

Thermal Degradation Studies and Kinetic Parameter of Biphenol and Butanediamine

Priyanka U. Belsare

Department of Chemistry, Mahatma Fule Art's Commerce and Sitaramji Chaudhari Science College Warud - 444906, India

Email: priyankabelsare45[at]gmail.com

Abstract: The present paper informs the thermal degradation studies of 2, 2' - biphenol - butanediamine - formaldehyde terpolymer. Initially this terpolymer was synthesized from 2, 2' - biphenol, butanediamine with formaldehyde by the polycondensation reaction in the presence of acid catalyst at temperature 150 °C. The terpolymer after purification were characterized by elemental analysis and spectral studies such as UV - Visible, FT - IR and ¹H - NMR spectra which were used to confine the most probable structure of synthesized terpolymer. Characterization was carried out by different physicochemical techniques viz. Number average molecular weight determines by Non - aqueous conductometric titration and Intrinsic viscosity by Ubbelohde Viscometer. Non isothermal thermogravimetric technique has been carried out for thermogravimetric study. Freeman - Carroll 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. By studying above method we concluded that this newly prepared terpolymer is thermally stable at high temperature.

Keywords: Polycondensation reaction, physicochemical studies, spectral studies, thermal behaviour and stability

1. Introduction

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 centre of thermal analysis [1, 2].

Materials that are used in everyday life have an immense impact on the development of the human society. During the Stone Age and Iron Age epochs, humans widely used stone or iron to make tools. In the present age, there is no question that polymers and plastics dominate our rapidly developing daily needs and show enormous potential for the development of new technologies. Constructive materials, such as polyolefins, polyesters or polyamides are preferentially made of standard polymeric materials. It is therefore obvious that the future of polymer chemistry will be influenced by the elaboration of new functional polymers. Nowadays, the development of various functional polymers is becoming increasingly important in specific areas of application.

2. Literature Survey

Gurnule and Bisen studied thermal decomposition of copolymer resin - II and its kinetics derived from 4 - hydroxybenzaldehyde, phenyl hydrazine and formaldehyde [3]. Physico - chemical and thermal degradation studies of 2, 2' - biphenol - ethylenediamine - formaldehyde resin has

been done by Bobde et al [4]. Thermal stability of polyureas derived from 4 - aryl - 2, 6 - bis - (4 - amino - phenyl) pyridines and diisocyanates have been studied by Tamami et al [5]. Terpolymers were synthesized by condensing 2, 4 - dinitrophenyl hydrazone of 4 - hydroxyacetophenone with substituted benzoic acids/phenols and formaldehyde in presence of NaOH or HCl as catalyst by Rath et al [6]. Dharkar and other researchers [7] synthesized the melamine - aniline - formaldehyde terpolymeric ligand and carried out its thermal degradation study.

3. Experimental

2, 2' - BPBDAF terpolymer was synthesized by condensation of 2, 2' - biphenol (1.86 gm, 0.1 mol) and butanediamine (2.01 gm, 0.2 mol) using the linkage of formaldehyde (15 ml, 0.4 mol) 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 °C in an oil bath for ten hours with frequent shaking [8 - 10]. 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 82 %. Scheme 1 represents proposed reaction for the formation of 2, 2' - BPBDAF terpolymer as follows. Figure 1 represents proposed reaction and synthetic details are reported in Table 1 for the formation of 2, 2' - BPBDAF terpolymer as follows.

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

Terpolymer	Reactants			Molar ratios	Catalyst 2M HCl (ml)	Reflux Temp. °C	Yield (%)	Time (hrs)
	2, 2' - Biphenol (2, 2' - BP) (mol)	Butanediamine (BDA) (mol)	Formaldehyde (F) (mol)					
2, 2' - BPBDAF	0.1	0.2	0.4	1: 2: 4	200	150	82.00	10

