Thermal Degradation Studies and Kinetic Parameters of Biphenol-Hexamethylenediamine-Formaldehyde Terpolymer

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Abstract: ***In the present research paper reports the thermal degradation studies of 2,2'-Biphenol (2,2'-BP), Hexamethylenediamine (HMDA) with Formaldehyde (F) (2,2'BPHMDAF-II) terpolymer. Terpolymer has been synthesized by the condensation of 2,2'-Biphenol and Hexamethylenediamine with formaldehyde in presence of 2M HCl as a catalyst using 1:2:4 molar ratios at temperature 150 ^{0}C. The terpolymer after purification was characterized by elemental analysis and spectral studies such as UV-Visible, FT-IR and ^{1}H-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 physico-chemical 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. Freeman-Carroll and Sharp-Wentworth methods have been applied for the calculation of kinetic parameters. 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. 2,2'-BPHMDAF-II terpolymer was synthesized to determine its thermal stability and which were proved to be thermally stable by studying above methods.***

Keywords: Polycondensation reaction, Spectral studies, Physicochemical techniques

1. Introduction

Terpolymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. The study of the thermal degradation of terpolymers has recently become a subject of interest. The development of new and improved polymers and their application in novel areas have led to innumerable new products. Since the modern history of thermogravimetry, thermal degradation of polymers and study of its kinetics has been at the center of thermal analysis.

The field of polymer technology is vast and the knowledge of this important field can enrich the productivity and use of these wonder materials. The large number of present and future applications of polymeric materials has created a great national need to carry out research and development in polymer science and engineering. Polymeric materials have a vast potential for exciting new applications in the foreseeable future. The thermal stability of copolymer has been studied by using the method of thermo gravimetric analysis (TGA) by several authors [1-6].

The thermal degradation study of copolymer which primarily decides the thermal stability, processability and important information about its practical applicability. The considerable afford has been made to improve the quality of copolymer either by introduction of a variety of functional monomers or by modifying methods. The terpolymers offered novelty and versatility; hence they occupy the pivotal position in the field of material science. Recently research papers on terpolymers are exploring diverse applications and synthesis methods. The progress in the field of terpolymer has been extensively rapid, as they are useful in packaging, adhesive, coating in electrical sensors, ion exchangers and organometalic semiconductors [7-10]. Additionally, terpolymers are being investigated for use in coatings, energy storage, and other functional materials.

2. Literature Survey

Khedkar et al synthesized characterize, and studied thermal behaviour of terpolymeric resin derived from m-cresol, hexamine and formaldehyde [11]. Tarase et al studied thermal degradation kinetics of 2,4-dihydroxypropiophenone-oxamide-formaldehyde terpolymer [12]. Thermal degradation kinetics of poly(methylphenylsiloxane) containing methacryloyl groups was investigated that different solid-state reaction mechanism was followed at different stages of degradation [13]. S. L. Oswal et al [14] synthesized and studied thermal properties of copoly (maleimidemethylmethacrylate), terpoly (maleimidemethylmethacrylate- acrylic acid) and terpoly(maleimide-methylmethacrylatemethyl-acrylic acid). The thermal behaviour was studied by TG and DSC techniques.

Shah et al [15] synthesized the terpolymer from salicylic acid - formaldehyde - resorcinol. The terpolymer was characterized by FTIR and elemental analysis. The thermal analysis (TGA) was performed at the heating rate of 10^{0}C/min. in nitrogen atmosphere. Butoliya et al [16] Studied Non-Isothermal Decomposition and Kinetic Analysis of 2,4-Dihydroxybenzoic Acid-Melamine-Formaldehyde and concluded that given copolymer has potential as matrix resin for long term applications at temperature up to 350 ^{0}C. Thermal properties of terpolymers with different monomer ratio were characterized by DSC and TG by synthesizing Heat-resistance ABS resin by emulsion polymerization of N-ptolylmaleimide (N-PTMI),butadiene–styrene latex (SB), AN and St [17].

3. Experimental

Materials

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

Synthesis

2,2’-BPHMDAF-II terpolymer was synthesized by condensation of 2,2’-biphenol and hexamethylenediamine using the linkage of formaldehyde with the molar ratios of 1:2:4 in presence of 2M hydrochloric acid (200 ml) as a catalyst. The mixture was heated at 150 ^{0}C in an oil bath for ten hours with frequent shaking [18-20]. 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 77.59 %. Figure 1 represents proposed reaction and synthetic details are reported in Table 1 for the formation of 2,2’-BPHMDAF-II terpolymer as follows.

