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Synthesis, characterization and thermal study of 2,2'-biphenoltetraethylenepentamine-formaldehyde terpolymer resin

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ABSTRACT

Terpolymer (2,2'-BPTEPAF) has been synthesized by using the monomers 2,2'-Biphenol and Tetraethylenepentamine with Formaldehyde in 1:1:2 molar proportion. The structure of newly synthesized terpolymer has been explicated on the basis of elemental analysis and various spectral studies i.e. UV-Visible, FT-IR and ¹H-NMR spectroscopy. Thermal degradation study has been carried out to ascertain its thermal degradation behavior and thermal stability. Kinetic parameters, such as activation energy (Ea), order of reaction (n) and frequency factor (z) have been evaluated by applying Friedman, Chang, Sharp-Wentworth and Freeman-Carroll methods. The activation energy calculated by using the Friedman (10.81 kJ/mol) and Chang (11.11 kJ/mol) methods have been found to be in close agreement with each other and activation energy calculated by Sharp-Wentworth and Freeman-Carroll methods are also in same manner.

Keywords: Synthesis, Thermogravimetric analysis, Energy of activation, Order of reaction, Frequency factor.

INTRODUCTION

Polymer science and technology has been developing rapidly due to its worldwide applications and attracted much attention towards the polymer scientists. Since last two decades, emphasis has been given on synthesis of thermally stable terpolymeric resins with reference to industrial applicability at elevated temperature, low production cost and ease of manufacture. Thermally stable terpolymers recently become beneficial to polymer chemist due to its superior characteristics. Many researchers were tried to improve the thermal stability by changing the monomer composition in polymer synthesis.

Terpolymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. In our laboratory, extensive work on thermal degradation of terpolymers has been undertaken [1, 2]. Peterson et al have carried out thermogravimetric analysis in inert as well as oxidative atmosphere [3]. Phenolic resins are known for their wide applications in various areas because of their thermal stability, easy availability, effectiveness and some of their excellent properties [4]. Jadhao et al have reported synthesis, characterization and thermal degradation study of 2,2'-dihydroxybiphenyl-urea-formaldehyde terpolymer resin [5, 6].

Chauhan [7] synthesized *p*-acetylpyridine oxime-*p*-methylacetophenone-formaldehyde (APOMAF) terpolymer resin and the Flynn–Wall–Ozawa (FWO), Kissinger–Akahira–Sunose (KAS), and Friedman methods are used to determine the apparent activation energy by various degradation models and again synthesized the terpolymer [8]

from (E)-4-acetylpyridine oxime (APO) with 4-hydroxyacetophenone (HA)/4-hydroxybenzaldehyde (HB) and formaldehyde (F) and the activation energy (E_a) values of the thermal decomposition were investigated with thermogravimetric analysis (TGA) by isoconversional Flyn-Wall-Ozawa method.

Masram et al [9] synthesized salicylicldehyde-ethylenediamine-formaldehyde (SdEDF) resin and its thermal degradation curve has been discussed in order to determine their Kinetic parameters from Freeman-Carroll and Sharp-Wentworth methods. Urade and co-workers studied the structural and thermokinetic parameters of terpolymeric resin derived from p-hydroxyacetophenone, bis (2-amino- 1, 3, 4-thiadiazole) and glycerol [10]. Thermal degradation and kinetics of terpolymer resin has been reported by Singru et al. [11, 12]. Ahmed et al. studied the thermokinetic studies of poly(o-toluidine) doped with perchloric acid [13]. Terpolymer resin 2,4-dihydroxybenzophenone-oxamide-formaldehyde has been reported by Butoliya et al [14]. Acrylic copolymers derived from 8-quinolinyl methacrylate have been reported in literature by Patel et al [15].

MATERIALS AND METHODS

Materials

2,2'-biphenol and tetraethylenepentamine of analytical grade purity which were 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'-BPTEPAF terpolymer was 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 146^{0} C in an oil bath for 6 hrs of continuous heating. The temperature of electrically heated oil bath was controlled with the help of a dimmerstat. Yellowish solid product was immediately removed, filtered and repeatedly washed with 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. Dried sample was dissolved in 8 % HCl and regenerated using 1:1 NaOH / water (v/v) with constant stirring and then it was filtered. This process was repeated twice. Resulting terpolymer sample was then washed with boiling water and dried in a vacuum at room temperature. Purified terpolymer was finely ground to pass through 300-mesh size sieve and kept in a vacuum over silica gel. Synthetic details of 2,2'-BPTEPAF terpolymer are shown in the Table 1 and its tentative structure has been given in Fig. 1.