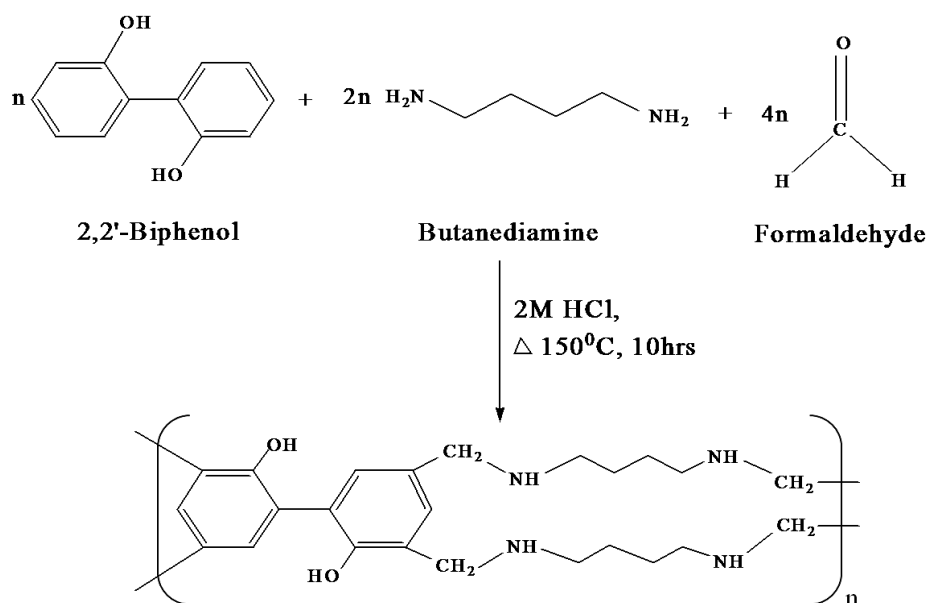


Figure 1: Proposed reaction for 2, 2' - BPBDAF terpolymer

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

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 [11, 12]. 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:

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

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

The intrinsic viscosity $[\eta]$ was determined by the corresponding linear plots using Ubbelohde viscometer [13-15] fabricated in our research laboratory at different concentrations ranging from 0.3 to 0.05 % of terpolymer in DMSO at 27 $^{\circ}\text{C}$. Intrinsic viscosity $[\eta]$ was calculated from relevant plots of Huggin's equation and Kraemer's equation. Huggin's [16] and Kraemer's [17] constants were determined by (1) and (2).

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

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

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

(1) been calculated.

(2)

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 [18] and Chang [19] techniques as follows:

Freeman-Carroll technique:

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

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 $\frac{\Delta \log (dw/dt)}{\Delta \log W_r}$ 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' - BPBDAF 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' - BPBDAF terpolymer

Terpolymer	C (%)		H (%)		N (%)		Empirical formula of the repeating unit	Empirical formula weight
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.		
2, 2' - BPBDAF	69.78	70.24	8.17	8.29	13.38	13.66	$C_{24}H_{34}N_4O_2$	410

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.

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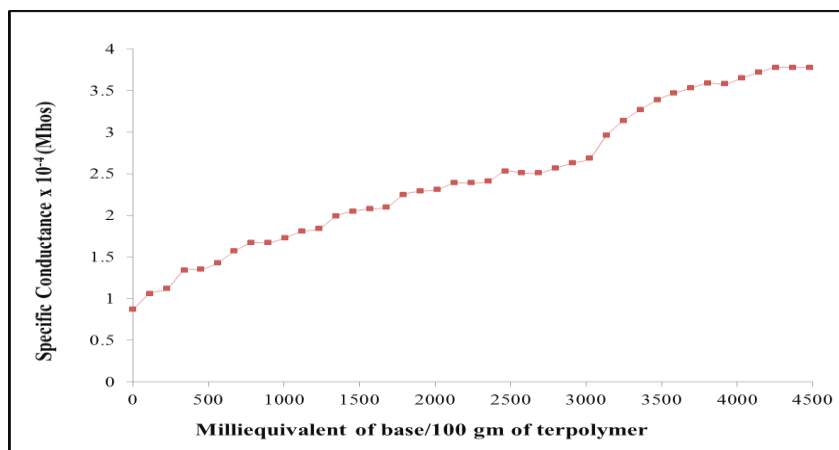


Figure 2: Conductometric titration curve of 2, 2' - BPBDAF terpolymer

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. 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' - BPBDAF 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' - BPBDAF	17.5	3632.09	0.85	0.253	0.259	0.512