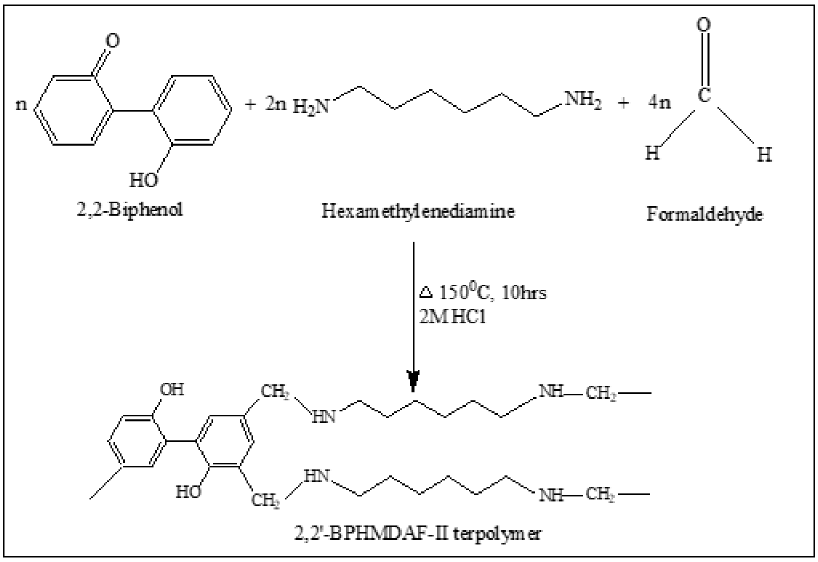

Figure 1: Proposed reaction for 2,2’-BPHMDAF-II terpolymer

Table 1: Synthesis details of 2,2’-BPHMDAF-II terpolymer

Terpolymer	Reactants			Molar ratio	Catalyst 2M HCl (ml)	Reflux Temp.^{0}C	Yield (%)	Time (hrs)
	2,2’-Biphenol (2,2’-BP) (mol)	Hexamethylene - diamine (HMDA) (mol)	Formaldehyde (F) (mol)					
2,2’BPHMDAF-II	0.1	0.2	0.4	04	200	150	77.59	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 were recorded on Perkin Elmer Spectrum RX-1 spectrophotometer in the range of 4000 to 400 cm^{-1} and ^{1}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 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 [21 & 22]. 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:

$$\overline{DP} = \frac{Totalmilliequivalentsofbaserequiredforcompleteneutralisation}{Milliequivalentsofbaserequiredforsmallestinterval}$$

$$\overline{Mn} = \overline{Dp} \times \textit{weight of repeat unit (monomer)}$$

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The intrinsic viscosity [η] was determined by the corresponding linear plots using Ubbelohde viscometer [23-25] fabricated in our research laboratory at different concentrations ranging from 0.3 to 0.05 % of terpolymer in DMSO at 27 ^{0}C. Intrinsic viscosity [η] was calculated from relevant plots of Huggin's equation and Kraemer's equation. Huggin's [26] and Kraemer's [27] constants were determined by (1) and (2).

$\eta_{sp}/C = [\eta] + K_1 [\eta]^2 .C$ (1)
$\ln \eta_{rel}/C = [\eta] + K_2 [\eta]^2 .C$ (2)
Where,
η_r is the relative viscosity,
$[\eta] = \lim C \rightarrow 0(\eta_{sp}/C)$,
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 ^{0}C per minute in air atmosphere in the temperature range 40-1000 ^{0}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 (Ea) 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 Freeman-Carroll [28] and Sharp-Wentworth [29] techniques as follows:

Freeman-Carroll technique:

$$\frac{\Delta log(^{dw}/_{dt})}{\Delta \log Wr} = \left(-\frac{Ea}{2.303\ R}\right).\frac{\Delta(\frac{1}{T})}{\Delta \log Wr} + n \qquad (5)$$

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 the energy of activation; R is gas constant; T is temperature and n is the order of reaction.

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

Sharp-Wentworth method:

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

where, dc/dt = Rate of change of fraction of weight with change in temperature;
β = Linear heating rate i.e. dT/dt;
c = Fraction of polymer decomposed at time t.

