Thermal Degradation Study of Copolymer Resin Resulting From O-Toluidine, Biuret and Formaldehyde

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Abstract

The copolymer o-TBF has been synthesized by condensation of o-Toluidine and biuret with formaldehyde in the presence of hydrochloric acid as a catalyst in the 1: 1: 2 molar proportion of reactants. The thermal decomposition behavior of o-TBF copolymer has been carried out by using TGA in static nitrogen atmosphere at a heating rate of 10 0C/min. Sharp-Wentworth and Freeman-Carroll methods have been applied to calculate the thermal activation energy(Ea), entropy change (ΔS), apparent entropy change (S*), free energy change (ΔF) and frequency factor (Z). The order of reaction (n) has been found to be 0.97.

Keywords: Thermal degradation, copolymer, condensation, thermal stability

Introduction

Due to global applications of polymeric materials, polymer science and technology have been developing rapidly and attracted much attention towards the polymer scientists. Thermal degradation studies of 2-hydroxy-4-methoxy acetophenone, guanidine and formaldehyde copolymer (Mishra PA et. al., 2022). Polymers have been found to be very useful applications as ion-exchange resins, adhesive, flame resistant fibers, coating materials, semiconductors and catalysts (Jiwatode MM et. al., 2017). Thermal analysis plays a vital role in studying the structure and properties of any material .Thermogravimetric analysis has been widely used to investigate the decomposition characteristics of polymeric matter (Liu C et. al., 2003).

Gurnule and coworkers have studied the thermal degradation of copolymer resin derived from 2-hydroxy-4-methoxybenzophenone,1,5-diaminonaphthalene and formaldehyde (Gurnule WB et. al., 2019). Chaudhary studied thermal microbial reactivity of copolymers and terpolymers of azo-N-4-bromophenyl substituted maleimide chain with acrylatesvinyls (Chaudhary et al., 2016). Synthesis and thermal degradation studies of aromatic based epoxy resins bearing salicylaldehyde and epichorohydrin group (Mahant RD, Gurnule WB., 2019). The kinetic study of non- isothermal decomposition of copolymer resin derived from 2,4-dihydroxypropiophenone, 1,5-diaminonaphthalene and formaldehyde has been reported (Gurnule WB et. al., 2019). Studied the thermal properties of copolymer derived from 2,4-dihydroxypropiophenone and 4-pyridylamine (Rahangdale SS et. al., 2019). Thermal study of polymers derived from acrylamide (Silva ME et. al., 2000).Comparative thermo kinetic study of terpolymeric resins derived from p-hydroxyacetophenone, resorcinol and glycerol has been reported (Kapse et al., 2014). Synthesis and thermal degradation studies of p-toluidine, ethylenediamine and formaldehyde (Kohod CG, Gurnule WB, 2019). Bisen et. al. synthesized and studied the kinetics of thermal decomposition of copolymer resin-II derived from 4-hydroxy benzaldehyde, phenyl hydrazine and formaldehyde (Bisen VR et. al. 2014).

In the present paper investigation it has been planned to study the synthesis, characterization and thermal degradation study of o-TBF copolymer resin derived from o-Toluidine and biuret with formaldehyde which has not been reported so far in literature. The Freeman-Carroll and Sharp-Wentworth methods have been applied for

the calculation of activation energy and kinetic parameters such as entropy change (ΔS), apparent entropy change (S*), free energy change (ΔF), frequency factor (Z) and order of reaction (n).

Synthesis of o-Toluidine–Biuret–Formaldehyde (o-TBF) Copolymer Resin

The four different types of o-TBF copolymer resins have been successfully synthesized and abbreviated as given in Table 1.

