Structural and Thermokinetic Parameters of Terpolymer Resin Derived from p-Hydroxybenzaldehyde, Urea and Ethylene Glycol

Amit N. Gupta[1]*, Vinay V. Hiwase[2], Ashok B. Kalambe[3] and N. T. Khaty[4]

[1]Department of Applied Chemistry, J. D. College of Engineering & Management, Nagpur, India
[2]Arts, Commerce and Science College, Arvi, Dist.-Wardha, India
[3]Department of Chemistry, Institute of Science, R.T.Road, Nagpur, India
[4]Department of Applied Chemistry, Priyadarshini College of Engineering, Nagpur, India Road, Delhi

(*MS received August 11, 2014; revised November 09, 2014*)

Abstract

Terpolymer abbreviated as HBUE-I was synthesized by polycondensation using monomers p-hydroxybenzaldehyde (0.1M), urea (0.1M) and ethylene glycol (0.3M) in the presence of polyphosphoric acid as catalyst at 120^{0}C. The molecular weight was determined by non-aqueous conductometric titration. Terpolymer was characterized by elemental analysis, FT-IR, 1H NMR and UV-Visible spectra. Thermokinetic parameters were calculated by using Freeman-Carroll (FC) and Sharp-Wentworth (SW) methods in the temperature range 170-500^{0}C. The values of the activation energy (Ea), frequency factor (A), apparent entropy change (ΔS^*) and free energy change (ΔG) were in good agreement. The order of degradation reaction determined by the FC method was confirmed by SW method.

Keywords: Polycondensation, Apparent Entropy, Free Energy, Thermal Degradation, Order of Degradation, Terpolymer.

*Corresponding author: angupta2020@gmail.com

1. Introduction

The superiority of terpolymer over copolymer with reference to improved electrical conducting ability, adequate ion exchange capacity and stability at elevated temperature have been attracting much attention in the area characterization of terpolymer since last two decades, obviously, opened up new horizon of research in polymeric materials [1-6]. Many coworkers have synthesized terpolymers using various functional phenolic monomers [7-11]. Synthesis and thermal property of terpolymer derived from p-hydroxybenzaldehyde-hiourea-ethylene glycol and p-hydroxybenzaldehyde-adipic acid-ethylene glycol were studied in our laboratory [12-13]. Thermogravimetric study of polymer provides information about the degradation pattern during heating and thermal stability reported by many coworkers [14-18]. The study of thermal behavior of polymers in argon at different temperature provides important information about its practical applicability at elevated temperature. In the literature several methods have been reported for the determination of thermokinetic parameters from thermal analysis [19-20]. Gurnule et al reported non-isothermal kinetic study of p-cresol-dithiooxamide-formaldehyde by using Freemen-Carroll and Sharp-Wentworth methods [21]. Masram et al reported a kinetic study of thermal degradation of resin derived from salicylaldehyde, ethylenediamine and formaldehyde [22]. Rahangdale et al studied thermal degradation of p-cresol-adipamide-formaldehyde copolymer [23]. Mallikarjun et al studied the thermal decomposition kinetics of Ni (II) chelates of

substituted chalcones by using Freemen-Carroll method [24]. Thakre et al recently reported themokinetic parameters of amberlite XAD-4 functioned with hydroquinone using Freemen-Carroll and Sharp-Wentworth methods [25].

Present paper deals synthesis, characterization and thermo kinetic parameters of HBUE-I terpolymer. The following methods were used to calculate thermokinetic parameters.

1.1 Freeman-Carroll method

In this method, activation energy and order of degradation are related to equation (1),

$$\frac{\log(dw/dt)}{\log W_r} \quad \frac{Ea}{2.303R} \quad \frac{(1/T)}{\log W_r} \quad n, \ldots\ldots(1)$$

Where, (dw/dt) = Rate of change in weight with time, W_r = Difference between weight loss at completion of reaction, and at time t, Where, (dw/dt) = Rate of change in weight with time, W_r = Difference between weight loss at completion of reaction, and at time t, E_a = Energy of activation and the n = Order of reaction.

