

## Synthesis, Characterization and Thermogravimetric Analysis of 2,2'-Biphenol Based Terpolymer Resins

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**Abstract:** The novel terpolymer resins (2,2'-BPTEPAF- I, II, III) have been synthesized by condensation polymerization of 2,2'-biphenol (2,2'-BP) and tetraethylenepentamine (TEPA) with formaldehyde (F) in presence of 2 M NaOH as a catalyst using varying molar ratios of reacting monomers. The composition of resins has been determined by elemental analysis. Spectral studies such as UV-Visible, FT-IR and  $^1\text{H}$  NMR spectra have been used to confine the most probable structures of newly synthesized terpolymer resins. Non-isothermal thermogravimetric analysis has been carried out to determine their mode of decomposition and relative thermal stability. Kinetic parameters such as energy of activation ( $E_a$ ), order of reaction ( $n$ ) and frequency factor ( $z$ ) has been calculated by applying Friedman, Chang and Sharp-Wentworth methods. The computed results are compared and elaborated.

**Keywords:** Synthesis, Characterization, Thermogravimetry, Kinetic parameters

### Introduction

Reactions of three component polymeric system by applying suitable method of synthesis have been the subject of interest for many investigators in order to study its high performance utility. In the present study, terpolymer comprises of three components, in which formaldehyde acts as a connecting link between two reacting monomers.

The terpolymer resins showing versatile applications and properties, attracted the attention of scientist and introduced the recent innovations in the polymer chemistry. They are found to be amorphous, crystalline or resinous in nature. The progress in this field has been extremely rapid as they are generally useful in high dielectric constant for energy storage capacitors<sup>1</sup>, packaging, adhesive and coatings in electrical sensors, ion-exchangers<sup>2,4,8-13</sup>, semiconductors<sup>5</sup>, activators, catalyst and thermally stable materials<sup>6,7,26</sup>.

Extensive research work has been carried out on the synthesis, characterization and thermogravimetry of terpolymers. Jadhav have synthesized and studied the thermal degradation properties of terpolymers based on 2,2'-biphenol<sup>14,15</sup>. Pratik Michael *et al.* studied the structural and thermal degradation of terpolymer derived from salicylic acid, guanidine and

formaldehyde<sup>16</sup>. Kobayashi and Kon-ishi synthesized resorcinol-acetone copolymer and studied its thermogravimetric analysis<sup>17</sup>. Singru and coworkers reported thermoanalytical study and kinetics of 8-hydroxyquinoline-5-sulphonic acid-oxamide-formaldehyde and *p*-cresol-oxamide-formaldehyde terpolymer resins<sup>18,19</sup>. Patel and coworkers synthesized and characterized acrylic copolymers derived from 8-quinoliny methyl methacrylate and studied its ion exchange properties<sup>20</sup>. Peterson *et al.* have carried out thermogravimetric analysis in inert as well as oxidative atmosphere<sup>21</sup>. The thermal stability of polymers and copolymers has been extensively studied by employing the method of thermogravimetric analysis by several authors<sup>22-25</sup>.

Study of thermal behaviour of terpolymers in air atmosphere at different temperature provides useful information about the nature of species produced at various temperatures due to degradation. Non-isothermal thermogravimetric analysis in which sample is subjected to condition of continuous increase in temperature at linear rate which provides the useful information about the degradation pattern and thermal stability.

Literature studies have revealed that no terpolymer has been synthesized using the monomer 2,2'-biphenol, tetraethylenepentamine and formaldehyde. In the present article, we present the synthesis of phenolic straight chain and branched terpolymers (2,2'-BP-TEPAF) by condensation terpolymerization reaction and characterized by elemental analysis, UV-visible, FT-IR, <sup>1</sup>H NMR spectra. Studies were further extended to thermogravimetric analysis in order to predict its thermal degradation pattern and kinetic parameters by implementing Friedman, Chang and Sharp-Wentworth method.

