Treatment of Thermogravimetric Kinetic Equations to Copolymer Derived from 4,4'-dihydroxybiphenyl

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ABSTRACT

4,4'-Dihydroxybiphenyl-4,4'-Diaminodiphenyl ether-Formaldehyde (4,4'-DBP-4,4'-DDE-F-I) copolymer has been synthesized by acid catalyzed (2M HCl) condensation polymerization between 4,4'-Dihydroxybiphenyl (4,4'-DBP) and 4,4'-Diaminodiphenyl ether (4,4'-DDE) with Formaldehyde (F). The structure of synthesized copolymer has been elucidated on the basis of elemental analysis and spectral techniques viz. UV–Visible, FT-IR and ^{1}H-NMR spectroscopy. Thermal analysis has been carried out for studying its thermal degradation behavior and kinetics. Thermal degradation curve has been discussed with minute details for each decomposition step. Friedman, Chang, Sharp-Wentworth, Freeman-Carroll and Coat Redfern methods have been implemented to evaluate the kinetic parameters such as Ea, n and ln(z).

Keywords: Condensation polymerization, Synthesis, Spectroscopic characterization, Thermogravimetry, Biphenol.

I. INTRODUCTION

Nowadays, the study of thermal degradation behavior and computation of kinetic parameters by implementing modern developing thermal degradation kinetic techniques is the subject of interest for many investigators. The interest is fully recognized because the kinetics is related with the decomposition mechanisms in which the thermal degradation takes place. Their mechanisms allow to study the salient features of kinetic equations and kinetic study is the initiative to postulates mechanisms for the thermal decomposition [1].

Variety of thermally stable copolymers has been synthesized in order to study their thermal degradation behavior and reaction kinetics for more and more advanced applications. Literature contains large information regarding the copolymerization of binary monomer systems however; researches are developing on investigation of modern methods of synthesis of terpolymers/copolymers, its characterization and thermal studies for its high performance utility.

Terpolymers exhibited renewed applications as semiconductors [2], high energy materials [3], thermally stable materials [4], antioxidants [5], optical lithography and microelectronics [6], fungicides in plants and tissues [7], biosensors [8], additives [9], ion exchangers/chelating agent [10] etc. Appreciable progress has been made by polymer scientists in many ternary systems such as linalool- styrene-methylmethacrylate [11], indene-

methylmethacrylate-acrylonitrile [12], styrene-acrylonitrile-chromium acrylate [13], isobutylene-acrylic ester –alkylboron halide [14], 2-ethoxyethyl methacrylate-styrene-maleic anhydride [15], styrene-acrylonitrile-maleic anhydride [16], anthranilic acid-thiourea-formaldehyde [17] etc.

A comprehensive kinetic model for high temperature free radical production of styrene, methylmethacrylate and acrylate resins have been reported by wei wang and robin hutchinson[18]. Boztung and Basan [19] have reported the synthesis and characterization of maleic anhydride-styrene-vinyl acetate terpolymer ester derivative. The thermal properties of emulsion terpolymers of *N*- p-tolylmaleimide/butadiene-styrene latex/acrylonitrile/styrene have been studied in detail by liting yang et al [20]. Also, number of paper has been published by our researchers from our laboratory on thermal degradation kinetics of terpolymers [21-25].

Jadhav M M have reported the synthesis, characterization and thermal degradation kinetics of copolymers derived from 2,2'-dihydroxybiphenyl-formaldehyde [26] copolymer and 2,2'-dihydroxybiphenyl, urea, formaldehyde [27] terpolymer. A detailed study has been done by Pradip Paik and Kamal K. Kar [28] on kinetics of thermal degradation and estimation of lifetime for polypropylene particles and its effect on particle size, involving the use of single as well as multiple heating rate techniques.

In the present communication, the synthesis, characterization, thermal degradation behavior and kinetics by TGA under nonisothermal conditions of copolymer derived from 4,4'-biphenol, 4,4'-oxydianiline and formaldehyde (4,4'-DBP-4,4'-DDE-F-I) has been studied. Activation energy (Ea), pre-exponential factor [ln(z)] and order of reaction (n) were determined for each degradation step using Friedman, Chang, Sharp-Wentworth, Freeman-Carroll and Coat-Redfern methods.