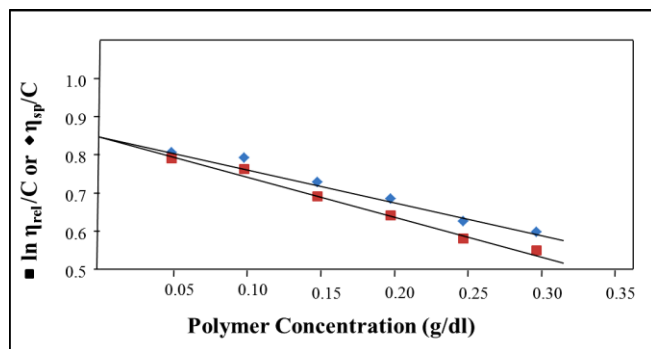


Figure 3: Viscometric plot of 2, 2' - BPBDAF terpolymer

UV - Visible spectra

The spectra displayed two characteristic broad bands between wavelengths 270 - 290 and 310 - 330 nm respectively. The more intense bands observed in between 270 - 290 nm have been accounted for $\pi \rightarrow \pi^*$, allowed transition of biphenyl moiety which attains coplanarity and shoulder merging (loss of fine structure). The later less intense band may be due to $n \rightarrow \pi^*$ electronic transition which indicates the presence of auxochromic - OH group.

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 hyperchromic 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. The spectra show bathochromic shift in λ_{max} of 24 - 30 nm from 246 nm to 270 - 290 nm and hyperchromic shift in ϵ_{max} in terpolymer. This is due to the conjugation of auxochromic and chromophoric group of terpolymer.

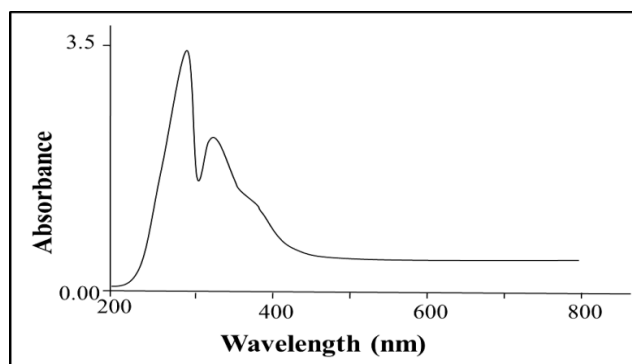


Figure 4: UV - Visible spectrum of 2, 2' - BPBDAF terpolymer

FT - IR spectra

The spectra show broad and strong bands, appeared in the region $3231 - 3353 \text{ cm}^{-1}$ may be assigned due to the stretching vibration of the phenolic - OH groups exhibiting intermolecular hydrogen bonding. The presence of a medium peaks in between $3056 - 3057 \text{ cm}^{-1}$ describes the $>NH$ stretching of secondary amine. Bending due to presence of secondary amine ($>NH$) show medium and strong bands in the region $1606 - 1607 \text{ cm}^{-1}$. The stretching vibration of $>C=C<$ in aromatics may be due to a medium bands, displayed in between $1492 - 1495 \text{ cm}^{-1}$. C - N stretching vibrations of aliphatic amines can be accounted

for $1278 - 1280 \text{ cm}^{-1}$, show medium and weak bands. One of the distinctive and characteristic strong bands appeared in the region $1220 - 1222 \text{ cm}^{-1}$ is due to C - O stretch in phenol.

The presence of methylene bridges (- CH_2 -) in the polymeric chain can be accounted by the presence of medium sharp, medium broad and sharp bands in between 1444 cm^{-1} , $1324 - 1354 \text{ cm}^{-1}$ and $753 - 755 \text{ cm}^{-1}$ for bending, wagging and rocking vibrations respectively. The presence of tetrasubstitution of aromatic ring is recognized from the medium bands appearing in between $1075 - 1077$ and 817 cm^{-1} respectively. Trisubstituted benzene ring show medium band at 795 cm^{-1} .

The results obtained in the present investigation are in well agreement with those reported in literature for the assignment of the most probable structures of newly synthesized terpolymers.