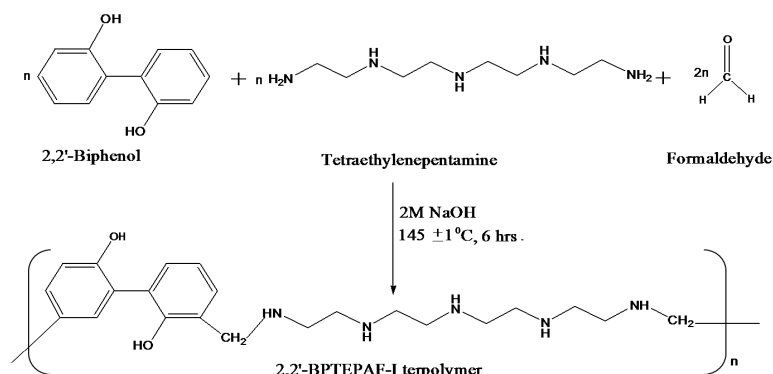
## Experimental

2,2'-Biphenol and tetraethylenepentamine are of analytical grade purity which was purchased from Acros Chemicals, Belgium. Formaldehyde (37%) was purchased from SD Fine Chemicals, India. All the used solvents like *N,N*-dimethylformamide, dimethyl sulphoxide, tetrahydrofuran, acetone, diethyl ether were procured from Merck, India.

### Synthesis

2,2'-BPTEPAF terpolymer resins were prepared by condensing 2,2'-biphenol and tetraethylenepentamine with formaldehyde in presence of 2 M NaOH as a catalyst in the various molar proportions of reacting monomers at 145±1 °C in an oil bath for six hrs of continuous heating. The temperature of electrically heated oil bath was controlled with the help of a dimmerstat. A wine red coloured solution was obtained after completion of reaction and the yellowish resinous solid product was formed after re-precipitation with 2 M HCl. The product was immediately removed, filtered and repeatedly washed with cold-distilled water, dried in air and powdered with the help of an agate mortar and pestle. The product obtained was extracted with diethyl ether to remove excess of 2,2'-biphenol-formaldehyde copolymer which might be present along with 2,2'-BPTEPAF terpolymer resin. Dried resin sample was dissolved in 8% NaOH and regenerated using 1:1 HCl/water (v/v) with constant stirring then it was filtered. This process was repeated twice. Resulting terpolymer resin sample was washed with boiling water and dried in a vacuum at room temperature. Purified terpolymer resin was finely ground to pass through 300-mesh size sieve and kept in a vacuum over silica gel<sup>26</sup>.

Similarly, other terpolymer resins *viz.* 2,2'-BPTEPAF-II, 2,2'-BPTEPAF-III were synthesized by varying the molar proportion of starting material, *i.e.* 2,2-biphenol, tetraethylenepentamine with formaldehyde in the ratio of 1:2:4 and 4:1:5. The chemical reaction of 2,2'-BPTEPAF-I terpolymer resin is given in Figure 1. Synthesis and physical data of 2,2'-BPTEPAF terpolymer resins are shown in Table 1.



**Figure 1.** Chemical reaction of 2,2'-BPTEPAF- I terpolymer resin

**Table 1.** Synthesis and physical data of 2,2'-BPTEPAF terpolymer resins

Terpolymer resins	Reactant			Catalyst 2 M NaOH (aq) mL	Yield, %
	2,2'-Biphenol, mol.	Tetraethylene- pentamine, mol.	Formal- dehyde, mol.		
2,2'-BPTEPAF-I	0.1	0.1	0.2	200	79.00
2,2'-BPTEPAF-II	0.1	0.2	0.4	200	81.05
2,2'-BPTEPAF-III	0.4	0.1	0.5	200	83.65