Synthesis of o-TBF-I copolymer resin

The new copolymer resin o-TBF-I was synthesized by condensing o-Toluidine (1.07 g, 0.1 mol) and biuret (1.03 g, 0.1 mol) and formaldehyde (7.50 ml, 0.2 mol) in molar ratio of 1:1:2 in the presence of 2M (200 ml) HCl as a catalyst at 122ºC ± 2ºC for 5 hrs in the round bottom flask attached with water condenser and was heated in an oil bath with occasional shaking to ensure thorough mixing. The temperature of oil bath was controlled by dime stat (Sanjiokumar et.al 2019, 2020, 2021, Santosh P., 2020). The resinous cream product obtained was removed immediately as soon as the condensation reaction was over. The reaction is shown as follows in Fig. 1.

The novel copolymer/activated charcoal composite was prepared by o-TBF copolymer and activated charcoal in 1:2 ratio. The copolymer was dissolved in 25 ml of DMSO and the activated charcoal was added into it and the mixture was subjected to ultrasonification for 3 hrs with constant stirring for 24 hrs at room temperature. After the specific time, the obtained composite was seperated, filtered and dried at 700C for 24 hrs.
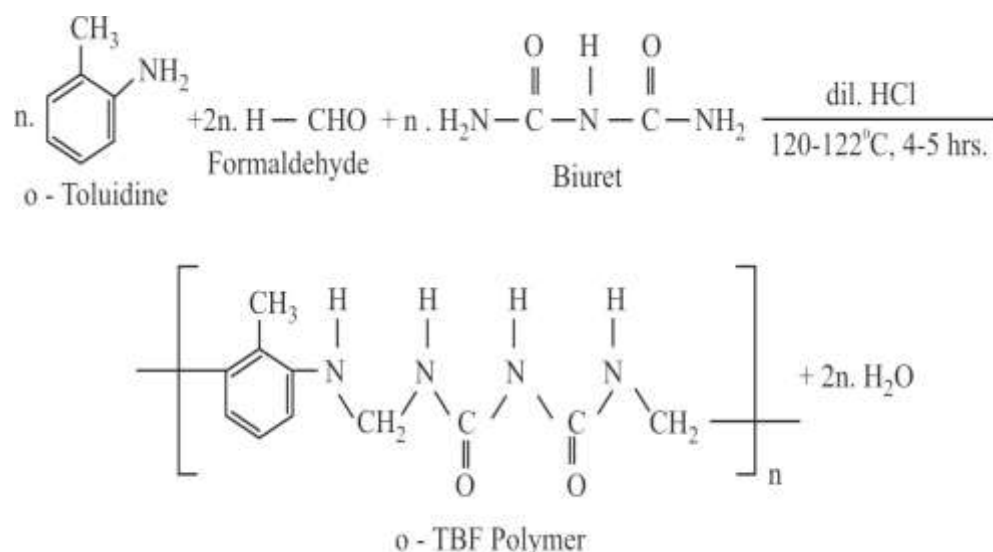

Fig. 1 : Structure of o-TBF Copolymer

Purification of Resins

The separated copolymer resin was washed with hot water and methanol to remove unreacted starting materials and monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove biuret-formaldehyde copolymer which might be present along with o-TBF copolymer. The product so obtained was further purified by reprecipitation technique. For this purpose the copolymer resin was dissolved in 10% aqueous sodium hydroxide solution, stirred well, filtered, and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v concentrated hydrochloric acid/distilled water) with constant and rapid stirring to avoid lump formation. The process of re-precipitation was repeated twice. The copolymer sample o-TBF-I thus obtained was filtered and washed several times with hot water, dried in air, powdered and kept in vacuum desiccators over silica gel. The yield of the copolymer resin was found to be 81%. Similarly other copolymer resins o-TBF-II, o-TBF-III and o-TBF-IV were synthesized by varying the molar ratios of the starting materials viz. (2:1:3), (3:1:5) and (4:2:7), respectively with little variation of experimental conditions. The samples, yields and reaction details are tabulated in Table 1.