The plot of $\frac{\log(dw/dt)}{\log W_r}$ verses $\frac{(1/T)}{\log W_r}$ gives a straight line, with a slope of ($-E_a/2.303R$). Energy of activation (E_a) can be determined from the slope and order of reaction (n) obtained with the help of intercept [26].

1.2 Sharp-Wentworth method

$$\log \frac{(d\ /dt)}{(1\ )^n} \quad \log A \quad \frac{E_a}{2.303RT} \quad \ldots\ldots\ldots(2)$$

Equation (2) has been used to evaluate the kinetic parameters. Where, (dα/dt) = Fraction of weight loss with time, β = Linear heating rate, A = Frequency factor, α = Fraction of molecule decomposed. By plotting the graph between $\log \frac{(d\ /dt)}{(1\ )^n}$ verses $\frac{1}{T}$, the straight line graph is obtained with a slope of ($-E_a/2.303R$) from which activation energy is calculated and frequency factor (A) evaluated from intercept. The change in apparent entropy (ΔS*) and change in free energy (ΔG) calculated by further calculations [27].

2. Experimental Section

2.1 Materials

All chemicals were AR grade or chemically pure grade, p-hydroxybenzaldehyde, urea, ethylene glycol and polyphosphoric acid were procured from s.d. fine chemicals, India.

2.2 Synthesis of HBUE-I terpolymer

A terpolymer resin abbreviated as HBUE-I was synthesized by polycondensation of monomers p-hydroxybenzaldehyde, urea and ethylene glycol in the presence of polyphosphoric acid. To a well-stirred and ice-cooled mixture of p-hydroxybenzaldehyde (0.1M), urea (0.1M) and ethylene glycol (0.3M), polyphosphoric acid (PPA) was added slowly with continuous stirring as a catalyst. The reaction mixture was left at room temperature for 30 minutes then heated on oil bath at 120°C ± 2°C for 5 hrs. The reaction mixture was cooled, poured on crushed ice and left over night [28].

Dark reddish brown solid was separated. The crude product was squeezed with ether so as to remove urea-glycol copolymer which might be formed along with HBUE-I. The terpolymer was further purified by dissolving in 0.1N NaOH solution and precipitated by dropwise addition of 1:1 HCl with constant stirring. The product was washed several times with hot water and cold water. The product was air dried and kept in vacuum over silica gel. Yield was found to be 75%. The scheme of synthesis of

HBUE-I is shown in figure 1.

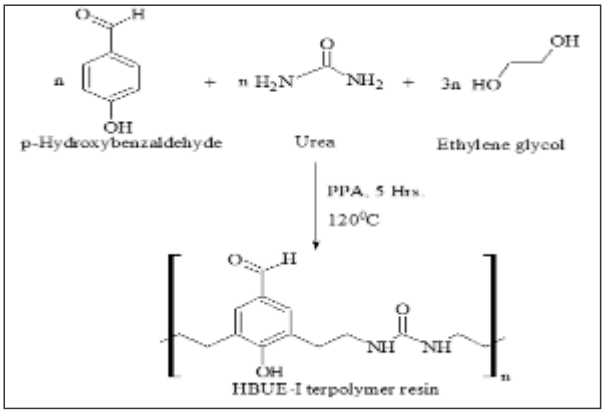

Figure 1: Synthesis scheme of HBUE-I terpolymer resin

3. Results and Discussion

HBUE-I terpolymer resin was dark reddish brown in color and soluble in DMSO and NaOH solution where as insoluble in acids and common organic solvents.

3.1 Elemental analysis and molecular weight determination (Mn)

Elemental analysis has been carried out in CIMFR unit, Nagpur, by analytical functional testing Vario MICRO CHN elemental analyzer (Germany). The number average molecular weight (*Mn*) was determined by non-aqueous conductometric titration in DMSO using 0.1M KOH in absolute alcohol as titrant [29]. From the graph of specific conductance against miliequivalents of KOH, first and last breaks were noted .The degree of polymerization (*Dp*) and the number average molecular weight (*Mn*) have been calculated using following equations (3) and (4).

$$\overline{Dp} \quad \frac{\text{Total Meq. of base required for last break}}{\text{Meq. of base required for first break}}$$

$\overline{Mn}$ $\overline{Dp}$ x Repeat unit weight ..... (4)

The repeating unit weight was obtained from elemental analysis. The elemental analysis and molecular weight determination data of HBUE-I terpolymer are tabulated in table 1.