### Spectral and thermal studies

Terpolymer resins were subject to elemental analysis for carbon, hydrogen and nitrogen on Elmentar Vario EL III Elemental Analyzer at Sophisticated Test and Instrumentation Centre, Cochin University of Science and Technology, Cochin. UV-Vis spectra of terpolymer resins in DMSO solvent recorded on JASCO V-630 UV-VIS spectrophotometer at Nagpur in the range of 200-850 nm at Department of Pharmacy, R.T.M. Nagpur University, Nagpur.  $^1\text{H}$  NMR studies were performed in DMSO as solvent on Bruker Advance-II 400 NMR spectrophotometer and FT-IR spectra were recorded in nujol mull on Perkin Elmer spectrum RX-I spectrophotometer in the range of  $4000\text{-}500\text{ cm}^{-1}$  at Sophisticated Analytical Instrumentation Facility (SAIF) Punjab University, Chandigarh. The non-isothermal thermogravimetric analysis of newly prepared terpolymer resins has been carried out using Perkin Elmer Diamond 3 II thermogravimetric analyzer in air atmosphere with a heating rate at  $10^\circ\text{C min}^{-1}$  in the temperature ranges from  $40\text{-}1000^\circ\text{C}$  at VNIT, Nagpur.

### Thermal analysis

Dynamic (non-isothermal) thermogravimetric analysis of all terpolymer resins have been carried out in air atmosphere with heating rate of  $10^\circ\text{C min}^{-1}$  by taking 5-6 mg of samples in platinum crucible. Thermograms were recorded in the temperature range  $40\text{-}1000^\circ\text{C}$ . Thermal activation energy ( $E_a$ ), order of reaction ( $n$ ) and frequency factor ( $z$ ) has been calculated from thermogravimetric data.

### 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. Kinetics parameters have been determined using Friedman<sup>27</sup>, Chang<sup>28</sup> and Sharp-Wentworth<sup>29</sup> techniques as follows:

### Friedman technique

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

Where,  $\alpha$  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

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

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.

### Sharp-Wentworth technique

$$\frac{\log\left(\frac{dc}{dt}\right)}{1-c} = \log\left(\frac{A}{\beta}\right) - \frac{E\alpha}{2.303RT} \quad (3)$$

Where,  $dc/dt$  = rate of change of fraction of weight with change in temperature;  $\beta$  = linear heating rate *i.e.*  $dT/dt$ ;  $c$  = fraction of polymer decomposed at time  $t$ .

Thus, a linear plot of  $\frac{\log\left(\frac{dc}{dt}\right)}{1-c}$  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.

## Results and Discussion

### Elemental analysis

The composition of terpolymer resins was assigned on the basis of elemental analysis and was found to be in good agreement with that of calculated values as shown in Table 2.

**Table 2.** Elemental analysis data of 2,2'-BPTEPAF terpolymer resins

Terpolymer resins	Monomer empirical formula	Monomer empirical Weight	Elemental analysis, %					
			C		H		N	
			Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
2,2'-BPTEPAF-I	C <sub>22</sub> H <sub>37</sub> N <sub>5</sub> O <sub>4</sub>	435	60.68	60.99	8.5	8.35	16.09	16.21
2,2'-BPTEPAF-II	C <sub>32</sub> H <sub>62</sub> N <sub>10</sub> O <sub>5</sub>	666	57.65	57.86	9.30	9.36	21.02	21.16
2,2'-BPTEPAF-III	C <sub>61</sub> H <sub>64</sub> N <sub>5</sub> O <sub>10</sub>	1026	71.34	71.45	6.23	6.42	6.82	7.67

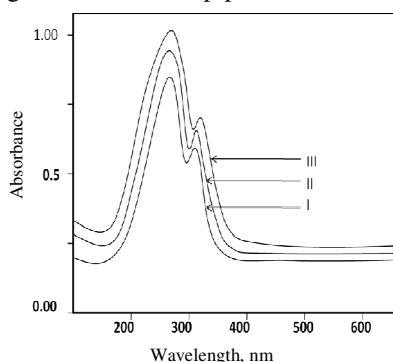
### UV-Visible spectra

UV-visible spectra of the 2,2'-BPTEPAF terpolymer resins give rise to a similar pattern is represented in Figure 2. The spectra of these terpolymer resins exhibit two absorption maxima at 270 to 280 nm and 310 to 330 nm. These observed positions for the absorption bands have different intensities. The more intense band which may be accounted for  $\pi \rightarrow \pi^*$  allowed transition of conjugation in aromatic ring. While the later and less intense band due to  $n \rightarrow \pi^*$  forbidden transitions of -OH group.

