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Synthesis, characterization and thermogravimetric analysis of copolymer resin-II

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Abstract : Condensation polymerization of *p*-Nitrophenol, 4,4'-Methylenedianiline and Formaldehyde catalyzed by 2M HCl has been carried out. The resin composition was determined on the basis of elemental analysis. Solution viscosity measurement was carried out to ascertain the characteristic functions and constants. The number average molecular weight was determined by conductometric titration in non-aqueous medium. The structure of newly synthesized copolymer has been elucidated and confirmed on the basis of spectral techniques i.e. UV–Visible, FT-IR and ^{1}H-NMR spectroscopy. Thermal analysis was performed in air atmosphere at the heating rates 10^0C/min for studying its thermal degradation behavior and kinetics. Thermal degradation curve has been discussed with minute details for each decomposition step. Freeman-Carroll, Sharp-Wentworth and Coat-Redfern methods have been implemented to evaluate the kinetic parameters such as activation energy, order of reaction and frequency factor. The data from Freeman-Carroll method has been used to determine various thermodynamic parameters i.e. entropy change (ΔS), free energy change (ΔF) and apparent entropy (S*). A detailed analysis of these methods for the treatment of constant heating rate with non-isothermal kinetic data is presented.

Keywords : Polycondensation; Resins; Thermogravimetry; Coat-Redfern; Freeman-Carroll.

INTRODUCTION

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 studying 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 has 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 papers 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, synthesis, characterization and thermal degradation behavior and kinetics by TGA at the heating rate of 10^0C/min under nonisothermal conditions of copolymer derived from p-nitrophenol and 4,4'-methylenedianiline using the linkage of formaldehyde has been studied. Activation energy (Ea), frequency factor (z) and order of reaction (n) were determined using Freeman-Carroll, Sharp-Wentworth and Coat-Redfern equations. Certain generalizations are made regarding the kinetic parameters obtained from mathematical kinetic equations. Computed results are compared and elaborated.

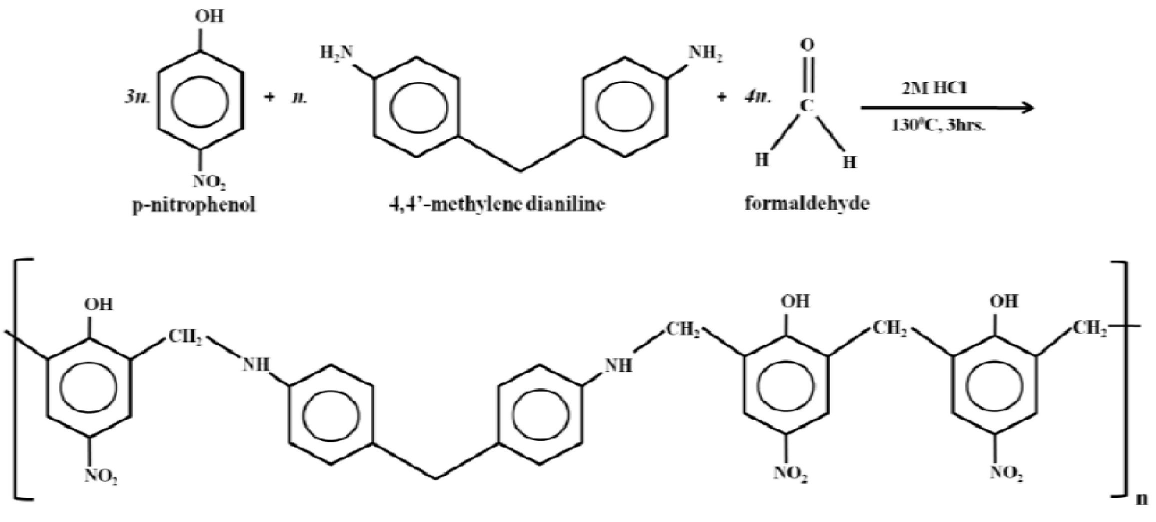
EXPERIMENTAL

Materials

All the chemicals used were of analytical grade purity. p-Nitrophenol and formaldehyde (37%) were purchased from S. D. Fine Chemicals, India. 4,4'-Methylene dianiline was purchased from Acros Chemicals, Belgium. Solvents like N, N-dimethylformamide, dimethyl sulphoxide, tetrahydrofuran, acetone and diethyl ether were procured from Merck, India.

Synthesis

p-NP-4,4'-MDA-F-II copolymer was synthesized by condensation polymerization method by using the molar proportion 3:1:4 of reacting monomers i.e. p-nitrophenol (4.17 gm, 0.3 mol) and 4,4'-methylenedianiline (1.98 gm, 0.1 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). The temperature of electrically heated oil bath was controlled with the help of a dimmerstat. The resinous dark reddish brown colored solid product was immediately removed, filtered and repeatedly washed with cold-distilled water, dried in air and powdered with the help of an agated mortar and pestle. 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 p-nitrophenol-formaldehyde copolymer, which might be present along with the *p*-NP-4,4'-MDA-F-II terpolymer. Finally the terpolymer was passed through 300-mesh size sieve and kept in a vacuum over silica gel[29].



p-NP-4,4'-MDA-F-II

Figure 1 : Chemical reaction of *p*-NP-4,4'-MDA-F-II copolymer

THEORETICAL CONSIDERATIONS

Characterization of copolymer

The intrinsic viscosity of newly synthesized copolymer has been evaluated using Tuan-Fuoss viscometer[30] fabricated in our research laboratory at different concentrations ranging from 1.00 to 0.031% of copolymer in dimethylformamide (DMF) at 30 °C. Intrinsic viscosity [η] was calculated from relevant plots of Huggins' equation (1) and Kraemer's equation 2 (Figure 2).

$$\eta_{sp}/_{C} = [\eta] + K_1\,[\eta]^2.C \qquad (1)$$

$$ln\eta_{rel}/_{C} = [\eta] + K_2.[\eta]^2.C \qquad (2)$$

Where η_{rel} = relative viscosity; $[\eta]=\lim_{c\to 0}(\eta_{sp}/C)$; K_1 = Huggin's constant; K_2 = Kraemer's constant.