3.2 IR spectra

IR spectrum of HBUE-I terpolymer was recorded at department of pharmacy, RTM Nagpur University, Nagpur, using FT-IR spectrophotometer, Shimadzu, model No-8101A. FT-IR spectrum of synthesized terpolymer is shown in figure 2.

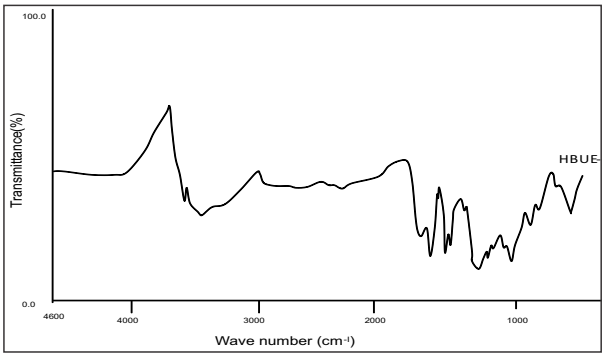

Figure 2: FT-IR spectrum of HBUE-I terpolymer

A medium peak at 3572 cm-1 was clearly due to N-H stretching of secondary amide group. A broad absorption band appeared in the region 3433 cm-1 was assigned to the stretching vibrations of phenolic hydroxyl (-OH) group exhibiting intermolecular hydrogen bonding. Peaks appeared at 2746 cm-1 and 2917 cm-1 were attributed to the –C-H- stretch in the

Table 1: Elemental analysis data, $\overline{Dp}$ and $\overline{Mn}$ of HBUE-I terpolymer

%C		%H		%N		Mol. Formula of repeating unit	Mol. Wt. of repeating unit	$\overline{Dp}$	Mol. Wt. $\overline{Mn}$
Cal	Found	Cal	Found	Cal	Found				
64.37	64.20	6.51	6.47	10.73	10.63	$C_{14}H_{17}O_3N_2$	261	16	4176

aldehyde (doublet due to Fermi resonance). A medium peak appeared at 1690 cm^{-1} was assigned to stretching in the carbonyl group of the amide (amide-I band). A peak at 1655 cm^{-1} was assigned to the C=O band (an aldehyde). A peak appeared at 1597 cm^{-1} was due to aromatic-ring. A peak appeared at 1560 cm^{-1} was assigned to N-H bending and C-N is stretching in HBUE-I terpolymer. The band at 1509 cm^{-1} was attributed to the coupling of N-H bending and C-N stretching absorption (amide-II band); clearly indicate the presence of secondary amide linkages. A peak appeared at 1469 cm^{-1} was due to -CH2- bending bridge coupled with aromatic ring. A peak appeared at 1384 cm^{-1} assigned to in plane bending vibration of phenolic –OH. A peak at 1345 cm^{-1} was due to aldehyde C-H bend in synthesized resin. The bands appeared at 1294, 1284 cm^{-1} were attributed to C-N stretching in CONH group. 1, 2, 3, 5- tetra substitution of aromatic ring was assigned due to the peaks at 1210, 1096 and 965 cm^{-1} and a peak at 831 cm^{-1} was due to the -CH2- (wagging) in HBUE-I [30-35]. FT-IR spectral data of HBUE-I terpolymer is tabulated in table 2.

3.3 ^{1}H NMR Spectrum

^{1}H NMR spectrum of HBUE-I terpolymer using DMSO solvent was scanned on NMR spectrophotometer SAIFNM100820A, at Sophisticated Test and Instrumentation Center (STIC),

Cochin University, Kerala, India. The 1H NMR spectrum of HBUE-I terpolymer is shown in figure 3.