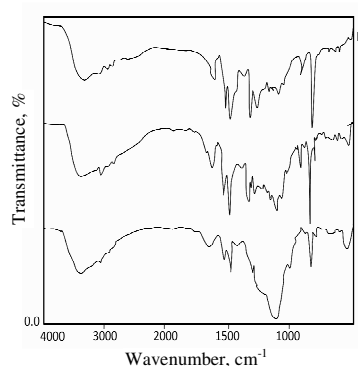
The auxochromic substituents (-OH) interacting with  $\pi$  electron of the benzene ring. This interaction stabilizes  $\pi^*$  state and thus lowers the energy as a result bathochromic shift is caused. The presence of phenolic hydroxyl group is responsible for bathochromic shift (shift toward longer wavelengths). Both bathochromic and hyperchromic effect of conjugation shown by chromophore (aromatic ring) and auxochrome (-OH) group in repeated unit of terpolymer resins.

### FT-IR spectra

The FT-IR spectra of 2,2'-BPTEPAF terpolymer resins are depicted in Figure 3 and IR spectral data are tabulated in Table 3. Broad and strong band appeared at  $3351\text{--}3397\text{ cm}^{-1}$ , which may be assigned to the stretching vibration of the phenolic -OH groups exhibiting intermolecular hydrogen bonding<sup>30,31</sup>. Short and weak band at  $3055\text{--}3062\text{ cm}^{-1}$  are indicate the presence of a >NH stretching (sec. amine) group. A medium broad band, displayed at  $1578\text{--}1602\text{ cm}^{-1}$ , may be due to bending vibration of secondary amine. Substituted aromatic ring show medium and short bands at  $1482\text{--}1484\text{ cm}^{-1}$ . Medium and short peak displayed at  $1371\text{--}1374\text{ cm}^{-1}$  suggested the presence of -CH<sub>2</sub>- bridge in terpolymer resins<sup>32</sup>. The presence of C-N stretch can be accounted by the presence of band at  $1154\text{--}1155\text{ cm}^{-1}$  and  $1143\text{--}1047\text{ cm}^{-1}$ . The presence of substitution on aromatic ring also shows sharp peak at  $756\text{--}758\text{ cm}^{-1}$ .



**Figure 2.** UV-Visible spectra of terpolymer resins 2,2'-BPTEPAF



**Figure 3.** IR spectra of terpolymer resins 2,2'-BPTEPAF

**Table 3.** IR frequencies spectral data of 2,2'-BPTEPAF terpolymer resins

Assignment	2,2'-BPTEPAF-I	IR Wavenumber, $\text{cm}^{-1}$ 2,2'-BPTEPAF-II	2,2'-BPTEPAF-III
-OH (Phenolic)	3397 b,st	3355 b,st	3361 b,st
>NH stretching (sec. amine)	3062 sh,w	3056 sh,w	3055 sh,w
Secondary amine bending	1602 m,b	1587 m,b	1578 m,b
-CH <sub>2</sub> - bridge	1371 m,sh	1372 m,sh	1374m,sh
C-N stretch	1155.57 m 1047.81 st,b	1154 m 1043sh	1155 m 1043m
Substituted aromatic ring	758 sh	756 sh	755 sh

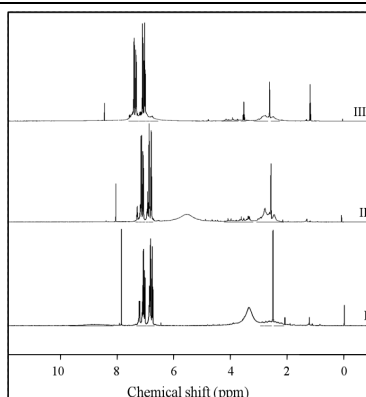
*sh- sharp; b- broad; st- strong; m- medium; w- weak*