Table 1 Synthesis and Physical Data of o-TBF Copolymer Resins

Copolymer Resin Abbreviation	Reactants			Molar ratio	Catalyst 2M/HCl (ml)	Reflux Temp. (K)	Time (hr)	Yield (%)	Melting point (K)
	o-Toluidine o-T (mol)	Biuret B (mol)	Formaldehyde F (mol)						
o-TBF-I	0.1	0.1	0.2	1:1:2	200	395	5	69	434
o-TBF-II	0.2	0.1	0.3	2:1:3	200	395	5	79	423
o-TBF-III	0.3	0.1	0.5	3:1:5	200	395	5	86	429
o-TBF-IV	0.4	0.2	0.7	4:1:6	200	395	5	78	442

Thermogravimetric Analysis

In non-isothermal or dynamic TGA, the sample is subjected to conditions increase in temperature at linear rate. The thermo gravimetric analysis was performed in with heating rate at 10 0C min-1 using 5-6 mg of samples in platinum crucible from temperature 40 0C to 8000C and thermogram is recorded for HMBPDANF-II. With the help of thermogravimetric data, the thermal activation energies (Eà), order of reaction (n), entropy change (ΔS), apparent entropy change (S*), free energy change (ΔF) and frequency factor (Z) were determined.

Theoretical Considerations

Thermogram was interpreted and analyzed to obtain information about the percentage weight loss at different temperatures which gives information about sample composition, product formed after heating. Kinetic parameters have been determined using Sharp-Wentworth and Freeman-Carroll methods as follows

Sharp- Wentworth Method

Using the equation derived by Sharp and Wentworth (Mishra PA et. al., 2022),

$\log(dC/dT)/(1-C) = \log(A/\beta) - Ea/2.303R \cdot 1/T$ ……………………………(1)

where,

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

β = linear heating rate dT/dt

The graph of   log (dC/dT)/(1-C) versus 1/T has been plotted. The graph is a straight line with activation energy (Ea) as slope and 'A' as intercept. The linear relationship confirms that the assumed order (n==1) is correct.

Freeman-Carroll Method

The straight line equation derived by Freeman and Carroll (Belsare PV et. al.

2015, Rathod YU et. Al., 2021), which is in the form of

$(\Delta\log(dW/dt))/\Delta\log Wr = n - Ea/2.303R \ (\Delta(1/T))/\Delta\log Wr$ ………………………………(2)

where,

dW/dt = Rate of change of weight with time.

Wr   = Wc-W

Wc = Weight loss at completation of reaction.

W   = Fraction of weight loss at time t.

Ea = Energy of activation.

n   = Order of reaction.

The plot between the terms $(\Delta\log(dW/dt))/\Delta\log Wr$ versus $(\Delta(1/T))/\Delta\log Wr$ gives a straight line. The slope, -Ea/2.303R, gives energy of activation (Ea) and intercept on Y-axis as order of reaction (n). The change in entropy (ΔS), frequency factor (Z), apparent entropy change(S*) can also be calculated by further calculations.

Result and Discussion

Thermogravimetric Analysis of o-TBF Copolymer

Thermogravimetric analysis of o-TBF copolymer resins have been carried out by using Thermogravimetric Analyser at heating rate of 10oCper minute. These methods were used to determine the kinetic parameters like, activation energy (Ea) and order (n) of the decomposition reaction. By using Freeman - Carroll methods, different thermodynamic parameters (Table 4) have been calculated such as, entropy change, free energy change apparent entropy change and frequency factor etc. However, the thermal data (Table 2 to 4) have been given. The numbers of water molecules associates with polymers have been suggested on the basis of thermal study. However, to economies the space, the thermal data (Table 2-4) for only

one representative case has been given. This initial weight loss may be due to moisture or solvent entrapped in the copolymer samples (Sanjiokumar S. Rahangdale et Sanjiokumar S. Rahangdale.al., 2020). The degradation of species with their corresponding mass loss is summarized in Table 2. The thermograms of o-TBF copolymer resins are shown in Fig. 2. The activation energy and decomposition temperature of copolymer is presented in the Table 3.