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

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-II terpolymer

Terpolymer	C (%)		H (%)		N (%)		Empirical formula of the repeating unit	Empirical formula weight
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.		
2,2'BPHMDAF-II	71.99	72.1	8.78	9.01	11.76	12.02	C28H42N4O2	466

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.

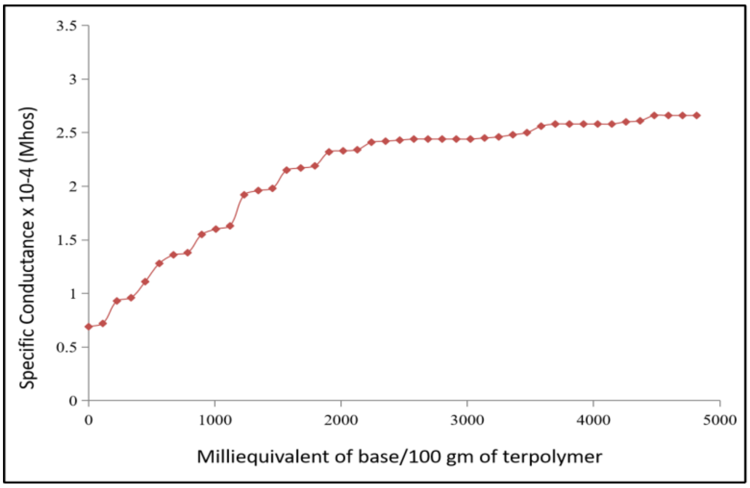

Figure 2: Conductometric titration curve of 2,2'-BPHMDAF-II terpolymer

Viscosity measurements were carried out using Ubbelohde viscometer. According to the above relations, the plots of η_{sp}/C and ln η_{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. 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-II	12.66	5902.66	0.57	0.272	0.258	0.530

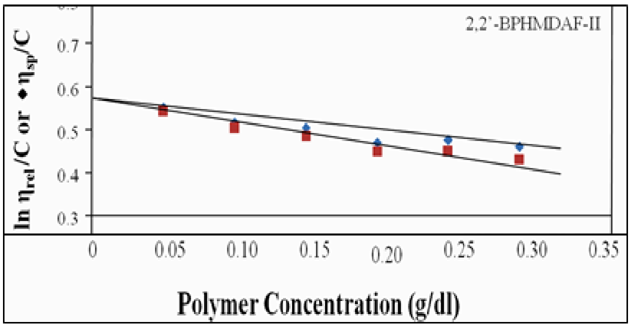

Figure 3: Viscometric plot of 2,2'BPHMDAF-II terpolymer

UV-Visible spectra

Figure 4 represents the UV-Visible spectrum of 2,2'BPHMDAF-II 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 290 and 330 nm respectively. The more intense band observed at 290 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 [30-31].

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 Σmax. Phenolic hydroxyl group is electron releasing and shifts the wavelength of maximum absorption to higher side and increases the intensity of secondary absorption band.