### <sup>1</sup>H NMR spectra

<sup>1</sup>H NMR spectral data of terpolymer resins are incorporated in Table 4 and spectrum is presented in Figure 4. Spectra reveal different patterns of peaks, since each of them possesses a set of protons having different proton environment. A singlet is observed due to proton of phenolic -OH group, observed at  $\delta$  7.99 - 8.19 ppm. A singlet is observed at  $\delta$  7.31-7.36 ppm and is due to unsymmetrical pattern of protons of phenol. A signal appeared in the region 2.51-2.56 ppm may be due to proton of methylene bridges (Ar-CH<sub>2</sub>-N) of polymer chain shows singlet. The singlet in the region 6.80-6.88 ppm is attributed to proton of -NH- bridge.

**Table 4.** <sup>1</sup>H NMR spectral data of 2,2'-BPTEPAF terpolymer resins

Nature of protons assigned	<sup>1</sup> H NMR Chemical shift ( $\delta$ ) ppm of Terpolymer resins		
	2,2'-BPTEPAF-I	2,2'-BPTEPAF-II	2,2'-BPTEPAF-III
Proton of Ar-OH (phenolic-OH)	7.99 s	8.1 s	8.19 s
Aromatic proton (unsymm. pattern)	7.36 s	7.34 s	7.31 s
Methylene proton of d, Ar-CH <sub>2</sub> -NH moiety	2.56 s	2.54 s	2.51 s
Proton of -NH bridge	6.88 s	6.83 s	6.80 s

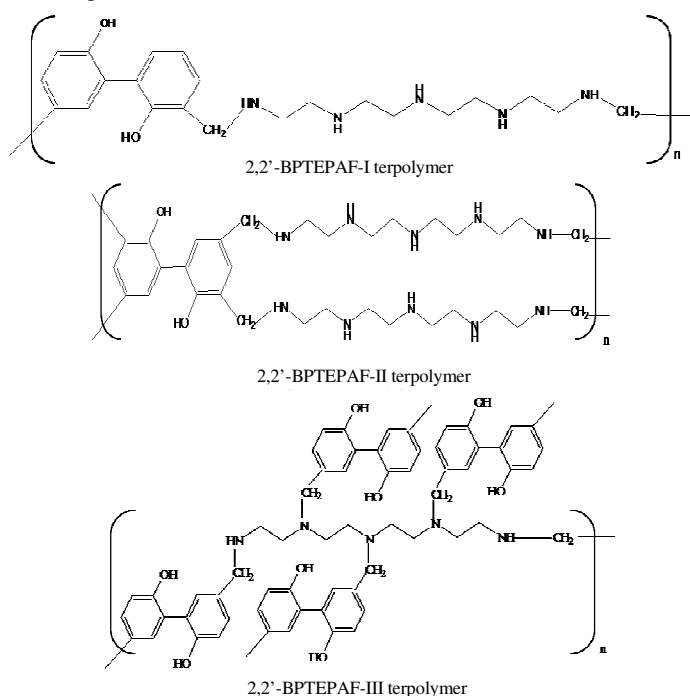


**Figure 4.** <sup>1</sup>H-NMR spectra of terpolymer resins 2,2'-BPTEPAF

### Thermogravimetric analysis

Decomposition pattern of terpolymer resin is shown in Figure 6. Thermogram of 2,2'-BPTEPAF-I terpolymer exhibited four step decomposition in the temperature range 40-1000 °C. The first step is of slow decomposition between 40 to 140 °C corresponds to 8.15% loss which may be attributed to loss of two water molecules which may be due to moisture entrapped in the terpolymer resin<sup>33,34</sup> against calculated 8.27% present per repeat unit of polymer. The second step decomposition starts from 140 °C to 220 °C which represents degradation of two hydroxyl groups (16.21% found and 16.09% calculated). The third step of decomposition starts from 220-310 °C corresponds to 57.28% loss of biphenyl ring against calculated 57.01%. Fourth step starts from 310 to 1000 °C corresponding to loss of complete tetraethylenepentamine moiety. Table 6 represents the thermal degradation data for 2,2'-BPTEPAF-I, II, III terpolymer resins. To obtain the kinetic parameters, the thermal degradation kinetic equations described by Sharp-Wetworth, Friedman and Chang was adopted. By using thermal decomposition data