II. METHODS AND MATERIAL

Materials

The chemicals 4,4'-Dihydroxybiphenyl and 4,4'-Diaminodiphenyl ether are of analytical grade purity which is purchased of Acros Chemicals, Belgium. Formaldehyde (37%) was purchased of S-Define Chemicals, India. All the solvents like N, N-dimethylformamide, dimethyl sulphoxide, tetrahydrofuran, acetone, diethyl ether used were doubly distilled.

Synthesis

4,4'-DBP-4,4'-DDE-F-I copolymer was prepared by condensation polymerization method by using the molar proportion 1:2:4 of reacting monomers i.e. 4,4'-Dihydroxybiphenyl (1.86 gm, 0.1 mol) and 4,4'-Diaminodiphenyl ether (4.00 gm, 0.2 mol) with formaldehyde (15 ml, 0.4 mol) in presence of 2M HCl as a catalyst at 130 ^{0}C in an oil bath for about 3 hrs of continuous heating with occasional shaking (Figure 1). Dark reddish brown colored solid product was immediately removed and filtered. It was purified by dissolving in 1:1 (v/v) conc. NaOH/water with constant stirring and filtered. The resulting polymer sample was washed several times with boiling water and dried in a desiccator at room temperature. Further dried polymeric sample extracted with diethyl ether to remove the excess 4,4'-biphenol-formaldehyde copolymer, which might be present along with the 4,4'-DBP-4,4'-DDE-F-I terpolymer. Finally the terpolymer was passed through 300-mesh size sieve and kept in a vacuum over silica gel [29].
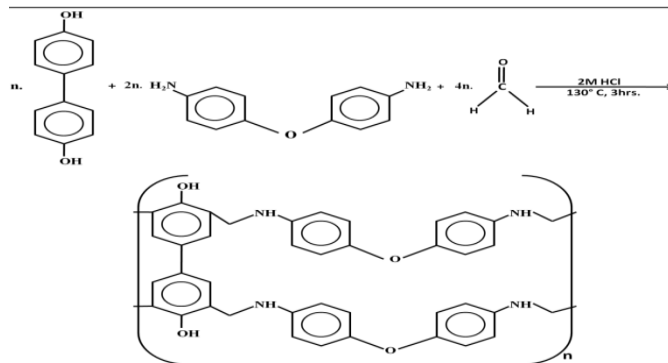

Fig. 1: Chemical reaction of 4,4'-DBP-4,4'-DDE-F-I copolymer.

Analytical and physicochemical studies

Copolymer was subject to elemental analysis for carbon, hydrogen and nitrogen on Perkin Elmer 2400 Elemental Analyser. UV-visible spectra were recorded by preparing solution in dimethylsulphoxide on Shimadzu UV-Visible double beam spectrophotometer fitted with automatic pen chart recorder on thermosensitive paper in the range of 200-850 nm. Infrared spectra was recorded using KBr pellet in nujol mull on Perkin-Elmer-spectrum RX-I spectrophotometer in the range of 4000-500 cm^{-1}. ^{1}H-NMR studies were performed in dimethylsulphoxide as solvent on Bruker Advance-II 400 MHz proton NMR spectrophotometer. All the analytical and spectral studies for newly synthesized copolymer were carried out at Sophisticated Analytical Instrumentation Facility (SAIF) Punjab University, Chandigarh.

Thermal studies

Non-isothermal thermogravimetric analysis of prepared copolymer has been carried out using Perkin Elmer, Pyris1 Thermogravimetric Analyzer, in air atmosphere with a heating rate 10 ^{0}C.min^{-1} in the temperature range 40-1000 ^{0}C. TGA was carried out at VNIT, Nagpur.

Theoretical considerations

Thermogram represents the relationship between change in mass on the temperature which gives information about sample composition, product formed after heating and kinetic parameters [30]. Kinetic parameters have been determined using Friedman [31-32], Chang [33], Sharp-Wentworth [34], Freeman-Carroll [35] and Coat- Redfern [36] techniques as given below.

Friedman technique

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

Where α is the conversion at time t. R is the gas constant (8.314 J/mol/K), and T is the absolute temperature (K). From the slope of the linear plot of ln(1-α) vs. 1/T, n can be obtained. The plot of ln(dα/dt) vs. 1/T should be linear with the slope Ea/R, from which Ea can be obtained.

Chang technique

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

A plot of [ln(dα/dt)/(1- α)^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 (-Ea/R) and ln(z) values, respectively.

Sharp-Wentworth technique

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

Where,

dC/dT = rate of change of fraction of weight with change in temperature

β is linear heating rate, dT/dt.