The number average molecular weight $(\overline{Mn})$ was determined by conductometric titrations in non-aqueous medium such as dimethyl sulphoxide (DMSO) against ethanolic KOH as a titrant by using 25 mg of sample. A plot of specific conductance against milliequivalents of base (ethanolic KOH) required for neutralization of 100 gm of copolymer has been plotted (Figure 3). From the plot, the first and final breaks were noted. The average degree of polymerization $(\overline{DP})$ and hence the number average molecular weight $(\overline{Mn})$ of all copolymers have been determined using the formula.

$$\overline{DP} = \frac{\text{Total milliequivalent of base required for complete neutralization}}{\text{Milliequivalents of base required for smallest interval}} \qquad (3)$$

$$(\overline{Mn}) = \overline{DP}\ x\ \textit{Repeat unit weight} \qquad (4)$$

Copolymer resin was subject to elemental analysis for carbon, hydrogen and nitrogen on Perkin Elmer 2400 Elemental Analyser. With the help of elemental data the empirical formula and empirical weights have been assigned to the new copolymer resin.

A UV-visible spectrum was recorded by preparing solution in dimethylsulphoxide on Shimadzu UV-Visible double beam spectrophotometer in the range of 200-850 nm. Infrared spectrum was recorded using KBr pellet in nujol mull on Perkin-Elmer RX-I spectrophotometer in the range of 4000-500 cm^{-1}. Nuclear Magnetic Resonance (^1H-NMR) spectrum of newly synthesized copolymer resin has been scanned on FT-NMR-Cryo magnet spectrum 400 MHz (Bruker) spectrometer. The elemental analysis and spectral studies for newly synthesized copolymer were carried out at Sophisticated Analytical Instrumentation Facility (SAIF) Punjab University, Chandigarh.

Thermogravimetric analysis

Thermogram represents the relationship between change in mass on the temperature which gives information about sample composition, product formed after heating and kinetic parameters[31]. Heating is performed under strictly controlled conditions and can reveal changes in the structure and other important properties of the material being studied. Kinetic parameters have been determined using Freeman-Carroll[32], Sharp-Wentworth[33] and Coat- Redfern[34] methods as given below.

Freeman and Carroll method

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

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 $\frac{\Delta\log\ (\frac{dw}{dt})}{\Delta \log \mathrm{Wr}}$ vs $\frac{\Delta(\frac{1}{T})}{\Delta \log \mathrm{Wr}}$ gives a straight line. The slope and intercept are equal to - (Ea/R) and n, respectively.

Sharp-Wentworth method

$$log\,\frac{dc/dt}{1-c} = log\left(\frac{A}{\beta}\right) - \frac{Ea}{2.303R} \cdot \frac{1}{T} \qquad \textbf{(6)}$$

Where dc/dt = rate of change of fraction of weight with change in temperature; β is linear heating rate, dT/dt; c is the fraction of polymer decomposed at time t.

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

Coat Redfern method

$$ln\left[\frac{g(\propto)}{T^2}\right] = ln\left\{\frac{AR}{qE_a}\left[1 - \frac{2RT}{E_a}\right]\right\} - \frac{E_a}{RT} \qquad \textbf{(7)}$$

Where q and A is the heating rate (^{0}C/min) and frequency factor respectively; *g(α)* 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)$^{1-n}$)/(T^2(1-n))] vs (1/T) or ln[-ln(1-α)/T^2] 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.

RESULT AND DISCUSSION

Viscosity measurement and number average molecular weight

Viscosity measurement was carried out at 300 K in Dimethyl Sulphoxide (DMSO) using Tuan-Fuoss Viscometer, at six different concentrations ranging from 1.00% to 0.031%. Reduced and inherent viscosity versus concentration was plotted for each set of data. The intrinsic viscosity [η] was determined by the corresponding linear plots (Figure 2). Huggin's (K_1) and Kraemer's (K_2) constants were determined by using equation 1 and 2 respectively (TABLE 1). According to the aforementioned relations, the plot of η_{sp}/C and ln η_{rel}/C against C was linear with slopes of K_1 and K_2 respectively. By extrapolating linear plot to zero concentration, intercepts on the viscosity function axis give [η] value in both the plots. The calculated values of the constants K_1 and K_2 in most cases favorably satisfied the relation $K_1 + K_2 = 0.5$[39]. It was observed that copolymer having higher $(\overline{\mathrm{Mn}})$ shows higher value of [η].

The number average molecular weight $(\overline{\mathrm{Mn}})$ of the copolymer has been determined by conductometric titration method in non-aqueous medium and 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 gm of each copolymer (Figure 3). There are several breaks before the complete neutralization of all phenolic hydroxyl groups (27). The first break in the plot was the smallest break and assumed that this corresponds to a stage in titration when an average one phenolic hydroxyl group of each chain was neutralized. It is observed that the molecular weight of copolymer was found to be 7763. This observation is in agreement with the trend observed by earlier workers[39,40]. The data obtained from viscometric and

TABLE 1 : Molecular weight and viscometric data of 4,4'-BP-4,4'-ODA-F-II copolymer

Copolymer	Empirical formula of repeat unit	Empirical weight of repeat unit (g)	DP	M_n	[η] (dL/g)	K_1	K_2	$K_1 + K_2$
p-NP-4,4'-MDA-F-II	$C_{35}H_{29}N_5O_9$	663	11.71	7763	1.10	0.23	0.26	0.49

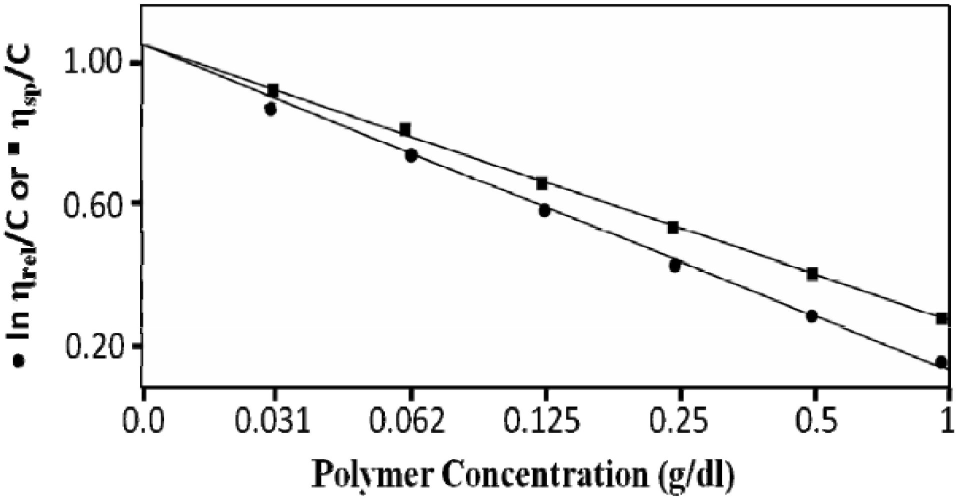


Figure 2 : Viscosity plot of *p*-NP-4,4’-MDA-F-II copolymer.