and then applying above methods the activation energy ( $E_a$ ), order of reaction ( $n$ ) and Frequency factor ( $z$ ) are calculated. The activation energies calculated by these methods are depicted in Table 5. The thermal stability of terpolymer predicted on the basis of the initial decomposition temperature is in concurrence with that predicted from the activation energy values. From the above spectral studies, the proposed structures of 2,2'-BPTEPAF-I, II, III terpolymer resins are given below.



**Figure 5.** Structures of 2,2'-BPTEPAF-I, II, III terpolymer resins

**Table 5.** Thermoanalytical data for each degradation step of 2,2'-BPTEPAF- I terpolymer resin

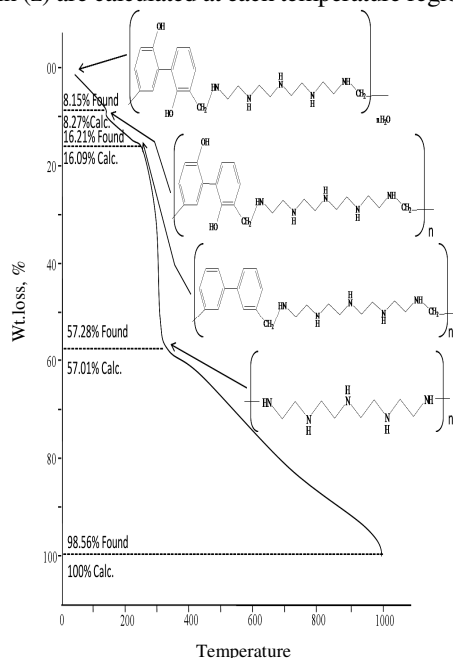
Kinetic equations	Decomposition steps								
	2,2-BPTEPAF-I			2,2-BPTEPAF-II			2,2-BPTEPAF-III		
	$E_a$	$n$	$z$	$E_a$	$N$	$z$	$E_a$	$n$	$z$
Friedman	10.81	1.8	11.09	10.90	1.4	10.91	12.97	1.7	11.29
Chang	11.11	1	11.14	11.40	1	10.98	13.63	1	11.29
Sharp-Wentworth	46.79	1	4.81	47.16	1	4.73	56.13	1	4.91

#### *Kinetics of thermal decomposition by Friedman, Chang and Sharp-Wentworth techniques*

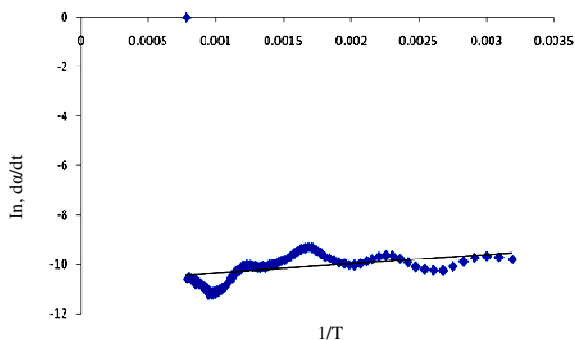
The analysis of thermograms indicates that the decomposition of terpolymer is four step process in which loss of water molecules present per repeat unit of polymer in first step. Due to fragmentation of straight chain and branch linked structure of terpolymer resins because of which it doesn't takes more time to attain the thermal equilibrium as well as at 1000 °C degradation process occurs up to final level without leaving behind the remaining moiety. The thermal stability of 2,2'-BPTEPAF terpolymer resins are concluded to be higher, may be due to the stronger intermolecular hydrogen bonding present in polymer structures because of

moisture entrapped in the terpolymer resin which would be more difficult to break and hence more resistant to higher temperature or it may be due to possibility of an linear and branched structure of terpolymer chain which gives stability to polymer chain.