Table 2: IR spectrum data of HBUE-I terpolymer

Observed frequency in cm-1	Assignment
3572 (m)	NH-stretching– secondary amide
3433 (broad)	Phenolic –OH group with intermolecular polymeric association
2746 (w), 2917 (m)	-C-H- stretching in aldehyde (doublet due to Fermi resonance)
1690 (m)	C=O amide (amide-I band)
1655 (s)	C=O band (aldehyde)
1597 (m)	Aromatic-ring
1560 (m)	N-H bending and C-N stretching band
1509 (m)	Coupling of N-H bending and C-N stretching (amide-II band)
1469 (m)	-CH2- bending bridge
1384 (m)	Phenolic –OH in plane bending
1345 (m)	Aldehydic C-H bending
1294(w), 1285(m)	C-N stretching band –CONH-
1210 (m), 1096 (m), 965 (w)	1,2,3,5 tetra substituted aromatic ring
831 (w)	-CH2-wagging

(m) = medium, (b) = broad, (s) = sharp, (w) = weak

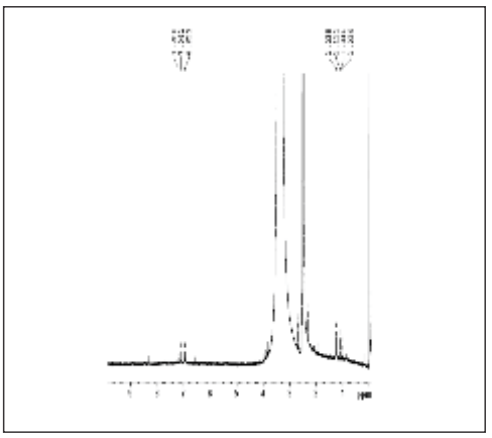

Figure 3: ^{1}H NMR spectra of HBUE– I terpolymer

The in the range 1.2 ppm was of -CH_2- in HBUE-I. The signal at 2.46 ppm was due to –CH_2-NH in HBUE-I terpolymer. The signal at 2.50 ppm was due to DMSO solvent. Signal at 3.3 ppm was assigned to secondary amine proton in terpolymer. Signal at 3.7 ppm was attributed to CH-OH moiety. The signal at 6.9 ppm was due to aromatic ring protons in HBUE-I. Signal at 7.2 ppm was due to C-NH in HBUE-I terpolymer. Weak signal 8.3 was due the aldehydic proton [36-38]. 1H NMR spectrum data are tabulated in table 3.

Table 3: ^{1}HNMR spectrum data of HBUE– I terpolymer

Chemical shift δ ppm	Nature of proton assigned
1.2	-CH_2-
2.46	CH_2-NH
2.50	DMSO solvent
3.30	N-H Variable
3.70	CH-OH
6.90	Aromatic proton (asymmetrical substitution pattern)
7.20	C-NH
8.30	-CHO

3.4 UV-Visible spectrum

UV-Visible spectrum of HBUE-I terpolymer in DMSO solvent recorded by UV-Visible double beam spectrophotometer, Schimadzu, model-1800 at the department of nanotechnology, Shivaji Science College, Nagpur. The electronic spectrum of the HBUE-I terpolymer is shown in figure 4.

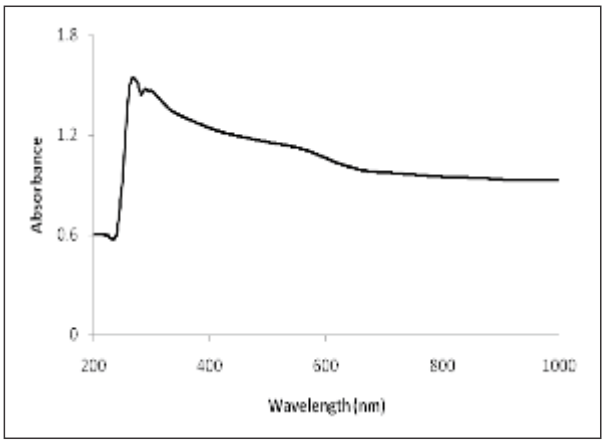

Figure 4: UV-Visible spectrum of HBUE-I terpolymer

A peak at 220.5 nm was assigned to n- * transition was due to C-NH- moiety and peak at 269.0 NM was assigned to * due to the aromatic ring. n- * transitions at 288.5 nm and 298.5 nm, these were due to >C=O in amide linkage and -CHO moiety [39]. The UV-Visible spectrum data are tabulated in below table 4.