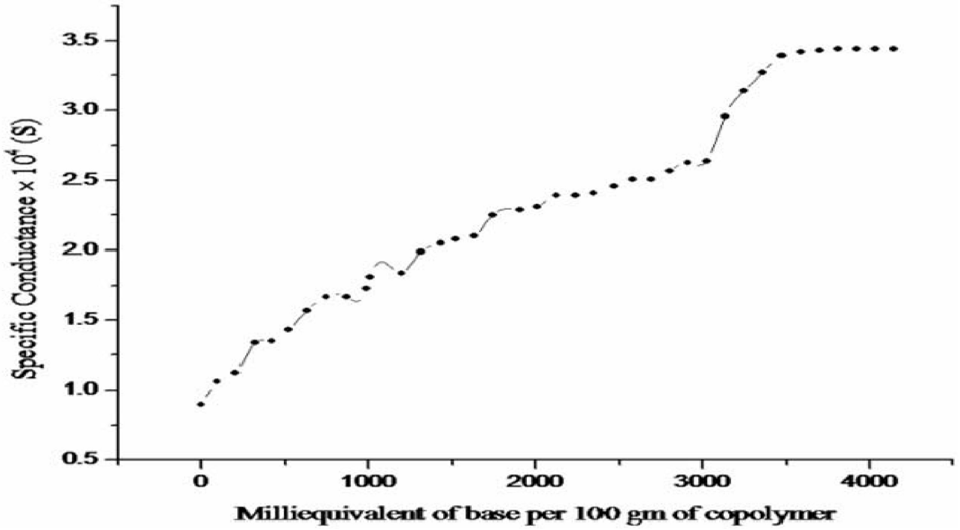


Figure 3 : Conductometric plot of *p*-NP-4,4’-MDA-F-II copolymer

conductometric studies have been incorporated in TABLE 1.

Characterization of *p*-NP-4,4’-MDA-F-II: 84.40 %

(A) UV-Visible (in DMSO-d_6 in the range 200-850nm)

The spectra exhibit two absorption maxima in region 250 and 330 nm. The former and less intense band may be due to n→π* transitions observed at 250 nm indicating the presence of 4,4'-methylenedianiline moiety. Hypsochromic shift observed in biphenyl may be due to introduction of -CH_2 group between two phenyl groups which destroys the conjugation. Later and more intense band observed at 330 nm may be accounted for π→π* transition might be due to chromophoric (-NO_2) group. The auxochromic substituents (-OH) interacting with π electron of the benzene ring. This interaction stabilizes π* state and thus lowers the energy as a result bathochromic shift is caused[35,36]. The hypsochromic shift of 10 nm from the basic value 260 to 250 nm and a bathochromic shift in λ_{max} of 30 nm from 300 to 330 nm may be due to conjugation effect and presence of –NO_2 group (chromophores). (Figure 4).

(B) FT-IR

3451.5 cm^{-1} (phenolic -OH str, b)[37], 2923.1 cm^{-1} (>NH Str, st), 2855.5 cm^{-1} (methylene -CH- str, st)[36], 1591.0 cm^{-1} (substituted aromatic ring C-C str. st), 1650.4 cm^{-1} (>C=C< str. in aromatics, m), 1286.7 cm^{-1} (C-N str. in amine, b), 1498.4 cm^{-1} (Asymm. N=O str, b), 1338.7 cm^{-1} (Symm. N=O str, b), 1217.2 cm^{-1} (>C-O str. in phenol, m), 965.4, 850.7 cm^{-1} (tetrasubstituted benzene ring, m), 1460.0 cm^{-1}, 1345-1350 cm^{-1}, 750-

770 cm^{-1}(Methylene bridge (-CH_2) modes bending, wagging, rock respectively) (Figure 5).

(C) ^{1}H-NMR (400 MHz, DMSO-d_6)

δ 10.8 (s, 1H, -OH)[36], δ 7.9 (s, 1H, Meta proton of –Ar-H), δ 3.5 (d, 1H, -CH_2-NH-Ar-), δ 3.1 (d, 2H, Methylene proton of Ar-CH_2-Ar linkage (4,4'-methylenedianiline moiety)), δ 6.8-6.9 (d, 1H, Proton orth to -CH_2-), δ 8.1 (d, 1H, Proton orth to -NH-) (Figure 6).

(D) Elemental analysis

Theoretically calculated C = 63.34%, H = 4.37%, N = 10.55%, O = 21.74%

Experimentally found C = 63.09%, H = 4.21%, N = 10.42%, O = 22.28%

Monomer empirical formula: ($C_{35}H_{29}N_5O_9$);

Empirical formula weight: (663).

Thermogravimetric analysis *p*-NP-4,4'-MDA-F-II copolymer

Thermogravimetric analysis of *p*-NP-4,4'-MDA-F-II has been performed at 10^0C.min^{-1} and the decomposition pattern with thermogravimetric (TGA) curve has been shown in Figure 7[38]. Thermogram of this copolymer depicted three step decomposition steps in the temperature range 50-600 ^{0}C (TABLE 3). First step is slow decomposition between 50 to 120 ^{0}C corresponds to 2.64% loss which may be attributed to water