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

Freeman and Carroll technique

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

Where

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

Wr = *Wc* − *W*

Wc = Weight loss at the completion of reaction

W = Total weight loss upto time t

Ea = Energy of activation

n = order of reaction

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

Coat Redfern technique

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

Where, q and A is the heating rate (⁰C/min) and frequency factor respectively. $g(\alpha)$ is equal to –ln(1-α) for n=1 and ([1-(1-α)ⁿ]/(1-n) for n≠1.

Thus a plot of either ln[(1-(1-α)¹⁻ⁿ)/(T²(1-n))] vs (1/T) or ln[-ln(1-α)/T²] vs (1/T) should results in straight line of slope [-Ea/R] for correct value of n, since it may be shown that for most values of Ea and for the temperature range over which reaction generally occurs the expression ln[(AR/qEa) (1-(2RT/Ea))] is constant.

III. RESULTS AND DISCUSSION

Characterization
Spectral Studies

4,4'-DBP-4,4'-DDE-F-I: 78%

UV-Visible (in DMSO-d₆ in the range 200-850nm)
Spectra exhibits two absorption maxima in the region 255 and 295 nm confirms n→ π* and π→π* transitions show the presence of -O- and biphenol groups respectively. (Fig. 2).

FT-IR 3400.1 cm⁻¹ (phenolic -OH str, b) [37], 2924.4 cm⁻¹ (>NH Str, st), 2855.0 cm⁻¹ (methylene -CH- str, st) [38], 1560.6 cm⁻¹ (substituted aromatic ring C-C str. st), 1662.8 cm⁻¹ (>C=C< str. in aromatics, m), 1340.7 cm⁻¹ (C-N str. in aromatic amine, b), 1170.9 cm⁻¹ (C-O str. in biphenyl ether, m), 1250.0 cm⁻¹ (>C-O str. in phenol, m), 1010.8, 837 cm⁻¹ (tetrasubstituted benzene ring, m) (Fig. 3).

¹H NMR (400 MHz, DMSO-d₆) δ 7.9 (s, 1H, -OH) [38], δ 7.4 (s, 2H, tetrasubstituted, Ar-H), δ 6.8 (d, 1H, -Ar-CH₂-NH), δ 7.2 (d, 2H, proton ortho to -NH), δ 7.3 (d, 2H, proton ortho to -O), δ 6.7 (s, 2H,-Ar-NH-CH₂-) (Fig. 4).

Elemental Analysis Monomer empirical formula: (C₄₀H₃₄N₄O₄); Empirical formula weight: (634).
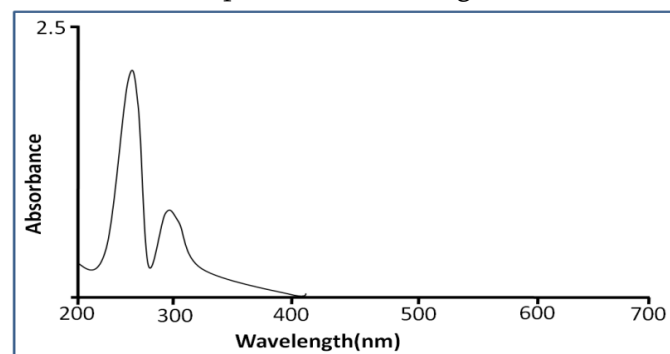

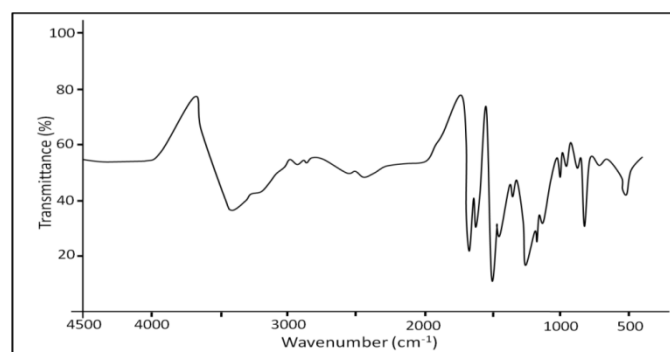**Fig. 2:** UV-visible spectra of 4,4'-DBP-4,4'-DDE-F-I

