 cm^{-1} . Strong C-O stretch in phenol is represented at 1220 cm^{-1} . The presence of methylene bridges

(-CH₂-) in polymeric chain can be accounted by the presence of medium, medium broad and sharp bands at 1443 cm^{-1} , 1350 cm^{-1} and 753 cm^{-1} for bending, wagging and rocking vibrations respectively. Medium band ascribed for the trisubstituted benzene ring at 800 cm^{-1} . Results obtained from spectral studies are in well agreement with those reported in literature [36, 37].

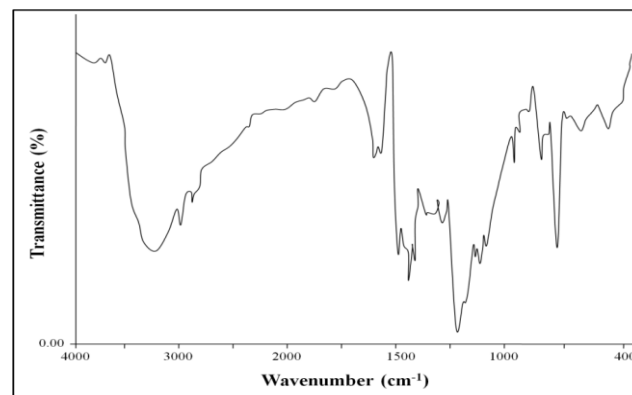


Figure 5: FT-IR spectrum of 2,2'-BPHMDAF terpolymer

¹H-NMR spectra

¹H-NMR spectrum of the terpolymer has been shown in Figure 6 which was recorded by using the solvent DMSO-d₆. ¹H-NMR spectral data calculated from graph has been interpreted as follows. A sharp singlet and doublet peak which appeared at δ 7.96 and 7.7 ppm may be assigned due to the presence of meta protons of aromatic groups [38]. Medium singlet observed at δ 7.2 ppm is may be due to hydroxyl protons of biphenol moiety [32, 39]. This significant downfield in chemical shift of proton of phenolic -OH groups clearly indicates intramolecular hydrogen bonding of -OH groups [31, 39, 40]. Amino protons of -CH₂-NH-CH₂- linkage appeared as medium singlet at δ 6.7 ppm. Triplet appeared in the region δ 4-4.1 ppm may be attributed to methylene protons of -NH-CH₂-CH₂- moiety [32]. Spectra show methylene proton of Ar-CH₂-NH- linkage appeared at δ 2.6 ppm. Further it was observed that quintet appeared at δ 1.4 ppm for methylene proton of -CH₂-CH₂-CH₂- linkage. The chemical shift (δ) ppm observed is assigned on the basis of the literature [40, 41, 42].

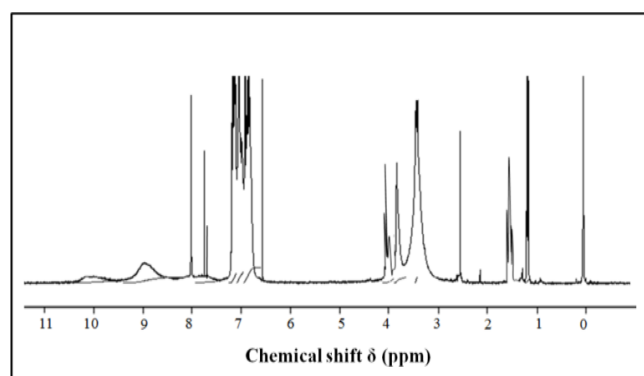


Figure 6: ¹H-NMR spectrum of 2,2'-BPHMDAF terpolymer

Thermogravimetry

The non-isothermal method is the most commonly used for performing the kinetic analysis of solid state reactions. A number of literatures on this matter have been published earlier in this journal [43-49]. Thermogravimetric technique

is found to be a precious method to evaluate the thermal decomposition pattern of the polymer. Rate of thermal decomposition for terpolymer has been determined using a thermogravimetric analyzer. Thermal degradation behavior of synthesized terpolymer (2,2'-BPHMDAF) in temperature range from 40 to 1000 °C has been integrated in Table 4 and decomposition pattern is shown in Figure 7.

Thermogravimetric study of 2,2'-BPHMDAF

terpolymer:

Initially, the first decomposition step is slow corresponds to 4.90 % weight loss which may be attributed due to the water of crystallization associated with terpolymer in the temperature range from 40 to 110 °C for one water molecule,

against calculated weight loss of 5.23 % present per repeat unit of the terpolymer. In the second step weight loss of 14.86 % found and 15.11 % calculated, has been observed from temperature 110 to 230 °C and is due to the degradation of two -OH groups attached to the biphenyl skeleton. The third step of decomposition starts from the temperature 230 to 530 °C corresponding to 66.43 % weight loss of biphenyl ring along with two side chains attached to hexamethylenediamine moiety against calculated 66.86 %. In the fourth or last step the remaining hexamethylenediamine moiety may degrades nearly at temperature 980 °C. Terpolymer is half decomposed at temperature 330 °C as given bellow.