TG of o-TBF-I Copolymer
Thermogram of the o-TBF -I copolymer is presented in Fig. 2 which exhibits three step decomposition in the temperature range 40 - 640 0C, after loss of water molecule (4.08 %

found and 4.20 % calculated). First step decomposition starts from 190 - 480 0C corresponding to the gradual mass loss of 39.97 % found and 39.95 % calculated which may be due to degradation of side chain attached to the aromatic benzene ring i.e., CH3 group. The second step decomposition starts from 480 - 510 0C corresponding the rapid mass loss of 63.81 % found and 63.08 % calculated which represents the degradation of aromatic nucleus with methylene group. The third step decomposition starts from 510 - 640 0C corresponding to the removal of all the biuret moiety with observed mass loss of 98.23 % against calculated 100 %.
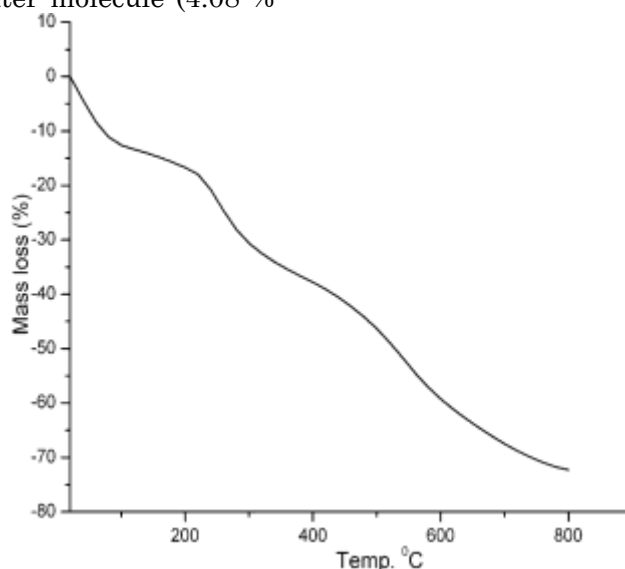

Fig. 2: TG plot of o-TBF-I copolymer

Table 2 Results of Thermogravimetric Analysis of o-TBF-I Copolymers

Temperature range (^{0}C)	Stage of decomposition	Species degraded	% Weight loss	
			Found	Calc.
40-190	--	Loss of water molecules	4.07	4.20
190-480	1st	Side chain attached to aromatic nucleus i.e. CH_3	39.96	39.95
480-510	2nd	Loss of aromatic nucleus and methylene linkage	63.80	63.08
510-640	3rd	Total loss of all biuret moiety	98.22	100

Table 3 Activation Energy and Decomposition Temperature of o-TBF Copolymers

Sr. No.	Copolymers	Decomposition Temp. (^{0}C)	Activation energy (KJ/Mole)	
			FC	SW
1	o-TBF -I	510	29.06	28.85

Table 4 Kinetic Parameters of o-TBF Copolymers

Sr. No.	Copolymers	Entropy change	Free energy change	Frequency factor	Apparent entropy change	Orderof reaction
		ΔS (J)	ΔF (KJ)	Z (S^{-1})	S (KJ)	N
1	o-TBF -I	-82.02	64.25	112.2	-124.16	0.97
2	o-TBF -II	-232.55	212.23	463.0	-657.04	0.96
3	o-TBF -III	-232.45	213.96	586.0	-655.41	0.91
4	o-TBF -IV	-226.20	195.13	616.0	-654.20	0.97

Discussion

From the observed TG data, Sharp-Wentworth and Freeman Carroll methods are employed to determine thermodynamic parameters (ΔS, ΔF, Z, S*) for the copolymer and its composite. The results could further reveal that, the copolymer and and its composite would have higher molecular weight and higher thermal stability in accordance with the activation energies.