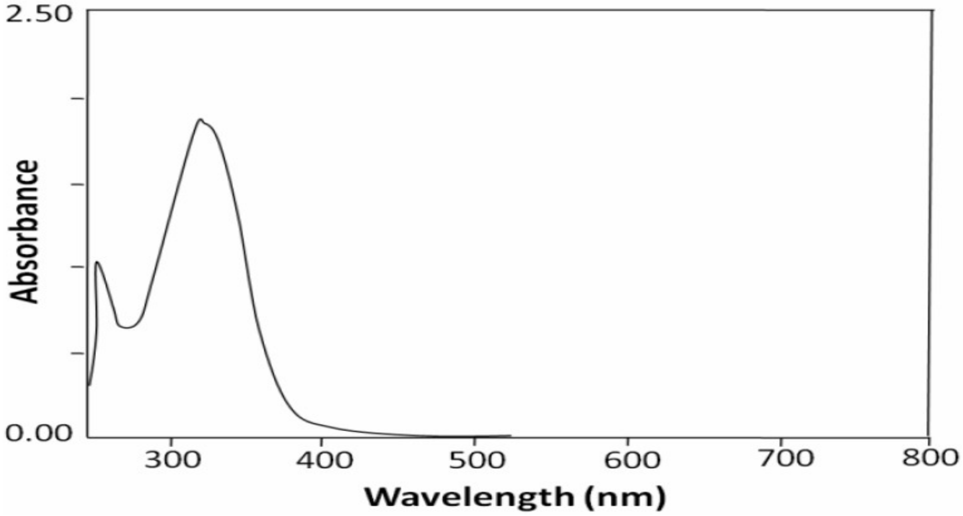


Figure 4 : UV-Visible spectra of *p*-NP-4,4'-MDA-F-II copolymer.