Table 4: UV-Visible spectrum data of HBUE-I terpolymer

Transition	Wavelength (nm)	Group / moiety assigned
n-	220.5	C-NH- moiety
*	269.0	Aromatic ring
n	288.5	>C=O in amide linkage
	298.5	-CHO group

3.5 Thermokinetic analysis

Thermogravimetric analysis (TGA) of HBUE-I terpolymer sample has been carried out by using Perkins Elmer Diamond TGA/DTA analyzer at a linear heating rate of 10°C min-1 in argon atmosphere up to 1000°C, at department of material science, VNIT, Nagpur. Thermogram of HBUE-I terpolymer is shown in below figure 5.

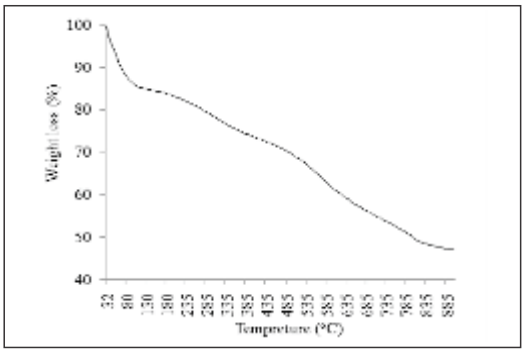

Figure 5: Thermogram of HBUE-I terpolymer

The initial loss up to 110°C was due to loss of water present in HBUE-I terpolymer. The degradation of terpolymer studied in the temperature ranges 170-500°C. The order of the reaction using Freeman-Carroll method was found to be 0.99~1.0, which was further confirmed by Sharp-Wentworth method [40-41]. Thermokinetic parameters were calculated and tabulated in table 5. FC method and SW method plots are shown in figure 6 and 7.

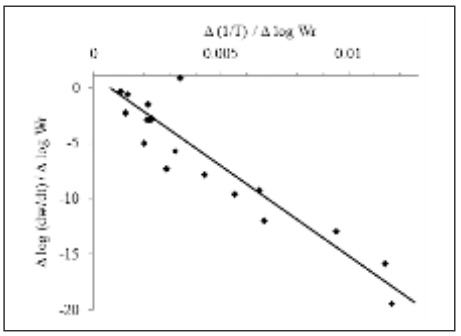

Figure 6: Freemen-Carroll Plot of HBUE-I terpolymer

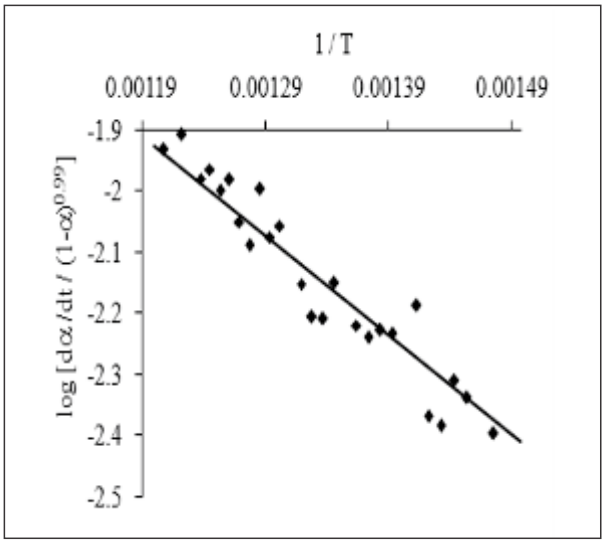

Figure 7: Sharp-Wentworth Plot of HBUE-I terpolymer

Table 5: Thermokinetic parameter data of HBUE-I terpolymer

Terpolymer	**HBUE-I**	
Temperature range (°C)	170°C – 500°C	
Method	FC*	SW#
Activation energy (Ea) in kJ	30.95	31.10
Frequency factor (A) in min-1	10.45	10.52
Apparent entropy change (ΔS*) in J/K	-233.15	-233.09
Free energy change (ΔG) in kJ	206.58	206.74
Order of reaction (n)	0.99	0.99