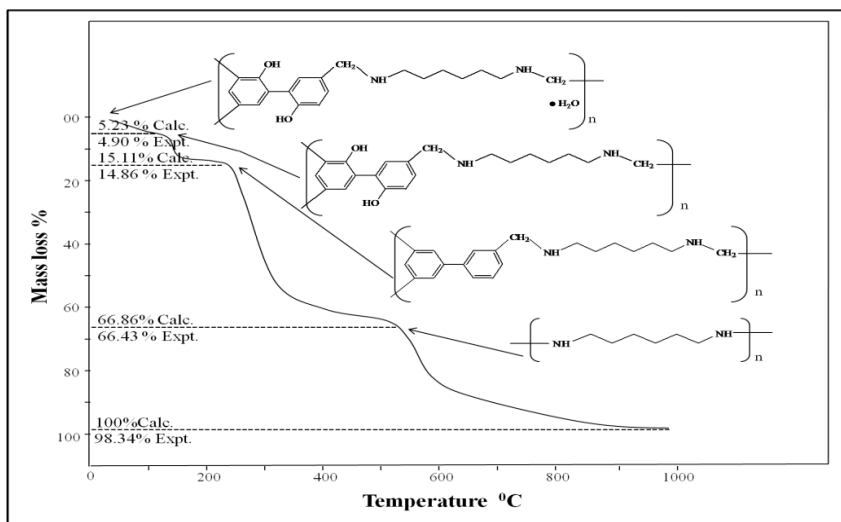


Figure 7: Decomposition pattern of 2,2'-BPHMDAF terpolymer

Table 4: Thermal degradation behavior of 2,2'-BPHMDAF terpolymer

Terpolymer	Stages of decomposition	Temp. Range (°C)	Species Degraded	Wt. Loss (%)	
				Expt.	Calc.
2,2'-BPHMDAF	First	40-110	Loss of one H ₂ O molecule	4.90	5.23
	Second	110-230	Loss of two -OH groups	14.86	15.11
	Third	230-530	Loss of biphenyl ring with two (-CH ₂) groups	66.43	66.86
	Fourth	530-980	Complete loss of Hexamethylenediamine moiety	98.34	100.00

The knowledge of activation energy from Freeman-Carroll method was further used to determine the thermodynamic parameters which are cited bellow such as entropy change, free energy change, frequency factor, apparent entropy change and order of reaction.

- 1) Activation Energy (E_a) - 11.013 (KJ/mol)
- 2) Entropy change (ΔS) - 8.141 (J)
- 3) Free energy change (ΔF) - 13.699 (KJ)
- 4) Frequency factor (z) - 429.50 (sec⁻¹)
- 5) Apparent entropy change (S*) - 23.62 (J)
- 6) Order of reaction (n) - 1.1

Kinetics of thermal decomposition by Friedman, Chang and Freeman-Carroll methods:

Kinetic parameters are obtained from the thermal degradation kinetic equations described by Friedman, Chang and Freeman-Carroll methods. Thermal decomposition data apply to the above methods to resolve the activation energy, order of reaction and frequency factor. The kinetic plots drawn from Friedman, Chang and Freeman-Carroll methods have been shown in Figures 8-12. The results of kinetic

parameters of above mentioned methods have been incorporated in Table 5.

The energy of activation calculated by Friedman and Chang methods are found to be in well agreement with each other. But Freeman-Carroll method shows slightly different observations. Order of reaction calculated from Chang method is found to be one and from Freeman-Carroll method is near about one. But order of reaction calculated by Friedman method not obeys first order kinetics perfectly as reported by Jacobs and Tompkin and Coats and Redfern [50, 51]. The thermal stability of 2,2'-BPHMDAF terpolymer is concluded to be higher, may be due to the stronger intermolecular hydrogen bonding present in terpolymer structure because of moisture entrapped in the terpolymer which would be more difficult to break and hence more resistant to higher temperature or it may be due to possibility of a linear structure of terpolymer chain which gives stability to terpolymer chain.

To obtain the useful information on the behavior of samples should be due to kinetic analysis. Fairly comparable results in the kinetic parameters *i.e.* E_a and z are obtained by Friedman and Chang may be due to analogy in mathematical model but somewhat slightly different observations are observed in Freeman-Carroll method. From abnormally low values of frequency factor, it may be concluded that decomposition reaction of 2,2'-BPHMDAF terpolymer can be classed as a "slow" reaction and no other possible reason can be given [50, 52]. The results 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 [53].

Due to complex phenomena of terpolymer degradation process in non-isothermal 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 terpolymer in non-isothermal conditions. As a consequence these kinetic parameters are fictive from the point of view of chemical kinetics.