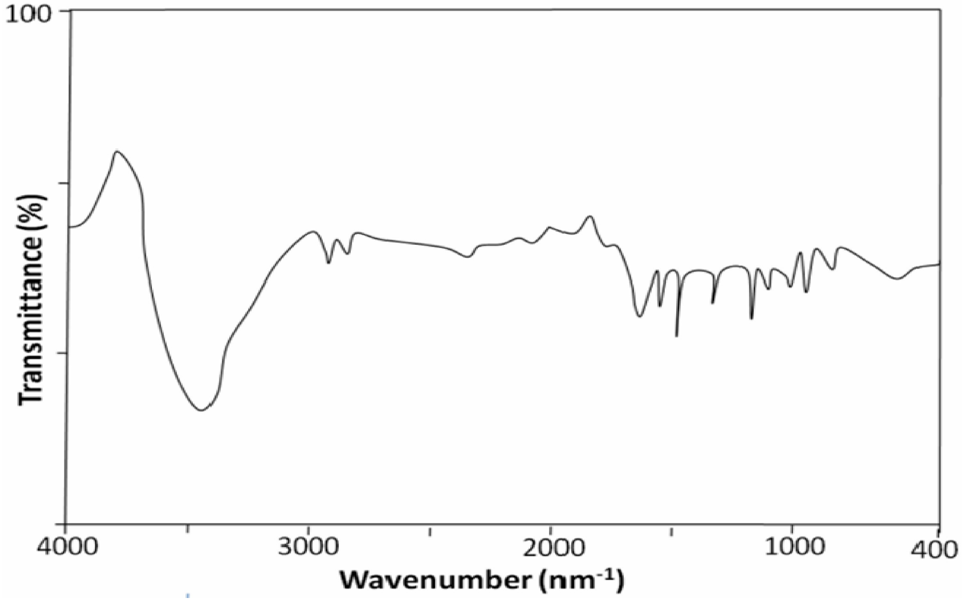


Figure 5 : FT-IR spectra of p-NP-4,4'-MDA-F-II copolymer

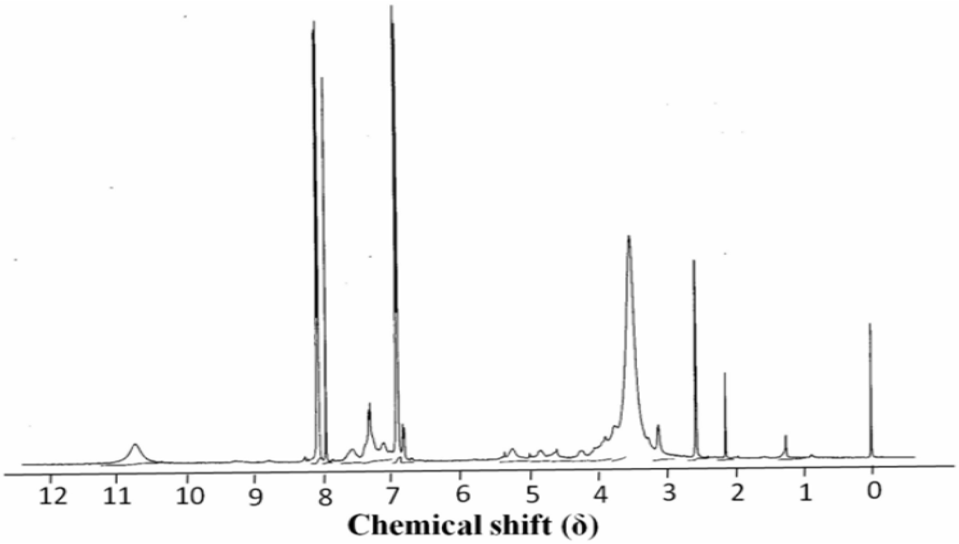


Figure 6 : 1H-NMR spectrum of *p*-NP-4,4'-MDA-F-II copolymer

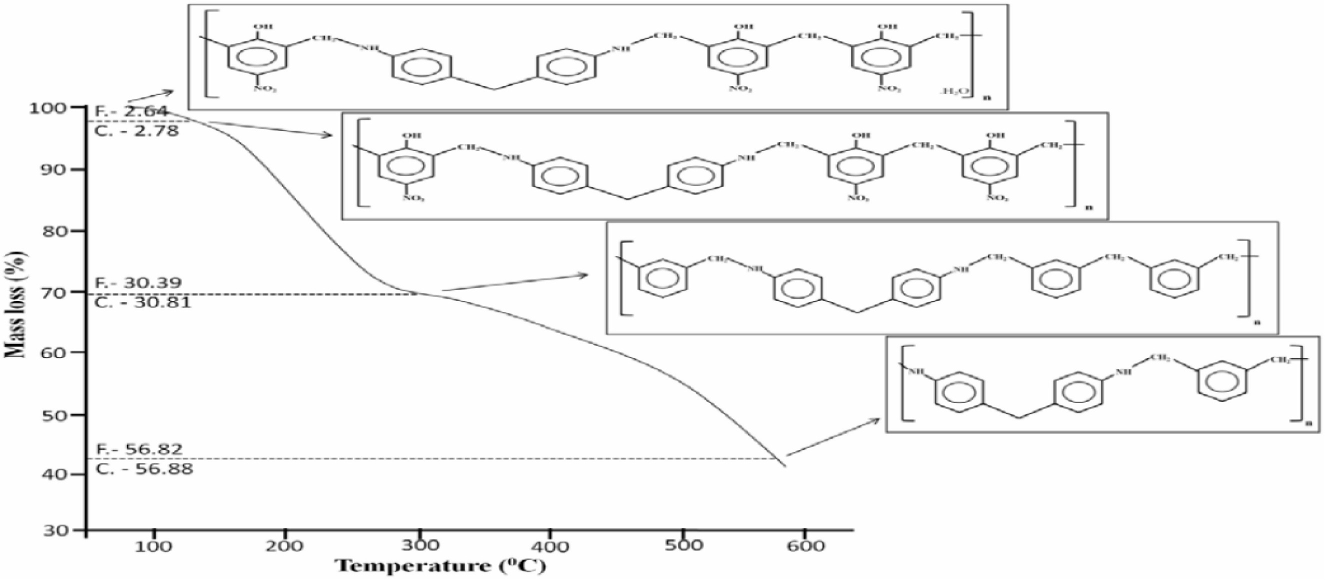


Figure 7 : Decomposition pattern of *p*-NP-4,4'-MDA-F-II copolymer.

of crystallization associated with copolymer resin[39], against calculated 2.78% present per repeat unit of the polymer. The second step of decomposition starts from 120-290 ^{0}C which represents the degradation of three (–OH) groups attached to the benzene skeleton and three (–NO_2) groups (30.39% found and 30.81% calculated). Third step of decomposition starts from 290-590 ^{0}C corresponding to 56.82% loss of two side benzene rings along with –CH_2 groups against calculated 56.88%. The thermal degradation by increasing temperature may be due to the increasing strain, instability and crosslinking of molecule by increasing thermal vibration. To decrease the strain and to maintain stability, the resin undergoes degradation. The synthesized copolymer is half decomposed at 210 ^{0}C observed from thermal data. The decomposition is due to pyrolysis of straight chain linked structure of copolymer and at 590 ^{0}C degradation process occurs upto final level leaving behind the remaining moieties.

Thermal analysis of *p*-NP-4,4'-MDA-F-II copolymer has been carried out and representative graphs for Freeman-Carroll (Figures 8 and 9), Sharp-Wentworth (Figure 10) and Coat-Redfern (Figure 11) methods has been plotted.

The kinetic parameters computed by the above mentioned kinetic equations and thermodynamic parameters such as entropy change (ΔS), free energy change (ΔF) and apparent entropy change (S*) calculated on the

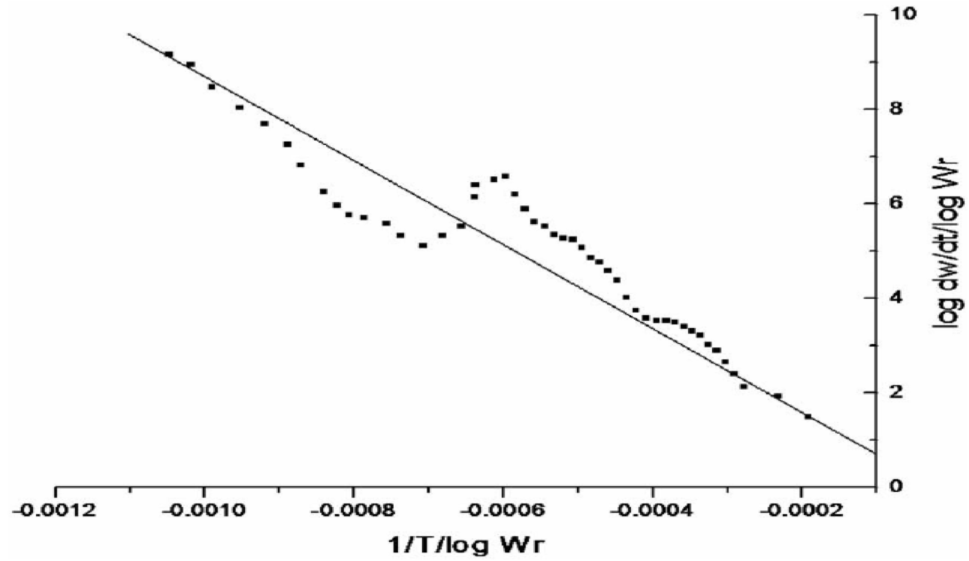


Figure 8 : Freeman-Carroll plot of *p*-NP-4,4'-MDA-F-II copolymer for calculation of activation energy

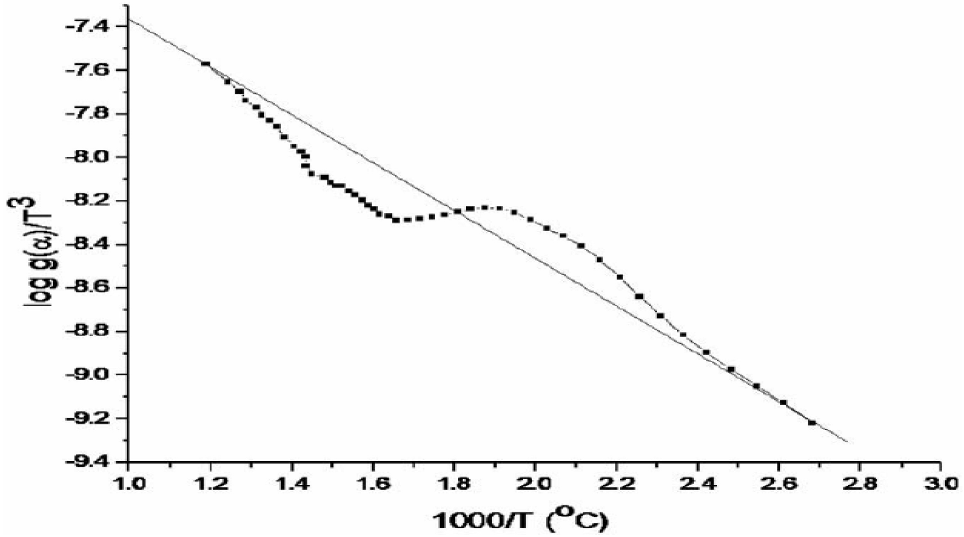


Figure 9 : Freeman-Carroll plot of *p*-NP-4,4'-MDA-F-II copolymer

basis of thermal activation energy estimated by Freeman- Carroll method are shown in TABLE 2 using the following equations.