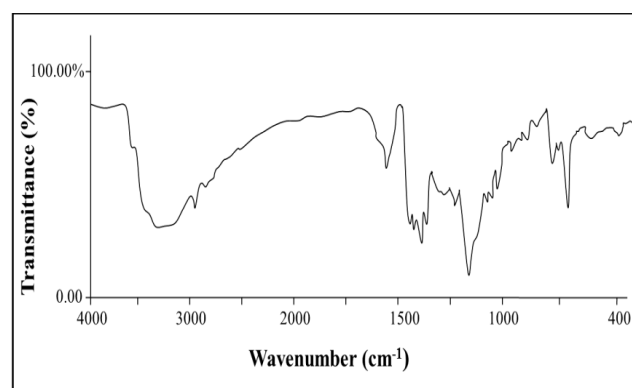


Figure 5: FT - IR spectrum of 2, 2' - BPBDAF terpolymer

^1H - NMR spectra

It has been found from spectral studies that different peaks and splitting pattern have been observed according to its electronic environments since each of them possesses a set of protons having different proton environment. A sharp, medium singlets and doublet have been observed at δ 7.6 ppm and are due to meta protons of phenol. A significant downfield in chemical shift of proton of phenolic - OH groups have been observed in between δ 7.1 - 7.2 ppm which is due to intermediate proton exchange reaction of phenolic - OH groups.^{121, 122, 126} Proton of amino group of - $\text{CH}_2 - \text{NH} - \text{CH}_2$ - linkage has been observed as singlets in the region δ 6.7 - 6.8 ppm. Methylene proton of $>N - \text{CH}_2 - \text{CH}_2$ - linkage resulted in the formation of triplet in between δ 5.1 - 5.3 ppm. Triplet observed in the region δ 4 - 4.1 ppm may be due to methylenic proton of - $\text{NH} - \text{CH}_2 - \text{CH}_2$ - linkage.¹²¹ Methylenic proton of Ar - $\text{CH}_2 - \text{N}$ - moiety which may be recognized as singlet signal appearing at δ 3.4 ppm. Similarly Ar - $\text{CH}_2 - \text{NH}$ - linkage has been observed as a singlet at δ 2.56 ppm. Quinted appeared in the region δ 1.4 - 1.5 ppm may be assigned for methylenic proton of - $\text{CH}_2 - \text{CH}_2 - \text{CH}_2$ - linkage.

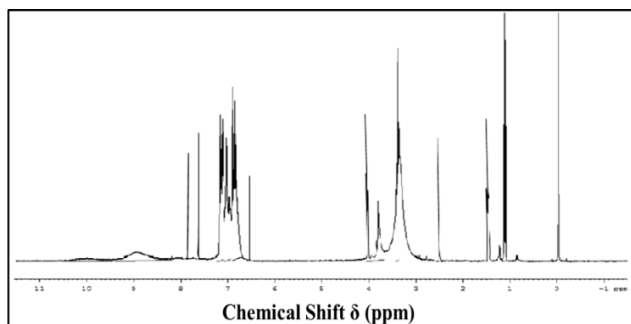


Figure 6: ^1H -NMR spectrum of 2, 2' - BPBDAF terpolymer

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. 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' - BPBDAF) in temperature range from 40 to 600 $^{\circ}\text{C}$ has been integrated in Table 4 and decomposition pattern is shown in Figure 7.

Thermogravimetric study of 2, 2' - BPDDAF terpolymer:

The thermogram displayed three stages of decomposition pattern with loss of one water molecule in the first step at temperature 120 $^{\circ}\text{C}$. The second and third stages of decomposition have been observed in the temperature ranges from 120 to 350 and 350 - 580 $^{\circ}\text{C}$ respectively for different group and moiety attached to terpolymer. During the second stage of decomposition corresponds to loss of two -OH groups attached to biphenyl skeleton of terpolymer. The third and last stage might be due to the degradation of biphenyl ring with one butanediamine moiety and two methylenic groups attached to it leaving behind the remaining moiety. The half decomposition temperature of terpolymer was found to be at 395 $^{\circ}\text{C}$.