*FC = Freeman-Carroll, SW# = Sharp-Wentworth

4. Conclusions

The data of elemental analysis, UV–Visible

spectrum, FT-IR spectrum and 1H NMR spectrum supports the structure of HBUE-I terpolymer. The thermokinetic parameters calculated by Freeman-Carroll method is in good agreement with those calculated by Sharp-Wentworth method [42]. Abnormal low values of frequency factor were due to 'slow' degradation of HBUE-I terpolymer. The negative values for entropy indicated that the activated polymer has a more ordered structure than the reactants. This was further supported by the low value of frequency factor. The SW - method provides a good approximation to a straight line as compared to the FC - method. The order n= 0.99~1.0 calculated from the intercept of FC-plot satisfy SW-equation with good approximation hence confirms the said order of degradation [43-44]. The terpolymer is found to be thermally stable up to 170°C.

5. Acknowledgements

The Authors are thankful to the Director Dr. M. T. Bharambe, Institute of Science, Nagpur, Dr. R. H. Limsey, Head of the Department of chemistry, Institute of Science, Nagpur for providing laboratory facilities, CIMFR unit, Nagpur for elemental analysis of the sample, Pharmacy Department, R.T.M. Nagpur University, Nagpur for FT-IR spectrum of the sample, Director STIC, Cochin University, Kerala for 1H NMR spectrum of the sample, Nanotechnology Department, Shivaji Science College, Nagpur for UV-Visible spectrum of sample and Department of Material Science, VNIT, Nagpur for TGA of the sample.

References

1. R. N. Singru. Thermal study of the newly synthesized organic polymer 8-HQ5-SAOF-II. Der Pharma Chemica, 3(5), (2011), 128-134.

2. R.N. Singru, V. A. Khati, W. B. Gurnule, A. B. Zade and J. R. Dontulwar. Studies on semiconducting, chelating and thermal properties of p-cresol-oxamide-formaldehyde terpolymer. Anal. Bioanal. Electrochem., 3(1), (2011), 67-86.

3. D. Urade, V. Hiwase and A. Kalambe. Synthesis and electrical conducting behaviour of resin derived from 2, 6-diaminopyridine and terphthalic acid. Chem. Sci. Trans., 1(3), (2012), 604-611.

4. R. Singru, A. B. Zade and W. B. Gurnule. Thermoanalytical study and kinetics of new 8-hydroxyquinoline 5-sulphonic acid-oxamide-formaldehyde terpolymer resins. E-J Chem. 6(S1), (2009), S171-S182.

5. D. T. Masram, K. P. Kariya and N. S. Bhave. Physicochemical and ion exchange studies of resin derived from p-hydroxybenzoic acid and pheynlenediamine with formaldehyde. Adv. Appl. Sci. Res. 2(4), (2011), 156-165.

6. P. A. Dhakite and W. B. Gurnule, Ion-exchange study of some new copolymer resins derived from 8-hydroxyquinoline- 5 sulphonic acid, biuret and formaldehyde. E-J Chem. 8(3), (2011), 1186-1199.

7. A. D. Kushwaha, A. B. Kalambe, V. V. Hiwase and D. N. Urade. Structural and antibacterial study of resin-II derived from p-nitrophenol, resorcinol and formaldehyde. J. Chem. Pharma. Res. 4(2), (2012), 111-1116.

8. V. V. Hiwase, A. B. Kalambe, S. S. Umare and K. M. Khedker, Ion-exchange study of some resins derived from p-hydroxyacetophenone, hexamine and formaldehyde. Acta Ciencia Indica, XXXIIIC(4), (2007), 615-622.