(A) Entropy change

$$\text{Intercept} = \log \frac{KR}{h\Phi E} + \frac{\Delta S}{2.303R} \qquad (8)$$

Where K = 1.3806 x 10^{-16} erg/deg/mole; R = 1.987 cal/deg/mole; h = 6.625 x 10^{-27} erg sec; Φ = 0.166; ΔS= change in entropy; E = activation energy from graph

(B) Free energy change

$$\Delta F = \Delta H - T\Delta S \qquad (9)$$

Where ΔH = Enthalpy change; T = Temperature in KΔS = Entropy change {from (6) used}

(C) Frequency factor

$$B_{2/3} = \frac{\log Z E_a}{R\Phi} \qquad (10)$$

$$B_{2/3} = \log 3 + \log[1 - 3\sqrt{1-\alpha}] - \log\ p(x) \quad (9)$$

Where, Z = Frequency factor, B = Calculated from equation (9); log p(x) = Calculated from Doyle table corresponding to activation energy.

(D) Apparent entropy change

$$S^* = 2.303R\ \log \frac{Zh}{RT^*} \qquad (11)$$

Where, Z = from relation[8]; T* = Temperature at which half of the compound is decomposed from it total loss.

TABLE 2 : Kinetic and thermodyanamic parameters corresponding to heating rate of 10 ^{0}C/min of 4,4'-BP-4,4'-ODA-F-II

Copolymer	T_{half}^a (^{0}C)	F-C			S-W			C-R			Entropy change ΔS (J)	Apparent entropy change S* (KJ)	Free energy change ΔF (sec^{-1})
		Ea	n	z	Ea	n	z	Ea	n	z			
4,4'-BP-4,4'-ODA-F-II	210	11.75	0.95	10.63	12.28	1.0	6.32	21.56	0.99	10.15	7.159	-22.71	10251.52

Units of Ea and ln(z) are kJ/mole and min^{-1} respectively; ^{a}Half decomposition temperature

TABLE 3 : Thermoanalytical data and decomposition temperature for p-NP-4,4'-MDA-F-II terpolymers.

Decomposition steps	Temp. Range (^{0}C)	Species Degraded	Wt. Loss (%)	
			Found	Calculated
1.	50-120	One H_2O molecule	2.64	2.78
2.	120-290	Three -OH$^-$ and Three –NO_2 groups	30.39	30.81
3.	290-590	Two side benzene rings along with (-CH_2) groups	56.82	56.88

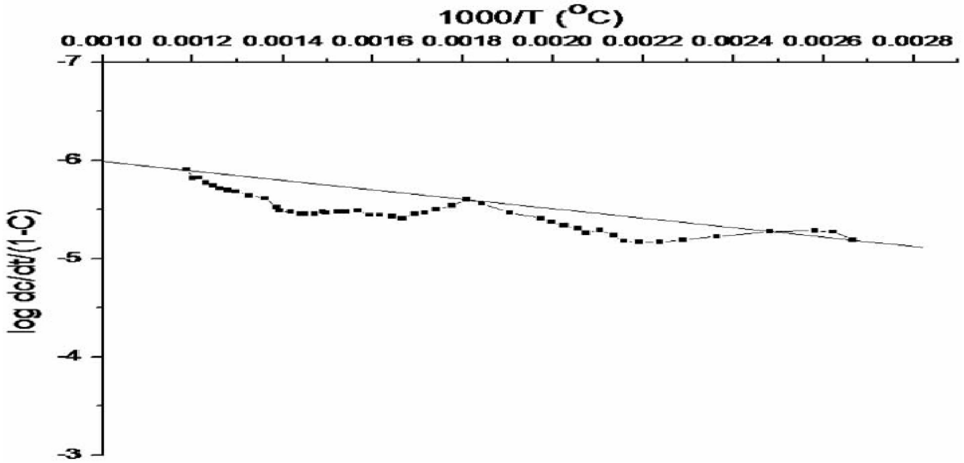


Figure 10 : Sharp-Wentworth plot of *p*-NP-4,4'-MDA-F-II copolymer

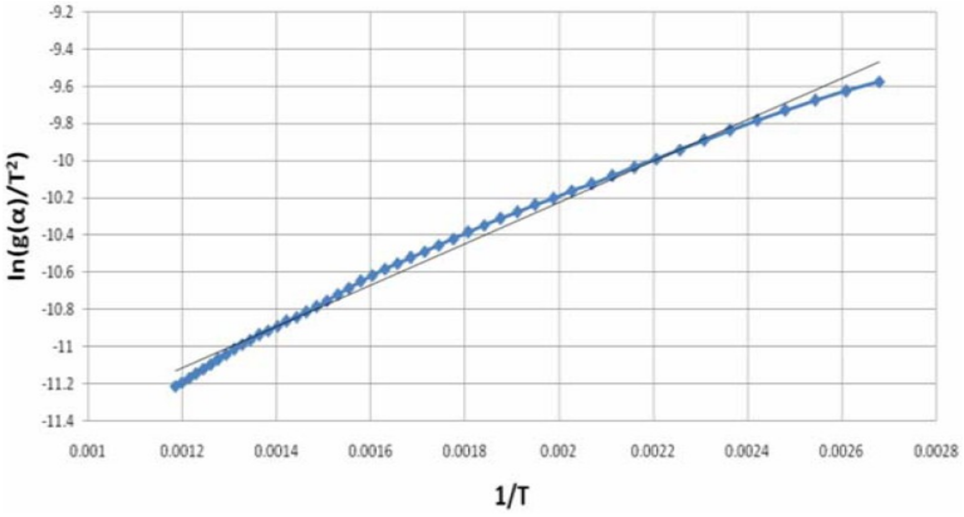


Figure 11 : Coat-Redfern plot of *p*-NP-4,4'-MDA-F-II copolymer

The thermal stability of *p*-NP-4,4'-MDA-F-II copolymer is concluded to be higher, may be due to the stronger intermolecular hydrogen bonding present in the polymer structure because of water of crystallization which would be more difficult to break and more resistant to higher temperature or it may be due to the possibility of almost linear structure of copolymer chain which gives stability to the polymer chain[40,41].