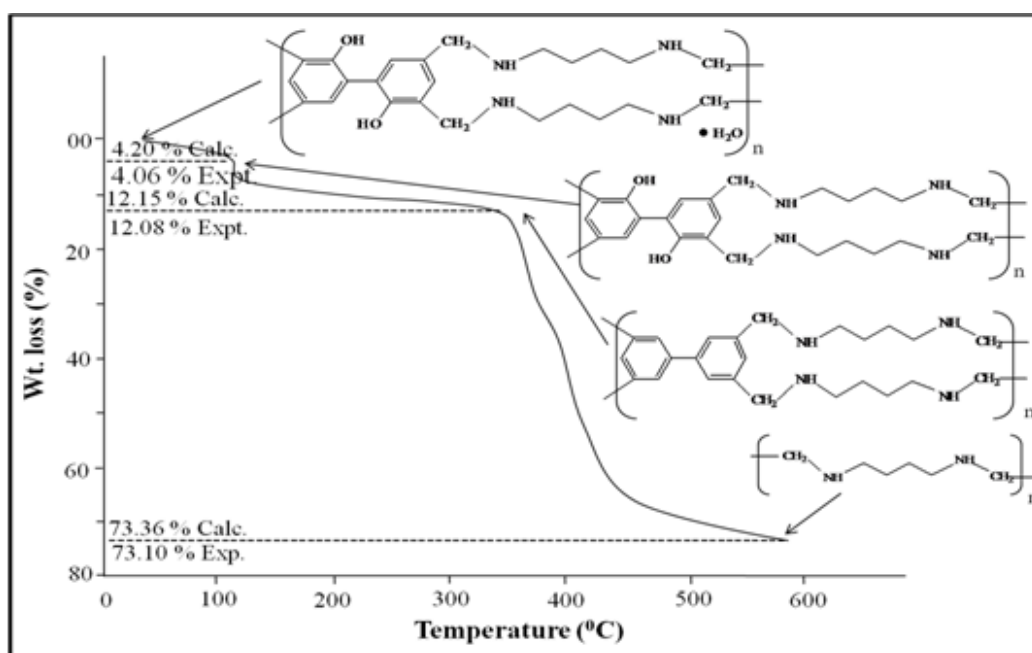


Figure 7: Decomposition pattern of 2, 2' - BPDDAF terpolymer

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

Terpolymer	Stages of Decomposition	Temp. Range ($^{\circ}\text{C}$)	Species Degraded	Wt. Loss (%)	
				Expt.	Calc.
2, 2' - BPBDAF	First	50 - 110	Loss of one H_2O molecule	4.52	4.59
	Second	110 - 280	Loss of two -SH and two - NH_2 groups	29.22	29.59
	Third	280 - 580	Loss of two phenyl rings with three (- CH_2) groups	77.84	78.06

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

- 1) Activation Energy (E_a) - 16.732 (KJ/mol)
- 2) Entropy change (ΔS) - 8.551 (J)
- 3) Free energy change (ΔF) - 20.11 (KJ)
- 4) Frequency factor (z) - 33.97 (sec^{-1})
- 5) Apparent entropy change (S^*) - 26.16 (J)
- 6) Order of reaction (n) - 0.98

Kinetics of thermal decomposition by Freeman - Carroll methods:

Kinetic parameters are obtained from the thermal degradation kinetic equations described by Freeman - Carroll method. 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 method has been shown in Figures 8 and 9. The results of kinetic parameters of above mentioned method has been incorporated in Table 5.

The energy of activation calculated by Freeman - Carroll method is near about one. The thermal stability of 2, 2' - BPBDAF 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. From abnormally low values of frequency factor, it may be concluded that decomposition reaction of 2, 2' - BPBDAF terpolymer can be classed as a "slow" reaction and no other possible reason can be given [20, 21]. 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 [22]. 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' - BPBDAF terpolymer

Methods	E_a	N	z
Freeman - Carroll	11.013	1.1	33.97

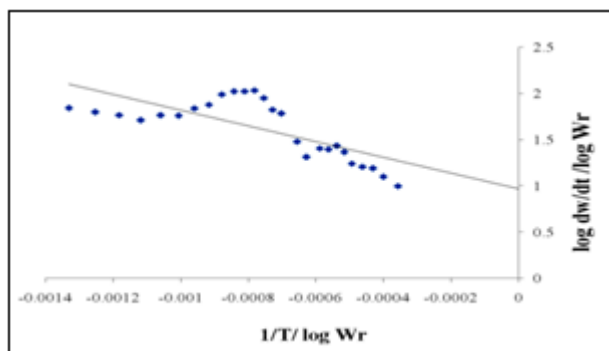


Figure 8: Thermal activation energy plot by Freeman - Carroll method of 2, 2' - BPBDAF terpolymer

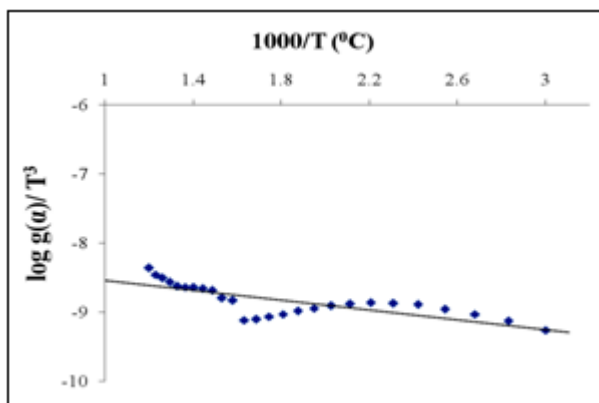


Figure 9: Freeman - Carroll plot of 2, 2' - BPBDAF terpolymer

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' - BPBDAF 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' - BPBDAF is thermally stable at higher temperature.

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