9. V. V. Hiwase, A. B. Kalambe, K. M. Khedkar and S. D. Deosarkar, Ion

exchange properties of resins derived from p-hydroxybenzaldehyde, resorcinol and formaldehyde. E-J Chem., 7(1), (2010), 287-294.

10. K. P. Dharkar, S. S. Ingle and A. B. Kalambe, Electrical conductivity properties of newly synthesised melamine-aniline-formaldehyde terpolymer and its polychelates. E-J Chem., 8(1), (2011), 127-130.

11. A. D. Kushwaha, V. V. Hiwase and A. B. Kalambe, Semiconducting behavior and antibacterial activity of some resins derived from p-nitrophenol, resorcinol and formaldehyde. Der. Pharma. Chemica., 4(1), (2012), 557-567.

12. A. N. Gupta, V. V. Hiwase and A. B. Kalambe, Semiconducting behavior and thermokinetic study of terpolymeric resin-i derived from p-hydroxybenzaldehyde, thiourea and ethylene glycol. J. Chem. Pharma. Res., 4(5), (2012), 2475-2482.

13. A. N. Gupta, V. V. Hiwase and A. B. Kalambe, Semiconducting behavior and thermokinetic study of terpolymeric resin-I derived from p-hydroxybenzaldehyde, adipic acid and ethylene glycol. Der Pharma Chemica, 4(3), (2012), 1153-1159.

14. S. K. Kapse, V. V. Hiwase and A. B. Kalambe, Structural and thermokinetic study of resin-I derived from p-hydroxyacetophenone, quinhydrone and melamine. Der Pharma Chemica, 4(1), (2012), 460-467.

15. D. Mathew, C. P. Reghunadhannair and K. N. Kinan, Pendant cyanate functional vinyl polymers and imido-phenolic-triazines thereof: synthesis and thermal properties. Eur. Polym.. J,. 36(6), (2000), 1195-1208.

16. D. T. Masram, N. S. Bhave and K. P. Kariya, Kinetic study of thermal degradation of resin derived from salicyladehyde, ethylenediamine and formaldehyde. E-J. Chem., 7, (2010), 564-568.

17. P. E. P. Michael, J. M. Barbe, H. D. Juneja and L. J. Paliwal, Synthesis, characterization and thermal degradation of 8-hydroxyquinoline-guanidine-formaldehyde terpolymer. Eur. Polym. J., 43(12), (2007), 4995-5000.

18. P. K. Roy, P. Surekha, C. Rajagopal and V. Choudhary, Thermal degradation studies of LDPE containing cobalt stearate as pro-oxidant. eXpess Polym. Lettre, 1, (2007), 208-216.

19. B. A. Shah, A. V. Shah and D. M. Shah, Synthesis, characterization and analytical applications of o-substituted benzoic acid chelating resin. Iran Polym. J., 15, (2006), 809-819.

20. J. Yangs, R. Miranda and C. Roy, Using the DTG curve fitting method to determine the apparent kinetic parameters of thermal decomposition of polymers. Polym. Degrad. Stab., 73, (2001), 455-461.

21. W. B. Gurnule and S. S. Katkamwar, Non-isothermal kinetic study of p-cresol-dithiooxamide-formaldehyde terpolymer. E-J Chem., 7(4), (2010), 1380-1390.

22. D. T. Masram, Thermal degradation study of salicylic acid, diaminonaphthalene and formaldehyde terpolymer. E-J Chem., 6(3), (2009), 830-834.

23. S. S. Rahangdhale and W. B.Gurnule, Synthesis and electrical conductance

studies of p-cresol-adipamide-formaldehyde copolymer. Arch. Appl. Sci. Res., 2(6), (2010), 53-58.

24. K. G. Mallikarjun, Thermal decomposition kinetics of Ni (II) chelates of substituted chalcones. E-J. Chem., 2, (2004), 05-109.