Fig. 3: FT-IR spectra of 4,4'-DBP-4,4'-DDE-F-I
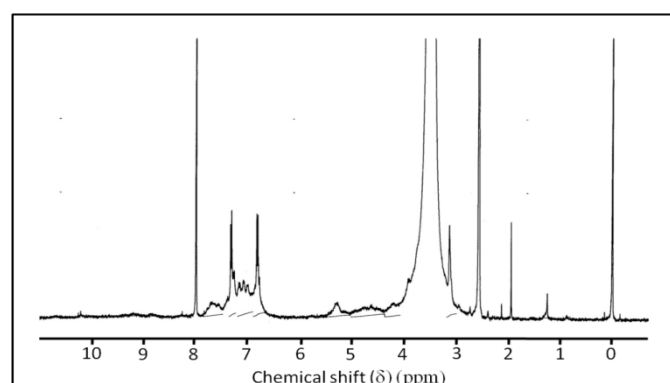

Fig. 4: ¹H-NMR spectra of 4,4'-DBP-4,4'-DDE-F I

Thermogravimetric analysis 4,4'-DBP-4,4'-DDE-F-I copolymer

Thermogravimetric analysis of 4,4'-BP-4,4'-ODA-F-I has been performed at 10 ⁰C.min⁻¹ and the decomposition pattern of a representative polymer

has been shown in Fig. 5. Thermogram of this copolymer depicted three step decomposition steps in the temperature range 40-1000 °C (Table 1). First step is slow decomposition between 40 to 120 °C corresponds to 10.40% loss which may be attributed to moisture entrapped in the molecule [39], against calculated 10.19% present per repeat unit of the polymer. The second step of decomposition starts from 130-320 °C which represents degradation of two (–OH) groups attached to the benzene skeleton and two –CH_2-NH – groups (23.34% found and 23.22% calculated). Third step decomposition starts from 330-1000 °C corresponding to 71.22% loss of two oxybiphenyl and –CH_2-NH- moieties against calculated 71.10% and consequently residue remained having the values (28.78% found and 28.90% calculated). The synthesized copolymer is half decomposed at 440 °C observed in thermal data.

Table 1 Thermal degradation behavior of 4,4'-DBP-4,4'-DDE-F-I copolymer.

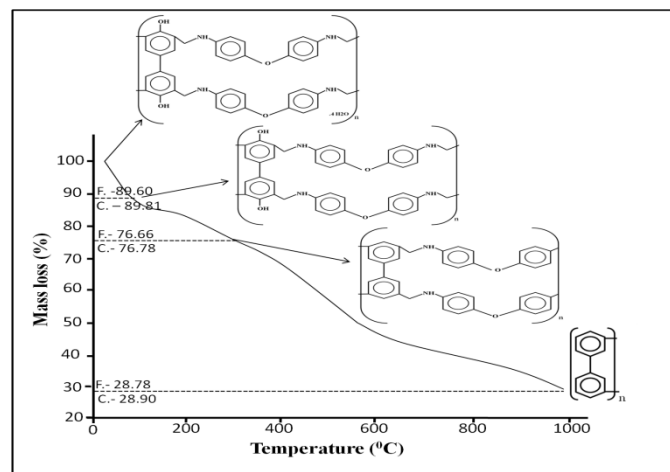| Decomposition steps	Temp. range (°C)	Wt. loss (%)		Species degraded
		Observed	Calculated	
1.	40-120	10.40	10.19	Four H_2O molecules
2.	120-320	23.34	23.22	two (–OH) and two –CH_2-NH – groups
3.	330-1000	71.22	71.10	two oxybiphenyl and –CH_2-NH – moieties

Fig. 5: Decomposition pattern of 4,4'-DBP-4,4'-DDE-F-I copolymer

Kinetics of thermal decomposition by Friedman, Chang, Sharp-Wentworth, Freeman-Carroll and Coat Redfern methods.

Thermogram represents three different degradation steps corresponding to loss of respective groups by fitting the thermogravimetric data to five thermal degradation kinetic techniques (viz. Friedman, Chang, Sharp-Wentworth, Freeman-Carroll and Coat-Redfern). The decomposition is due to pyrolysis of straight chain linked structure of copolymer and at 1000 °C degradation process occurs upto final level leaving behind the remaining biphenyl moiety. The thermal stability of 4,4'-DBP-4,4'-DDE-F-I copolymer is concluded to be higher, may be due to the stronger intermolecular hydrogen bonding present in polymer structure because of water of crystallization which would be more difficult to break and hence more resistant to higher temperature [40] or it may be due to possibility of an almost linear structure of copolymer chain which gives stability to polymer chain [41]. In case of copolymer the removal of four water molecules is complete and is probably crystal water or moisture entrapped in the molecule.