Activation energy calculated by Sharp-Wentworth method agrees well with the Freeman–Carroll method and Coat-Redfern method shows fairly good observations (TABLE 2). Thermodynamic parameters have been calculated[42] on the basis of thermal activation energy and the values are cited in Table 2. Similarity of values indicates a common reaction mode. From abnormally low values of frequency factor (z), it may be concluded that decomposition reaction of *p*-NP-4,4'-MDA-F-II copolymer resin can be classed as a "slow" reaction[43,44]. The low positive values of entropy (ΔS) indicate that the activated polymer has a more ordered structure than the reactants and the reactions are slower than normal which were further supported by low z values. It is difficult to draw any unique conclusion from the magnitude of thermal activation energy as decomposition mechanism is expected to be complicated. However, in Freeman-Carroll (Figures 8 and 9), Sharp-Wentworth (Figure 10) and Coat-Redfern (Figure 11) methods, some abnormal points were ignored to get a clear picture of most of the points. It is expected that decomposition of the copolymer is not obeying first order kinetics perfectly[45]. These observations are in harmony with the findings of Jacobs and Tompkin[46], Coat Redfern[34] and other earlier researchers[47].

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

CONCLUSIONS

Synthesis of targeted copolymer *p*-NP-4,4'-MDA-F-II has been confirmed which is supported by results obtained from the spectral analysis. The -CH_2- group as the methylene linkage between phenol and amine shows the formation of condensation product. Thermogram obtained has shown three degradation stages, first indicating degradation of water molecule; second step shows degradation of three -OH and three –NO_2 groups and third represents loss of two side benzene rings along with –CH_2 groups. Activation energy calculated by Sharp-Wentworth method agrees well with the Freeman–Carroll method and Coat-Redfern method also shows fairly good observations. Low values of collision frequency factor may be concluded that the decomposition reaction can be classified as 'slow reaction' and order of reaction is found to be nearly equal to one. The decomposition reaction was started at higher temperature, indicating a terpolymer *p*-NP-4,4'-MDA-F-II is thermally stable at higher temperature.

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REFERENCES

[1] J.A.Conesa, A.Marcilla, J.A.Caballero, R.Font; Comments on the validity and utility of the different methods for kinetic analysis of thermogravimetric data, J.Anal.Appl.Pyrol., **58/59**, 617-633 **(2001)**.

[2] A.Pron, P.Rannou; Processible conjugated polymers: From organic semiconductors to organic metals and superconductors, Progress in Polymer Science, **27(1)**, 135-190 **(2002)**.

[3] J.Wolfrum, G.W.Ehrenstein; Interdependence between the curing, structure, and the mechanical properties of phenolic resins, J.Applied Polymer Science, **74(13)**, 3173-3185 **(1999)**.

[4] M.V.Tarase, W.B.Gurnule, A.B.Zade; Thermal degradation studies of terpolymer resins derived from 2,4-dihydroxypropiophenone, biuret and formaldehyde, Ultra Chemistry, **3(1)**, 41-48 **(2007)**.

[5] William Dickstein, Ottp vogl; Functional polymers. XXVI. Co- and terpolymers involving methacrylates, N-vinylpyrollidone, and polymerizable ultraviolet stabilizers and antioxidants, Journal of Macromolecular Sciences: Part A, **23(4)**, 387-402 **(1986)**.

[6] M.Angelopoulos; Conducting polymers in microelectronics, J.Res. and Dev., **45(1)**, 57-75 **(2001)**.

[7] Noah Ben-Shalom, Cuneyt Aki, Ruti Ardi, Riki Pinto; Elicitation effects of chitin oligomers and chitosan sprayed on the leaves of cucumber (Cucumis sativus) and bean (Phaseolus vulgaris) plants, Israel Journal of Plant Sciences, **50(3)**, 199-206 **(2002)**.

[8] D.D.Borole, U.R.Kapadi, P.P.Mahulikar, D.G.Hundiwale; Glucose oxidase electrodes of a terpolymer poly(aniline-co-o-anisidine-co-o-toluidine) as biosensors, European Polymer Journal, **41(9)**, 2183-2188 **(2005)**.

[9] A.I.Hopwood, H.J.Coles; Liquid crystalline polymers as additives to enhance the device properties of low molecular mass liquid crystals, Polymer, **26(9)**, 1312-1318 **(1985)**.

[10] M.M.Jadhav, L.J.Paliwal, N.S.Bhave; Ion-exchange properties of 2,2'-dihydroxybiphenyl-urea-formaldehyde terpolymer resin, Desalination, **250**, 120-129 **(2009)**.

[11] A.Shukla, A.K.Shrivastava; Terpolymerization of linalool, styrene and methyl methacrylate: Synthesis, characterization and a kinetic study, Polymer Plastics Technology and Engineering, **41(4)**, 777-793 **(2002)**.

[12] H.F.Naguib, S.M.Mokhtar, S.Z.Khatil, M.Z.Elsabee; Polymerization kinetics of indene, methyl methacrylate and acrylonitrile and characterization of their terpolymer, Journal of Polymer Research, **16(6)**, 693-702 **(2009)**.

[13] P.Shukla, A.K.Shrivastava; Terpolymerization of styrene, acrylonirtile and chromium acrylate: Synthesis and properties, Polymer, **35(21)**, 4665-466 **(1994)**.

[14] K.Mashita, S.Yasui, M.Hirroka; Alternating copolymerization of isobutylene and acrylic ester with alkylboron halide, Polymer, **36(15)**, 2973-2982 **(1995)**.

[15] C.S.Sanmathi, Prasannakumar, B.S.Sherigara; Terpolymerization of 2-ethoxyethyl methacrylate, styrene and maleic anhydride, Determination of Reactivity Ratios, **27(3)**, 243-249 **(2004)**.

[16] V.V.Zaitseva, T.G.Tyurina, S.Yu.Zaitsev; Copolymerization of styrene with acrylonitrile and maleic anhydride, Polymer Science Series B, **51(1-2)**, 13-19 **(2009)**.

[17] R.S.Azarudeen, M.A.S.Ahamad, D.Jeyakumar, A.R.Burkanudeen; An eco-friendly synthesis of a terpolymer resin: Characterization and chelation ion-exchange property, Iranian Polymer Journal, **18(10)**, 821-832 **(2009)**.