Table 5: Thermoanalytical data of 2,2'-BPHMDAF terpolymer

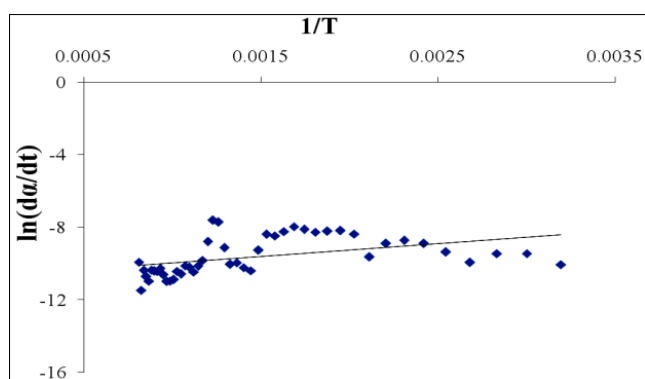


Figure 8: Friedman activation energy plot of 2,2'-BPHMDAF terpolymer

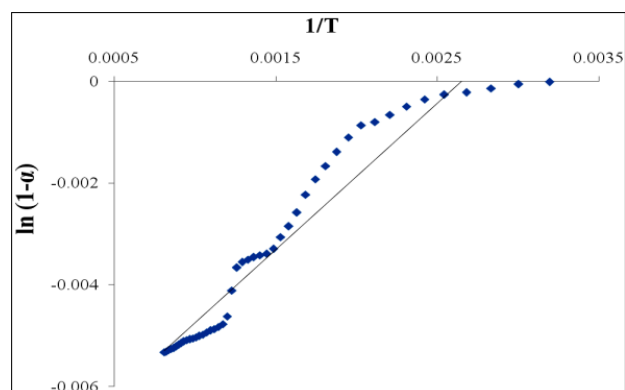


Figure 9: Friedman order of reaction plot of 2,2'-BPHMDAF terpolymer

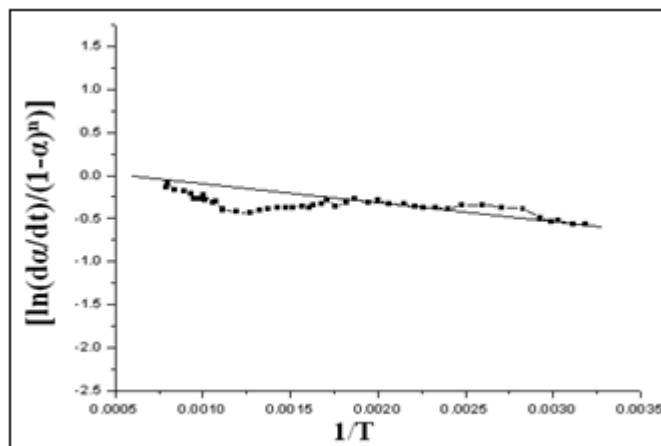


Figure 10: Chang plot of 2,2'-BPHMDAF terpolymer

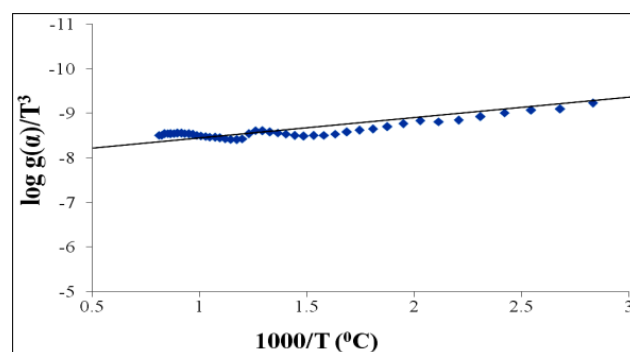


Figure 11: Freeman-Carroll plot of 2,2'-BPHMDAF terpolymer

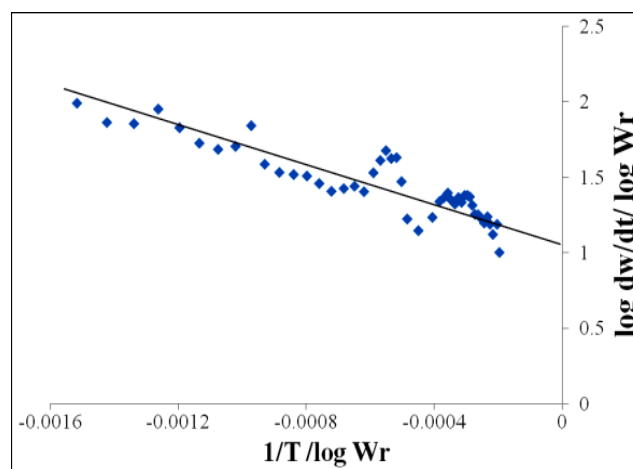


Figure 12: Freeman-Carroll activation energy plot of 2,2'-BPHMDAF terpolymer

5. Conclusion

- 1) The structure of the terpolymer was proposed on the basis of spectral studies *i.e.* UV- VIS, FT-IR, ^1H NMR and physicochemical analysis.
- 2) The thermal stability of 2,2'-BPHMDAF terpolymer is concluded to be higher, may be due to the stronger intermolecular hydrogen bonding present in terpolymer structure.
- 3) The decomposition reaction was started at higher temperature, indicating a terpolymer 2, 2'-BPHMDAF is thermally stable at higher temperature.

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