Kinetic parameters for 4,4'-DBP-4,4'-DDE-F-I copolymer have been calculated using Friedman method (1) for each decomposition step. Activation energy (Ea) has been obtained from the plot between ln(dα/dt) vs. (1/T) (Fig. 6) and order of reaction (n)

from the plot between ln(1-α) vs (1/T) (Fig. 7). Values of ln (z) are calculated at each temperature region from (1) with the help of Ea and n. The results from Friedman are shown in Table 2. The kinetic parameters show that Ea, n and ln(z) are different for different thermal decomposition reactions as the thermogram is divided into three different zones.

Table 2 Kinetic parameters of thermal degradation of 4,4'-DBP-4,4'-DDE-F-I copolymer calculated by Friedman method.

Decomposition steps	Ea	n	ln(z)
1.	45.66	1.5	16.09
2.	13.43	1.0	8.48
3.	40.62	4.00	12.49

Units of Ea and ln(z) are kJ/mole and min^{-1} respectively.

Table 3 Kinetic parameters of thermal degradation of 4,4'-DBP-4,4'-DDE-F-I copolymer calculated by Chang method.

Decomposition steps	Ea	n	ln(z)
1.	46.13	1.5	16.17
2.	13.30	1.0	8.71
3.	44.62	4.0	13.09

Units of Ea and ln(z) are kJ/mole and min^{-1} respectively.

Table 4 Kinetic parameters of thermal degradation of 4,4'-DBP-4,4'-DDE-F-I copolymer calculated by Sharp-Wentworth method.

Decomposition steps	Ea	n	ln(z)
1.	19.81	1.5	6.9
2.	5.84	1.0	3.6
3.	17.50	4.0	5.4

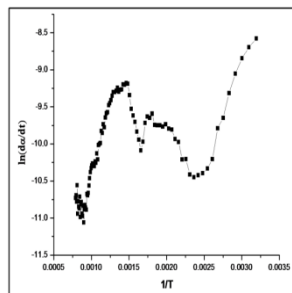Units of Ea and ln(z) are kJ/mole and min^{-1} respectively.

Fig. 6: Friedman plot of 4,4'-DBP-4,4'-DDE-F-I copolymer for activation energy.
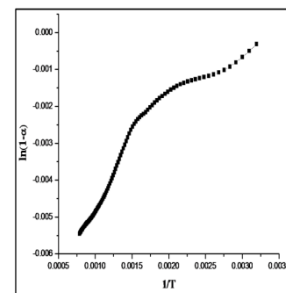
Fig. 7: Friedman plot of 4,4'-DBP-4,4'-DDE-F-I copolymer for the order of reaction.

Figure 8 has shown Chang method (2) gives the plot between $[\ln(d\alpha/dt)/(1-\alpha)^n]$ vs. (1/T) for 4,4'-DBP-4,4'-DDE-F-I at the heating rate 10 ^{0}C.min^{-1} which is used to calculate Ea and ln(z) of respective degradation reaction for best fitted value of n, which corresponds to correct reaction order for each respective thermal decomposition step (Fig. 8). Varied values of activation energy and frequency factor are observed at each degradation step which indicates degradation of respective group as shown in Table 3.
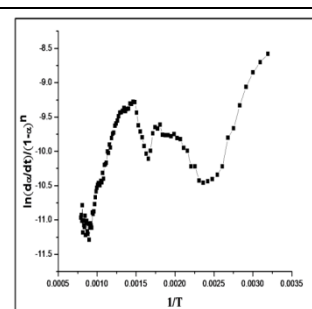

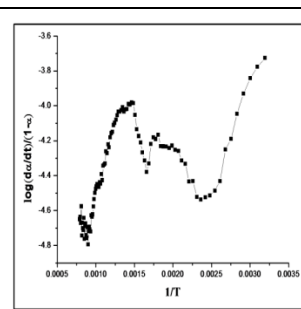**Fig. 8:** Chang plot of 4,4'-DBP-4,4'-DDE-F-I copolymer

Fig.9: Sharp-Wentworth plot of 4,4'-DBP-4,4'-DDE-F-I copolymer

Also kinetic parameters for different thermal degradation zones have been calculated by Sharp-Wentworth method (3) shown in Table 4. Ea and ln (z) values are calculated from the plot between $log \dfrac{dc/dt}{1-c}$ vs. $\dfrac{1}{T}$ with best fitted values of n for each respective degradation reaction (Fig. 9).