The activation energy calculated by Sharp-Wentworth method (Fig. 2) and using thermal decomposition data, which is in agreement with the activation energy calculated by Freeman-Carroll method (Table 3). Thermodynamic parameters have been evaluated on the basis of thermal activation energy and these values are presented in the Table 3. From the result of kinetic parameters it is observed that the copolymer resins prepared from a higher molar ratio of o-toluidine and biuret exhibited a lower rate of decomposition suggesting the order of stability as o-TBF-I<o-TBF-II <o-TBF-III <o-TBF-IV of these copolymer resins. This fact is further supported by the increasing order of melting point (viz. o-TBF-I <o-TBF-II<o-TBF-III < o-TBF-IV). These order of stability may be due to the possibility of on almost linear structure of the copolymer having higher molar ratio of o-toluidine and biuret which may give rise to a stable structure to the copolymer chain (Mahant RD et. al., 2019).

Thermodynamic parameters have been calculated by using the data of the Freeman Carroll method (Table 4) (Kohod CG et. al., 2019). The values of these thermodynamic parameters for all the copolymer resins are about the same. The similarities of the values indicate a common reaction mole [36, 37]. From the abnormally low values of frequency factor (Z) it may be concluded that the decomposition reaction of o- TBF resins can be classed as a "slow" reaction. There seems to be no other obvious reason (Gupta PM et. al., 2022).

The negative values for entropy (ΔS) indicate that the activated polymer has a more ordered structure than the reactants and the reactions are slower than normal. This is further supported by low Z values (Gurnule et. al., 2019). Higher value of activation energy suggests the higher stability (Nandekar et. al. 2012). Thus the order of thermal activation energy is o-TBF-I <o-TBF-II <o-TBF-III <o-TBF-IV.

Conclusion

Copolymer o-TBF was synthesized by condensation polymerization technique from o-toluidine and biuret with formaldehyde in the presence of acid catalyst. The proposed structure of the copolymer has been determined from the physico-chemical analysis, elemental analysis, UV-Visible, FT-IR and1H-NMR spectral studies. Activation energy calculated by both Sharp-Wentworth and Freeman-Carroll methods are in good agreement with each other. The negative values for entropy indicate that the activated polymer has more ordered structure than the reactants. Low value of frequency factor may be concluded that the decomposition reaction of copolymer can be classified as slow reaction. Thermogravimetric study concluded that o-TBF copolymer resin is stable even at high elevation temperature.