[18] W.Wang, R.Hutchinson; A compresensive kinetic model for high temperature free radical production of styrene/methylmethacrylate/acrylate resins, AIChE Journal, **57(1)**, 227-238 **(2011)**.

[19] A.Boztug, S.Basan; Characterization and synthesis of maleic anhydride-styrene-vinyl acetate terpolymer ester derivative, Journal of Material Science, **39**, 6843-6846 **(2004)**.

[20] L.Yang, A.Yi, S.Lin; Synthesis and thermal properties of emulsion terpolymers of *N*- p-tolylmaleimide/butadiene-styrene latex/acrylonitrile/styrene, Journal of Thermal Analysis and Calorimetry, **104**, 1153-1158 **(2011)**.

[21] R.N.Singru, A.B.Zade, W.B.Gurnule; Synthesis, characterization and thermal degradation studies of copolymer resins derived from p-cresol, melamine and formaldehyde, Journal of Applied Polymer Science, **109(2)**, 859-868 **(2008)**.

[22] S.S.Butoliya, W.B.Gurnule, A.B.Zade; Study of nonisothermal decomposition and kinetic analysis of 2,4-dihydroxybenzoic acid –melamine-formaldehyde copolymer, E-Journal of Chemistry, **7(3)**, 1101-1107 **(2010)**.

[23] R.N.Singru, A.B.Zade, W.B.Gurnule; Thermoanalytical study and kinetics of new 8-hydroxyquinoline 5-sulphonic acid, oxamide, formaldehyde terpolymer resins, E-Journal of Chemistry, **3(1)**, 41-48 **(2007)**.

[24] M.V.Tarase, A.B.Zade, W.B.Gurnule; Resin-I: Synthesis, characterization and ion-exchange properties of terpolymer resins derived from 2,4-dihydroxypropiophenone, biuret and formaldehyde, Journal of Applied Polymer Science, **108(2)**, 738-746 **(2008)**.

[25] S.S.Rahangdale, A.B.Zade, W.B.Gurnule; Thermal degradation studies of 2,4-dihydroxyacetophenone, dithiooxamide and formaldehyde terpolymer, J.Ultra Science, **19(2)**, 213-218 **(2007)**.

[26] M.M.Jadhav, L.J.Paliwal, N.S.Bhave; Thermal studies of 2,2'-dihydroxybiphenyl-formaldehyde copolymer resin, Thermans., **2004**, 250 **(2004)**.

[27] M.M.Jadhav, L.J.Paliwal, N.S.Bhave; Resin II: Thermal degradation studies of terpolymer resins derived from 2,22 -dihydroxybiphenyl, urea and formaldehyde, J. of Applied Polymer Science, **101(1)**, 227-232 **(2006)**.

[28] Paik Pradip, Kar Kamal; Kinetics of thermal degradation and estimation of lifetime for polypropylene particles: Effect of particle size, Polymer Degradation and Stability, **93**, 24-35 **(2008)**.

[29] R.Manavalan, M.M.Patel; Chelation ion-exchange properties of salicylic acid/thiourea/trioxane terpolymers, Die Makromolekulare Chemie, **184(4)**, **717-723** **(2003)**.

[30] P.P.Kalbende, A.B.Zade; Ion-exchange studies of copolymer derived from 4,4'-biphenol, Journal of Macromolecular Science-Part: A, Taylor and Francies, **51(1)**, 37-48 **(2013)**.

[31] M.N.Radhakrishanan Nair, G.V.Thomas, M.R.Gopinathan Nair; Thermogravimetric analysis of PVC/ELNR blends, Polym.Degrad.Stab., **92**, 189-196 **(2007)**.

[32] E.S.Freeman, B.J.Carroll; The application of thermoanalytical techniques to reaction kinetics. The thermogravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate, Phys.Chem., **62**, 394 **(1958)**.

[33] J.B.Sharp, S.A.Wentworth; Kinetic analysis of thermogravimetric data, Anal.Chem., **41(14)**, 2060 **(1969)**.

[34] A.W.Coats, J.P.Redfern; Kinetic parameters from thermogravimetric data, Nature, **201(4914)**, 68-69 **(1964)**.

[35] A.I.Vogel; Textbook of Practical Organic Chemistry Longman Scientific & Technical England, Longman Group UK Ltd, **(1989)**.

[36] R.M.Silverstein, G.C.Bassley, T.C.Morrill; Spectrometric Identification of Organic Compounds, 5th Edition, Singapore, Wiley, **(1991)**.

[37] K.Nakanishi; Infrared Absorption Spectroscopy Practical, Tokyo, Nolden Day and Nankodo, **(1967)**.

[38] X.G.Li, M.R.Huang, G.H.Guan, T.Sun; Polymer International, **46**, 289-297 **(1998)**.

[39] P.E.P.Michael, J.M.Barbe, H.D.Juneja, L.J.Paliwal; Synthesis, characterization and thermal degradation of 8-hydroxyquinoline-guanidine-formaldehyde terpolymer, Europian Polymer Journal, **43**, 4995-5000 **(2007)**.

[40] M.M.Jadhao, L.J.Paliwal, N.S.Bhave; Journal of Applied Polymer Science, **96**, 1605 **(2005)**.

[41] T.Ozawa; Journal of Thermal Analysis, **7(3)**, 601-617 **(1985)**.

[42] A.K.Singh, A.P.Sinha, K.K.Singh; Asian J.Chem., **10(2)**, 241 **(1998)**.

[43] D.T.Masram, K.P.Kariya, N.S.Bhave; High Performance Polymers, **22**, 1004-1016 **(2010)**.

[44] H.Zhao, Y.Z.Wang, D.Y.Wang, B.Wang, B.Wu, D.Q.Chen; Polymer Degradation and Stability, **80**, 135 **(2003)**.

[45] A.S.Aswar, R.G.Mahale, P.R.Kakde, S.G.Bhadange; J.Ind.Chem.Soc., **75**, 395 **(1998)**.

[46] P.W.M.Jacobs, F.C.Tompkins; Chemistry of the Solid State, WE Garner Publication, London, 188 **(1955)**.

[47] R.N.Singru, A.B.Zade, W.B.Gurnule; Journal of Applied Polymer Science, **109(2)**, 859 **(2008)**.