Kinetic parameters for 2,2'-BPTEPAF terpolymer resins have been calculated using Friedman, Chang and Sharp-Wentworth method. In Friedman method Activation energy ( $E_a$ ) of three terpolymer resins have been obtained from the plot between  $\ln(d\alpha/dt)$  vs.  $(1/T)$  and order of reaction ( $n$ ) from the plot between  $\ln(1-\alpha)$  vs.  $(1/T)$  as shown in Figures 7 and 8 respectively. Values of  $\ln(z)$  are calculated at each temperature region with the help of  $E_a$  and  $n$ .



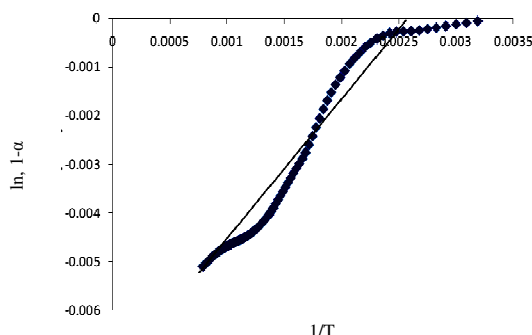
**Figure 6.** Decomposition pattern of 2,2'-BPTEPAF- I terpolymer resin



**Figure 7.** Friedman activation energy plot of 2,2'-BPTEPAF- I terpolymer resin

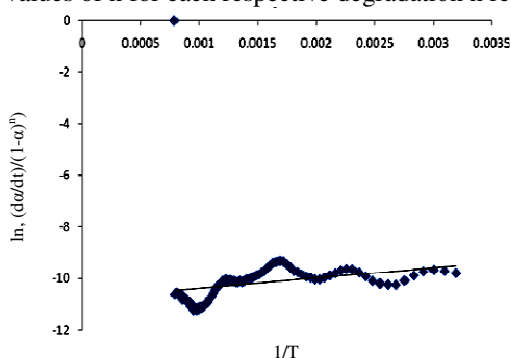
Figure 9 shows Chang method gives plots between  $[\ln(d\alpha/dt)/(1-\alpha)^n]$  vs.  $(1/T)$  for 2,2'-BPTEPAF at the heating rate  $10\text{ }^\circ\text{C.min}^{-1}$  which is used to calculate  $E_a$  and  $\ln(z)$  of respective degradation reaction for best fitted value of  $n$  (from Friedman equation), which corresponds to correct reaction order for each respective thermal decomposition step.





**Figure 8.** Friedman order of reaction plot of 2,2'-BPTEPAF- I terpolymer resin

Also kinetic parameters for different thermal degradation zones have been calculated by Sharp-Wentworth method.  $E_a$  and  $\ln(z)$  values are calculated from the plot between  $\frac{\log\left(\frac{dc}{dt}\right)}{1-c}$  vs.  $\frac{1}{T}$  with best fitted values of  $n$  for each respective degradation  $n$  reaction (Figure 10).



**Figure 9.** Chang plot of 2,2'-BPTEPAF- I terpolymer resin

By using thermal decomposition data and then applying the Friedman method (representative Friedman plots of 2,2'-BPTEPAF terpolymer resin are shown in Figures 7 and 8. Activation energy is calculated which is in agreement with the activation energy is calculated by Chang plot (Figure 9) for the polymer has been shown.

A plot of percentage mass loss vs. temperature is shown in Figure 5 for a representative 2,2'-BPTEPAF terpolymer resin. From the TG curves, the thermoanalytical data and decomposition temperature has been determined for different stages as given in Table 6.