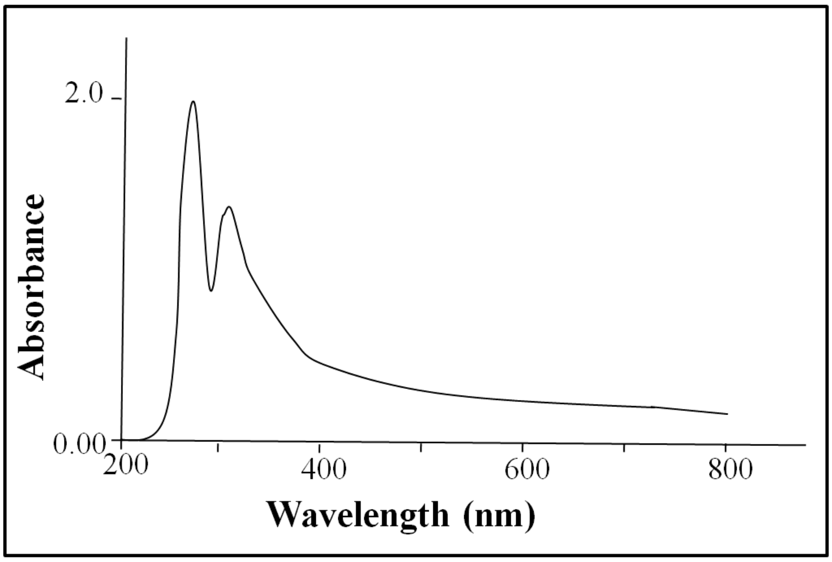

Figure 4: UV-Visible spectrum of 2,2'-BPHMDAF-II terpolymer

FT-IR spectra

Figure 5 represents the broad and strong bands appeared at $3272 m^{-1}$ of the phenolic -OH groups exhibiting intermolecular hydrogen bonding. The presence of a weak bands at 3065 cm^{-1} describes the >NH stretching of secondary amine. The medium and strong bands at 1606 cm^{-1} assigned for >NH bending vibrations of secondary amine. The stretching vibration of >C=C< in aromatics may be due to a medium and weak bands, displayed in between 1493 cm^{-1}. The C-N stretch in aliphatic amine may be accounted by the medium and weak bands appeared at 1278 cm^{-1}. Strong C-O stretch in phenol is represented at 1221 cm^{-1}. The presence of methylene bridges (-CH2-) in polymeric chain can be accounted by the presence of medium, medium broad and sharp at 1444 cm^{-1} ,1351 cm^{-1} and 753 cm^{-1} for bending, wagging and rocking vibrations respectively. The presence of tetrasubstitution of aromatic ring is recognized from the medium bands appearing in the region 1073 and 816 cm^{-1} respectively.

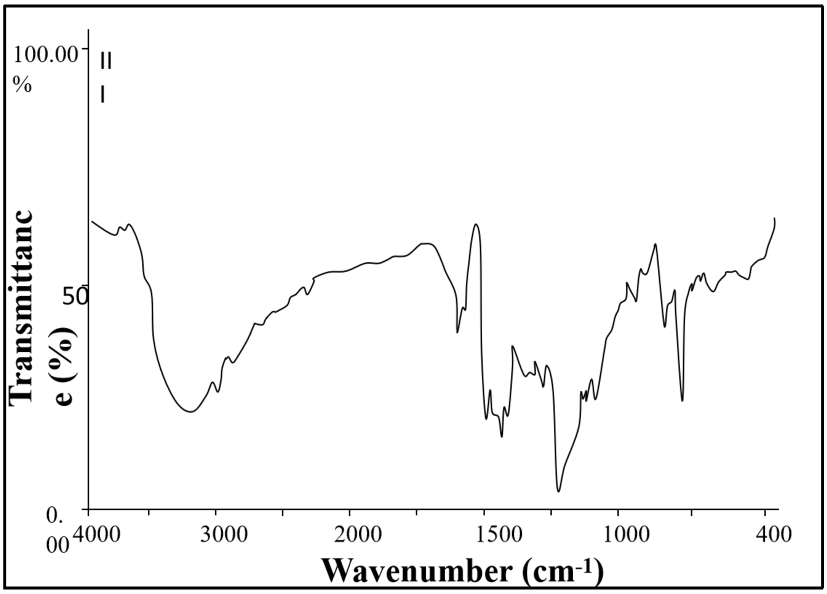

Figure 5: FT-IR spectrum of 2,2'BPHMDAF-II terpolymer

^{1}H-NMR spectra

^{1}H-NMR spectrum of the terpolymer has been shown in Figure 6 which was recorded by using the solvent DMSO-d_6. ^{1}H-NMR spectral data calculated from graph has been interpreted as follows. A sharp singlet and doublet peak which appeared at δ 8 and 7.9 ppm may be assigned due to the presence of meta protons of aromatic groups. Medium singlet observed at δ 7.2 ppm is may be due to hydroxyl protons of biphenol moiety [32]. This significant downfield in chemical shift of proton of phenolic -OH groups clearly indicate intramolecular hydrogen bonding of -OH groups. Amino protons of $-CH_2-NH-CH_2-$ linkage appeared as medium singlet at δ 6.5 ppm. Triplet appeared in the region δ 4.1-4.2 ppm may be attributed to methylene protons of $-NH-CH_2-CH_2-$ moiety [32]. Spectra show methylene proton of $Ar-CH_2-NH-$ linkage appeared at δ 2.7 ppm. Further it was observed that quinted appeared at δ 1.5 ppm for methylene proton of $-CH_2-CH_2-CH_2-$ linkage. The chemical shift (δ) ppm observed is assigned on the basis of the literature [33].