Similarly, using the Freeman-Carroll technique (4) kinetic parameters has been calculated. Fig. 10 shows representative plot of $\frac{\Delta \ln (\frac{d\alpha}{dt})}{\Delta \ln (1-\alpha)}$ vs $\frac{\Delta (\frac{1}{T})}{\Delta \ln (1-\alpha)}$ for 4,4'-DBP-4,4'-DDE-F-I. The slope and intercept for each step are computed from (4), which is equal to (Ea/R) and n respectively (Table 5).

Table 5 Kinetic parameters of thermal degradation of 4,4'-DBP-4,4'-DDE-F-I copolymer calculated by Freeman-Carroll method.

Decomposition steps	Ea	n	log z
1.	12.57	2.5	0.56
2.	8.96	1.3	0.35
3.	18.72	1.05	3.36

Units of Ea and ln(z) are kJ/mole and min^{-1} respectively.

Table 6 shows kinetic parameters evaluated by using Coat Redfern (5) method by plotting ln[(1-(1-α)$^{1-n}$)/(T^2(1-n))] vs (1/T) for 4,4'-DBP-4,4'-DDE-F-I, should results in straight line of slope [-Ea/R] for correct value of n (Fig. 11) .

Table 6 Kinetic parameters of thermal degradation of 4,4'-DBP-4,4'-DDE-F-I copolymer calculated by Coat Redfern method.

Decomposition steps	Ea	n	log z
1.	17.44	0.9	13.08
2.	16.59	0.9	12.15
3.	37.26	0.9	13.81

Units of Ea and ln(z) are kJ/mole and min^{-1} respectively.
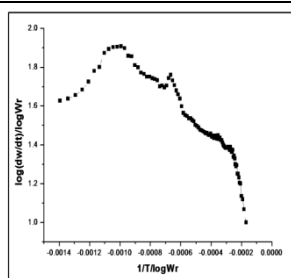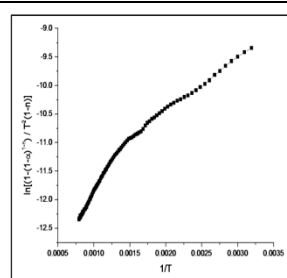
plot of 4,4'-DBP-4,4'-DDE-F-I copolymer	plot of 4,4'-DBP-4,4'-DDE-F-I copolymer	

A plot of percentage mass loss vs temperature is shown in Fig. 5 for a representative 4,4'-DBP-4,4'-DDE-F-I copolymer. From the TG curves, the thermoanalytical data and decomposition temperature has been determined by utilizing five different kinetic equations for different stages as given in Table 1. This kinetic analysis should be a starting point to obtain the useful information on the behavior of samples.

Fairly comparable results for kinetic parameters viz. Ea, n and ln(z) are obtained by Friedman and Chang which are nearly equal may be due to analogy in mathematical model. Also results by Sharp-Wentworth, Freeman-Carroll and Coat-Redfern methods are in similar order.

From the above discussion, it is therefore concluded that for each technique, the values of Ea, n and ln(z) depend on calculation technique used as well as degrading species at a particular step. Total calculations obtained from different kinetic models demonstrated that the numerical value of kinetic parameters depends on the mathematical model used to analyze the experimental data [28]. Low values of log z revealed that decomposition reaction of copolymer may be slow.

By using above mentioned kinetic techniques fairly comparable results are obtained which represents versatility and great utility of thermal degradation kinetic equations in thermogravimetry.

IV. CONCLUSIONS

1. Synthesis of targeted copolymer 4,4'-DBP-4,4'-DDE-F-I has been confirmed which is supported by results obtained by the spectral analysis.
2. Thermogram obtained has shown three degradation stages indicating degradation of water molecule, two –CH$_2$-NH – groups and two oxybiphenyl and –CH$_2$-NH– moieties. Friedman, Chang methods show nearly similar values of

Fig. 10: Freeman-Carroll

Fig. 11: Coat- Redfern

kinetic parameters may be due to resemblance in mathematical model whereas and Sharp-Wentworth, Coat Redfern and Freeman-Carroll methods shows different observations.

3. The values of kinetic parameters are significantly controlled by level of degradation and calculation technique used to analyze the experimental data.

V. ACKNOWLEDGEMENT

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Cite this article as :