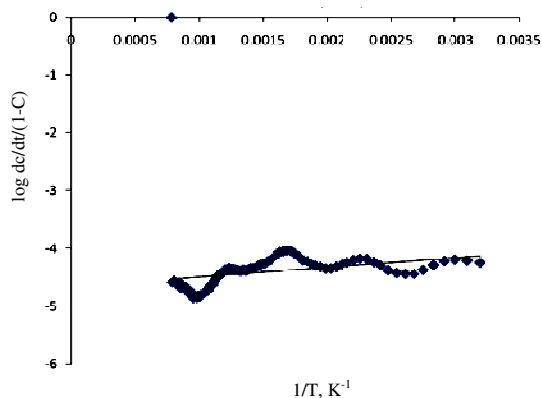
This kinetic analysis should be a starting point to obtain the useful information on the behavior of samples. Fairly comparable results in the kinetic parameters *i.e.*  $E_a$  and  $z$  are obtained by Friedman and Chang may be due to analogy in mathematical model but somewhat different observations are observed in Sharp-Wentworth method.

The energy of activation calculated by Friedman and Chang method are found to be in will agreement with each other. But Sharp-Wentworth method shows different observations. Order of reaction calculated from Sharp-Wentworth and Chang method is found to be one. But order of reaction calculated by Friedman method not obeys first order kinetics perfectly as reported by Jacobs and Tompkin<sup>35</sup> and Coats and Redfern<sup>36</sup>.

**Table 6.** Thermal degradation behavior of 2,2'-BPTEPAF-I terpolymer resin

S.No.	Terpolymer	Temp. °C Range, °C	Half decomposition temperature, °C	Stage of decomposition	Species Degraded	Wt. Loss, %	
						Found	Calc.
1	2,2'- BPTEPAF-I	40-140	310	First	Loss of two H <sub>2</sub> O molecules	8.15	8.27
		140-220		Second	Loss of two hydroxyl groups	16.21	16.09
		220-310		Third	Loss of Biphenyl ring with two (-CH <sub>2</sub> ) groups	57.28	57.01
		310-1000		fourth	Complete loss of TEPA moiety	98.56	100.00
2	2,2'- BPTEPAF-II	40-150	371	First	Loss of three H <sub>2</sub> O molecules	8.13	8.10
		150-180		Second	Loss of two hydroxyl groups	13.13	13.21
		180-600		Third	Loss of Biphenyl ring and one side chain of TEPA attached to biphenyl ring	71.35	71.92
		600-1000		Fourth	Complete loss of TEPA moiety	97.62	100.00
3	2,2'- BPTEPAF-III	40-130	319	First	Loss of two H <sub>2</sub> O molecules	3.81	3.50
		130-200		Second	Loss of eight hydroxyl groups	16.97	16.76
		200-600		Third	Loss of four Biphenyl ring with five (-CH <sub>2</sub> ) groups	81.74	81.77
		600-1000		Fourth	Complete loss of TEPA moiety	98.28	100.00

The thermogravimetric analysis of all the three terpolymer resins prepared has been carried out but, the thermal data and kinetic plots for only one representative case are given in Figures 7-10.

**Figure 10.** Sharp-Wentworth plot of 2,2'-BPTEPAF-I terpolymer resin

By using above mentioned techniques fairly good straight-line plots are obtained which represents versatility and great utility of thermal degradation mathematical equations in thermal studies and attempts are developing to implement the model free kinetic equations.

## Conclusion

Synthesis of targeted terpolymer resins (2,2-BPTEPAF) has been confirmed which is supported by the results obtained by the elemental analysis and spectral data. Presence of

spectral peaks of methylene bridge in the spectral data confirms the formation of terpolymer resins. The thermogram shows four degradation steps for all the terpolymers *i.e.* in first step loss of water molecule, in second step hydroxyl group, in third step biphenyl ring and in fourth step loss of complete tetraethylenepentamine moiety. The activation energy values calculated from Friedman and Chang method are in well agreement with each other due to resemblance in the mathematical model and with some variation in Sharp-Wentworth method.

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