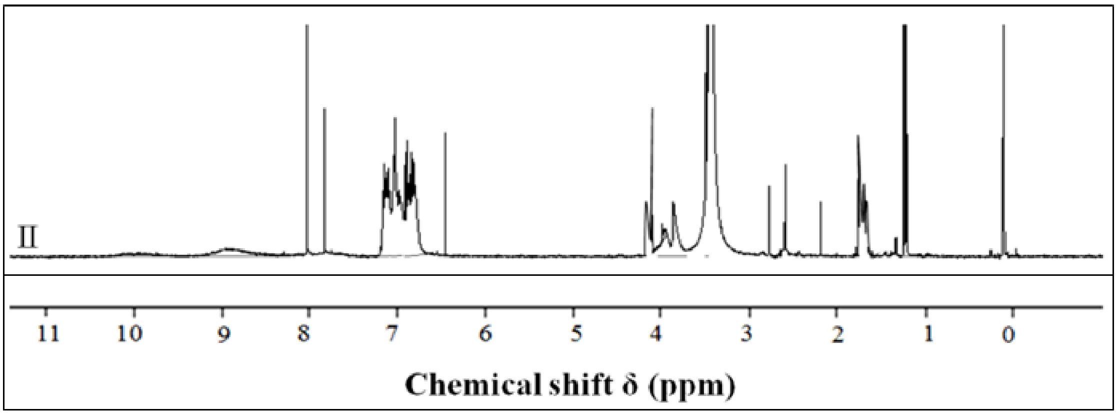

Figure 6: ^{1}H-NMR spectrum of **2,2'BPHMDAF-II** terpolymer

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 [34-40]. 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-II) in temperature range from 40 to 1000 ^{0}C has been integrated in Table 4 and decomposition pattern is shown in Figure 7.

Thermogravimetric study of 2,2'-BPHMDAF-II terpolymer:

Initially, the first decomposition step is slow corresponds to 3.57 % weight loss which may be attributed due to the water of crystallization associated with terpolymer in the temperature range from 40 to 120 ^{0}C for one water molecule, against calculated weight loss of 3.72 % present per repeat unit of the terpolymer. In the second step weight loss of 10.28 % found and 10.74 % calculated, has been observed from temperature 120 to 210 ^{0}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 210 to 540 ^{0}C corresponding to 76.33% weight loss of biphenyl ring along with two side chains attached to hexamethylenediamine moiety against calculated 76.44%. In the fourth or last step the remaining hexamethylenediamine moiety may degrades nearly at temperature 980 ^{0}C. Terpolymer is half decomposed at temperature 340 ^{0}C as given bellow.