Fig. 1- Structure of 2,2'-BPTEPAF terpolymer

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E		(
Tetraethylenepentamine Formaldehyde		(%)
(mol.)	(aq) ml	
0.2	200	79.00
	(mol.) 0.2	(mol.) (aq) ml 0.2 200

Table1. Synthetic details of 2,2'-BPTEPAF terpolymer

Spectral and thermal studies

Terpolymer was subjected to elemental analysis for carbon, hydrogen and nitrogen on Elementar Vario EL-III Elemental Analyzer at Sophisticated Test and Instrumentation Centre, Cochin University of Science and Technology, Cochin. UV-Visible spectrum of terpolymer in DMSO solvent was recorded on JASCO V-630 UV-VIS spectrophotometer in the range of 200-800 nm at Department of Pharmacy, R.T.M. Nagpur University, Nagpur. ¹H-NMR studies were performed in DMSO as solvent on Bruker Advance-II 400 NMR spectrophotometer and FT-IR spectrum was recorded in nujol mull on Perkin Elmer spectrum RX-I spectrophotometer in the range of 4000-400 cm⁻¹ at Sophisticated Analytical Instrumentation Facility (SAIF) Punjab University, Chandigarh. The non-isothermal thermogravimetric analysis has been carried out using Perkin Elmer Diamond 3-II thermogravimetric analyzer, in air atmosphere at VNIT, Nagpur.

Thermal Analysis

Non-isothermal thermogravimetric analysis of terpolymer has been carried out in air atmosphere with heating rate of $10 \,{}^{0}\text{C}$ min⁻¹. Thermogram was recorded in the temperature range 40-1000 ${}^{0}\text{C}$. Thermal activation energy (Ea), order of reaction (n) and frequency factor (z) have been calculated from thermogravimetric data.

Theoretical considerations

Thermogram expresses the dependence of change in mass with temperature which gives information about sample composition, product formed after heating and kinetic parameters. Kinetics parameters have been determined using Friedman [16], Chang [17], Sharp-Wentworth [18] and Freeman-Carroll [19] methods as follows:

Friedman method:

$$ln\left(\frac{d\alpha}{dt}\right) = ln(z) + nln(1-\alpha) - \frac{Ea}{RT}$$
(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(d α /dt) vs. 1/T should be linear with the slope E_a/R , from which E_a can be obtained.

Chang method:

$$ln\frac{\frac{d\alpha}{dt}}{(1-\alpha)^n} = \ln(z) - \frac{E_a}{RT}$$
(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.

(3)

Sharp-Wentworth method: $log \frac{dc/dt}{1-c} = log \left(\frac{A}{\beta}\right) - \frac{Ea}{2.303R} \cdot \frac{1}{T}$

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 $\frac{1}{r}$ 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.

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Freeman and Carroll method:

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

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. E_a = Energy of activation; n = Order of reaction.

The $\Delta \log (dw/dt)$ and $\Delta \log Wr$ values were 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.

RESULTS AND DISCUSSION

Elemental analysis

The composition of terpolymer 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.

Table2. Elemental analysis data of 2,2'-BPTEPAF terpolymer

		Monomon amainiaal	Elemental Analysis (%)					
Terpolymer	Terpolymer Monomer empirical formula		С		Н		Ν	
		weight	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
2,2'-BPTEPAF	$C_{22}H_{37}N_5O_4$	435	60.68	60.99	8.5	8.35	16.09	16.21



Fig. 2- UV-Visible spectrum of terpolymer resin 2,2'-BPTEPAF

UV-visible spectra

UV-visible spectrum of 2,2'-BPTEPAF terpolymer is represented in Fig. 2. Which exhibit two absorption maxima at 271 and 310 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 is due to $n \rightarrow \pi^*$ forbidden transitions of -OH group.

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The auxochromic substituents (-OH) interacting with π electron of the benzene ring. This interaction stabilizes π^* state and thus lowers the energy. The presence of phenolic hydroxyl group is responsible for bathochromic shift. Both bathochromic and hyperchromic effect of conjugation shown by chromophore (aromatic ring) and auxochrome (-OH) group in repeated unit of terpolymer.

FT-IR spectra

The FT-IR spectrum of 2,2'-BPTEPAF terpolymer is represented in Fig. 3 and the corresponding data is reported in Table 3. Broad and strong band appeared at 3397 cm⁻¹ which may be assigned to the stretching vibration of the phenolic -OH groups exhibiting intermolecular hydrogen bonding [20, 21]. Medium and weak band at 3062 cm⁻¹ indicates the presence of >NH stretching (sec. amine) group. Medium band displayed at 1602 cm⁻¹ may be due to bending vibration of secondary amine. Medium and short peak displayed at 1371 cm⁻¹ for methylene (-CH₂-) bridge. The presence of C-N stretch can be accounted by the presence of band at 1155 and 1047 cm⁻¹. The presence of substitution on aromatic ring also shows medium and sharp peak at 758 and 1482 cm⁻¹.



Fig. 3- FT-IR spectrum of 2,2'-BPTEPAF terpolymer

Table3. IR frequencies of 2,2'-BPTEPA	AF terpolyme	er
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Assignment	IR				
Assignment	Wavenumber (cm ⁻¹)				
-OH (Phenolic)	3397 b,st				
>NH stretching (sec. amine)	3062 m,w				
>NH bending (secondary amine)	1602 m				
-CH ₂ - (methylene bridge)	1371 m,sh				
C-N stretch	1155 m l				
	1047 st,b				
Substituted enematic since	1482 m,sh]				
Substituted aromatic ring	758 sh J				

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

¹H- NMR spectra

¹H-NMR spectrum is represented in Fig. 4 and spectral data is given in Table 4. Spectrum reveals different patterns of peaks, since each of them possesses a set of protons having different proton environment. The significant singlet signal appeared at the region δ 7.99 ppm can be assigned to phenolic proton of Ar-OH. A doublet observed at δ 7.35 ppm is due to unsymmetrical pattern of protons of phenol. Singlet of methylene proton of Ar-CH₂-NH- linkage observed at δ 2.56 ppm. A triplet observed at δ 4.1 ppm is due to methylene proton of -NH-CH₂-CH₂- linkage. The amino proton of CH₂-NH-CH₂- linkage gives doublet at δ 2.4 ppm.