25. A. M. Thakre, V. V. Hiwase and A. B. Kalambe, Synthesis and thermokinetic parameters of amberlite XAD-4 functionalized with hydroquinone. Arch. Appl. Sci. Res., 4(2), (2012), 1150-1154.

26. E. S. Freeman and B. Carroll, The application of thermoanalytical techniques to reaction kinetics, thermogravimetic evaluation of the kinetics of the decomposition of calcium oxalate monohydrate. J. Phy. Chem., 62, (1958), 94-397.

27. J. B. Sharp and S. A. Wentworth, Kinetic analysis of thermogravimetric data. Anal. Chem., 41(14), (1969), 2060-2062.

28. J. D. Joshi, N. B. Patel and S. D. Patel, Synthesis, characterization and ion-exchange study of poly[(2,4-dihydroxy benzophenone)butylene] resin and its polychelates with transition metals. Iran Polym. J., 15(3), (2006), 219-226.

29. D. B. Patel, W. B. Gurnule and A. B. Zade, Synthesis, characterization and ion-exchange properties of a terpolymer derived from 4-hydroxybenzophenone, biuret and formaldehyde. Der Pharma Chemica, 3(3), (2011), 341-353.

30. R. M. Silverstein and F. X.Webster, Spectrometric identification of organic compounds. 6th ed. John Willey (NY): (1998), 217-248.

31. H. Dudley and I. Fleming, Spectroscopic methods in organic chemistry. McGraw Hill, London (UK): (1975).

32. R. T. Morrison and R. N. Boyd, Organic Chemistry, Prentice Hall India Pvt. Ltd (New Delhi); (2004).

33. L. J. Bellamy, Infra red spectra of complex mol. Vol-1., Chapman and Hall London: (1958), 142-160;.

34. L. D. Field, S. Sternell and J. R. Kalman, Org struct. from spectra, John Willey and Sons (NY), (1969), 29.

35. P. S. Kalsi, Spectroscopy of organic compounds. New age international (New Delhi): (2004), 9-20.

36. D. N. Urade, V. V. Hiwase and A. B. Kalambe, Structural and thermokinetic parameters of terpolymeric resin derived from p-hydroxyacetophenone, bis (2-amino- 1, 3, 4 -thiadiazole) and glycerol. J. Chem. Pharma. Res., 4(1), (2012), 732-740.

37. M. Karunakaran, C. T. Vijaykumar, C. Magesh and T. Amudha, Terpolymer resin-II – thermal and metal ion binding properties of resorcinol-thiourea-formaldehyde terpolymer resin. IJEST, 3(1), (2011), 162-176.

38. T. K. Pal and R. B. Kharat, Salicylic acid-biuret-trioxane terpolymer resins and their ion-exchange properties. Angew Makromol. Chem., 113, (1989), 55-68.

39. B. L. Hirani, S. N. Paliwal, J. Choudhary and P. R. Choudhary, Synthesis, characterization and Copolymerization of N-(phenylamino)maleimide with MMA. E-J Chem., 4(2), (2007), 265-271.

40. S. S. Butoliya, W. B. Gurnule and A. B.

Zade, Study of non-isothermal decomposition and kinetic analysis of 2, 4-dihydroxybenzoic acid-melamine-formaldehyde copolymer. E-J Chem., 7(3), (2010), 1101-1107.

41. K. M. Khedkar, V. V. Hiwase, A. B. Kalambe and S. D. Deosarkar, Synthesis, characterization and thermal study of terpolymeric resin derived from m-cresol, hexamine and formaldehyde. E-J Chem., 9(4), (2012); 1911-1918.

42. T. Ozawa, Temperature control modes in thermal analysis. Pure Appl Chem. 72(11), (2000), 2083-2099.

43. P. W. M. Jacobs and F. C. Tompkin, Chemistry of solid state, WI Graver Pub London; (1955).

44. W. B. Gurunule, H. D. Juneja, L. J. Paliwal, Thermal analysis of 8-hydroxyquinoline-melamine-formaldehyde tercopolymer. Orient. J. Chem., 15(2), (1999); 283-288.

****