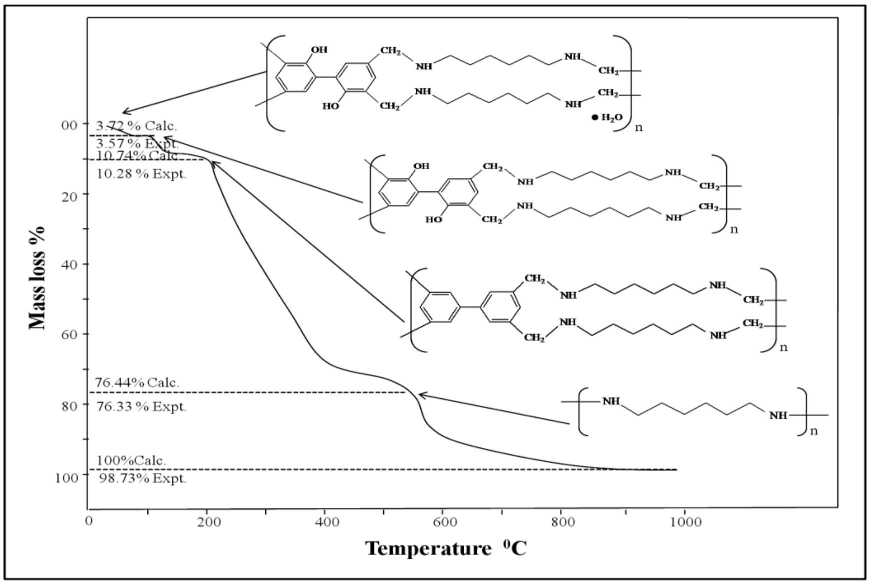

Figure 7: Decomposition pattern of 2,2'BPHMDAF-II terpolymer

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

S. No.	Terpolymer	Temp. Range (0C)	Stages of decomposition	Species Degraded	Wt. Loss (%)	
					Expt.	Calc.
1.	2,2``-BPHMDAF-II	40-120	First	Loss of one H2O molecule	3.57	3.72
		120-210	Second	Loss of two -OH groups	10.28	10.74
		210-540	Third	Loss of biphenyl ring and one Hexamethylenediamine moiety with four (-CH2) groups	76.33	76.44
		540-980	Fourth	Complete loss of Hexamethylenediamine moiety	98.73	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) Half decomposition temperature of terpolymer - 340 (^{0}C)
2) Activation Energy by Freeman-Carroll - 12.178 (KJ/mol)
3) Activation Energy by Sharp-Wentworth method - 11.956 (KJ/mol)
4) Entropy change - -8.301(J)
5) Free energy change - 15.001(KJ)
6) Frequency factor - 401.97 (sec^{-1})
7) Apparent entropy change - -23.69 (J)
8) Order of reaction - 1.1

Kinetics of thermal decomposition by d Freeman-Carroll and Sharp-Wentworth methods:
Kinetic parameters are obtained from the thermal degradation kinetic equations described by Freeman-Carroll and Sharp-Wentworth 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 Freeman-Carroll and Sharp-Wentworth methods have been shown in Figures 8-10.

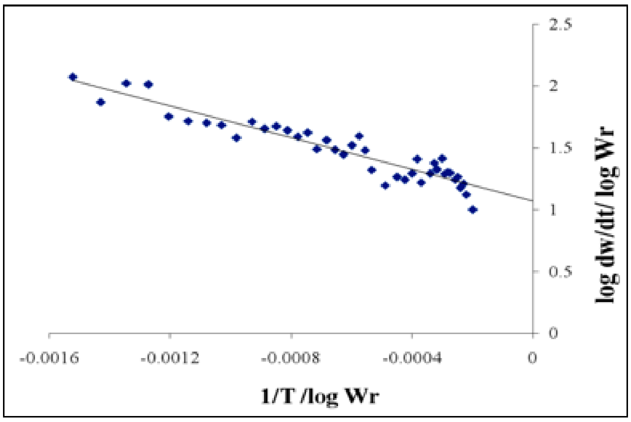

Figure 8: Thermal activation energy plot by Freeman-Carroll method of 2,2‟-BPHMDAF-II terpolymer

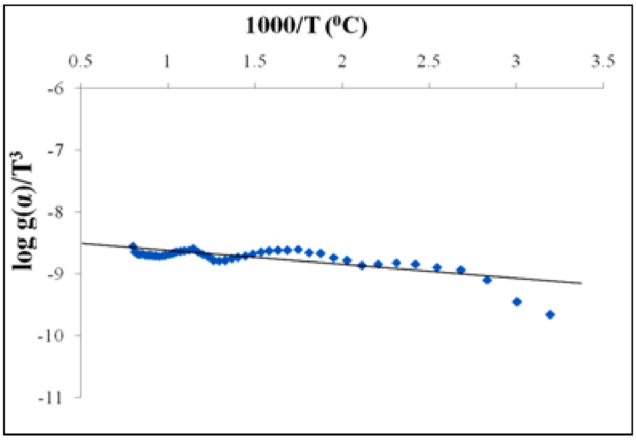

Figure 9: Freeman-Carroll plot of 2,2‟-BPHMDAF-II terpolymer

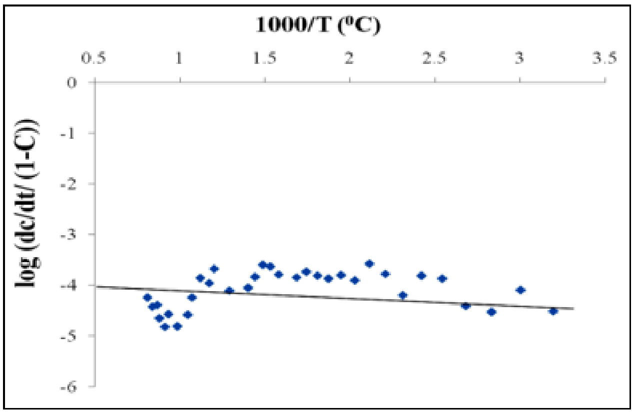

Figure 10: Sharp-Wentworth plot of 2,2‟-BPHMDAF-II terpolymer

Conclusion

1) The structure of the terpolymer was proposed on the basis of spectral studies i.e. UV- VIS, FT-IR, ^{1}H NMR and physicochemical analysis.
2) The thermal stability of 2,2'-BPHMDAF-II 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-II is thermally stable at higher temperature.

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