Thermogravimetric analysis

Thermogram of terpolymer is shown in fig. 5 which exhibited four step of decomposition in the temperature range 40-997 0 C. The first step is slow decomposition between 40 to 140 0 C corresponds to 8.15% loss and may attributed to loss of two water molecules which may be due to moisture entrapped in the terpolymer [22, 23] against calculated 8.27% present per repeat unit of polymer. The second step decomposition starts from 140 0 C to 210 0 C which represents degradation of two hydroxyl groups (16.21% found and 16.09% calculated). The third step of decomposition starts from 210-510 0 C corresponds to 50.99 % loss of biphenyl ring against calculated 50.57 %. Fourth step starts from 510 to 997 0 C corresponding to loss of side chain of tetraethylenepentamine moiety.



Fig. 5- Decomposition pattern of 2,2'-BPTEPAF terpolymer

Table5. Thermokinetic parameters of 2,2'-BPTEPAF terpolymer

Methods	Energy of activation (E)	Order of reaction	Frequency factor	
wienious	Energy of activation (E_a)	(n)	(z)	
Friedman	10.81	1.8	11.09	
Chang	11.11	1	11.14	
Sharp-Wentworth	46.79	1	4.81	
Freeman-Carroll	43.99	1.2	3	

Table6. Thermal degradation behavior of 2,2'-BPTEPAF terpolymer

Decomposition stops	Half decomposition temp. (^{0}C)	Temp.	Wt. Loss (%)		Spacios Degradad	
Decomposition steps		Range (⁰ C)	Exp.	Calc.	Species Degraded	
1		40-140	90.05	90.53	Loss of two H ₂ O molecules	
2	510	140-210	82.61	82.71	Loss of two hydroxyl groups	
3		210-510	50.99	50.57	Loss of Biphenyl ring	
4		510-997	28.75	28.46	loss of side chain of TEPA moiety	







Fig. 7- Friedman plot of 2,2'-BPTEPAF terpolymer for order of reaction



Fig. 8- Chang plot of 2,2'-BPTEPAF terpolymer



Fig. 9- Sharp-Wentworth plot of 2,2'-BPTEPAF terpolymer for activation energy



Fig. 10- Freeman-Carroll plot of 2,2'-BPTEPAF terpolymer for activation energy and order of reaction

Thermogravimetric degradation pattern of the terpolymer has been carried out and shown in fig. 5. Activation energy and order of reaction Plots for Friedman, Chang, Sharp-Wentworth and Freeman-Carroll methods are graphically shown in the figures 6, 7, 8, 9 and 10 respectively.

A plot of percentage mass loss vs temperature is shown in Fig. 5 for the TG curve, 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 sample. Fairly comparable results in the kinetic parameters i.e. Ea, n and ln(z) are obtained by Friedman and Chang which might be due to analogy in mathematical model. Also, fairly similar results with slight variations obtained by Sharp-Wentworth and Freeman-Carroll methods are given in Table 5. Low values of frequency factor in Sharp-Wentworth and Freeman-Carroll method revealed that decomposition reaction of terpolymer may be slow and no other possible reason can be given. However, in Friedman, Chang, Freeman-Carroll and Sharp-Wentworth plots most of the assigned points did not fall on straight line, which indicates that decomposition of terpolymer is not obeying first order of reaction perfectly [24, 25, 26].

It is therefore concluded from the above discussion that for each method, the values of kinetic parameters depend on calculation technique used and also on degrading species at a particular step. Due to complex phenomena of polymer 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 polymers in non-isothermal conditions. By using above techniques, fairly similar results 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. First order of reaction has been observed by Chang and Sharp-Wentworth methods while variations occurred in Freidman and Freeman-Carroll. This is expected since the decomposition of terpolymer is known to obey first-order kinetics but not perfectly as reported by Jacobs and Tompkin [27] and Coats and Redfern [28].

CONCLUSION

Synthesis of targeted terpolymer has been confirmed which is supported by the results obtained by the elemental analysis and spectral data. The presence of $-CH_2$ - bridge in the FT-IR spectra shows the formation of terpolymer chain. Friedman and Chang methods show nearly similar values of kinetic parameters may be due to resemblance in mathematical model whereas results obtained from Sharp-Wentworth and Freeman-Corroll methods are in good correlation with each other. The high value of energy of activation shown in Sharp-Wentworth and Freeman-Corroll relative to thermal energy suggest that the 2,2'-BPTEPAF terpolymer is thermally stable upto 997^oC.

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