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References

1. Bawankar SV, Kukade SD (2015). Synthesis, characterization and thermal degradation study of new terpolymeric material. Int. J. Res. Biosci. Agri. Tech., 2, 292-300.
2. Belsare PU, Zade AB, Dhore MS (2015). Thermal degradation studies of terpolymer derived from 2-aminothiophenol and butanediamine. Res. J. Pharm. Biol. Chem. Sci., 6(2), 1284-1290.
3. Bisen VR, Gurnule WB. (2014). Kinetics of thermal decomposition of copolymer resin-II derived from 4-hydroxybenzaldehyde, phenyl hydrazine and formaldehyde. Res. Pharm. Biol. Chem. Sci., 5(4), 1283-1297.
4. Chaudhary J, Jinger S, Purohit S (2016). Polymer structures: Studies on thermal and microbial reactivity of copolymers and terpolymers of [Azo-N-4-Bromophenol] substituted meleimide chain with a crylates/ vinyls.IJESRT, 5(10), 471-479. Dontulwar J (2016). Synthesis and characterization of high performance polymer resin 1-N-4-SAHDF-1. Int. J. Pharm. Sci. Rev. Res., 39(1), 260-264.
5. Gurnule WB, Das NC (2019). Kinetic study of non-isothermal decomposition of copolymer resin derived from 2, 4-dihydroxypropiophenone, 1, 5-diaaminonaphthalene and formaldehyde. Materials Today: Procedings, 15, 611-619.
6. Gurnule WB, Khobragade J, Ahamed M (2015). Synthesis, spectral, morphology and thermal degradation kinetics studies of copolymer. Chem. Sci. Rev. Lett., 3(12), 1329-1340.
7. Gurnule WB, Bisen VR (2017). Thermal degradation study of copolymer resin derived from 4-hydroxybanzaldehyde, phenyl hydrazine and formaldehyde. IJRBAT, 2(5), 472-479.
8. Gurnule WB, Das NC (2019). Thermal degradation studies of copolymer resin-III derived from 8-hydroxyquinoline-5-sulphonic acid-thiosemicarbazide-formaldehyde. IJCESR, 6(1), 2394-0697.
9. Jiwatode MM, Kariya KP, Berad BN (2017). Thermal degradation of terpolymer derived from 2, 4-dihydroxy acetophenone, propylenediamine and formaldehyde. World J. Pharm. Sci., 5(7), 51-60.
10. Kapse SK, Hiwase VV, Kalambe AB, Kene JD (2014). Comparative thermokinetics study of terpolymeric resins derived from p-hydroxyacetophenone, resorcinol and glycerol. Res. J. Chem. Sci., 4(2), 81-86.
11. Kohad CG, Gurnule WB (2018). Thermal degradation studies of copolymer resin derived from 8-hydroxyquinoline, hexamethylenediamine and formaldehyde. Res. J. Pharma. Biol. Chem. Sci., 9(5), 393-402.
12. Liu C, Yu J, Sun S, Zhang J, He J (2003). Thermal degradation studies of cyclic olefin copolymers. Polym. Degrad. Stab., 81, 197-205.
13. Masram DT (2009). Thermal degradation study of salicylic acid, diaminonaphthalene and formaldehyde terpolymer. E-J. Chem, 6(3), 830-834.
14. Michael PEP, Barbe JM, Juneja HD (2016). Synthesis, characterization and thermal degradation of 8-hydroxyquinoline-guanidine-formaldehyde terpolymer. Europ. Polym. J., 43 (12), 4995-5000.
15. Nandekar KA, Dontulwar JR, Gurnule WB (2012). Thermal behavior of newly synthesized copolymer derived from salicylic acid and thiosemicarbazide. Der Pharma Chemica, 4(4), 1644-1652.
16. Rahangdale SS, Das NC, Vajppai K, Gurnule WB (2019). Synthesis, characterization and thermaldegradation studies of copolymer derived from 2, 4-dihydroxypropiophenone and 4-pyridylamine. Int. J. Rec. Scientific Res., 10(4), 31772-31778.
17. Sanjiokumar S. Rahangdale, Nisha Tiwari, Manish Tiwari, Wasudeo B. Gurnule (2020). Antimicrobial Screening of Polymeric Resin Derived From 2, 2'-Dihydroxybiphenyl, Bouret and Formaldehyde, Alochana Chakra. IX (V), 74-84.
18. Sanjiokumar S. Rahangdale, Narayan C. Das, Kiran S. Vajpai And Wasudeo B. Gurnule(2020), Synthesis, Characterization And Thermal Degradation Study Of Copolymer Resin-Ii: Resulting From 2-Hydroxy, 4-Methoxybenzophenone, 1, 5-Diaminonaphthalene And Formaldehyde. IJRBAT, VIII (1) 194-204.

19. Sanjiokumar S. Rahangdale, Dinesh D. Kamdi, Jyotsna V. Khobragade And Wasudeo B. Gurnule (2020), Separation Of Toxic Metals Ions From Waste Water Using Pyrogallol-Biuret-Formaldehyde Copolymer Resin. IJRBAT, VIII (3) 259-268.

20. Santosh P. Chakole, S. S. Rahangdale, Ketki S. Misar, Kiran S. Vajpai, W. B. Gurnule (2020), Synthesis and Characterization of Copolymer Resin Derived from 2, 2'-Dihydoxybiphenyl, Ethylenediamine and Formaldehyde, Alochana Chakra. IX (V), 666-673.

21. S. S. Rahangdale, S. P. Chakole, K. S. Vajpai and W. B. Gurnule (2021), Synthesis, Characterization And Photoluminescent Studies Of Organic Copolymer Derived From 2, 2'-Dihydroxybiphenyl And Propylenediamine. JETIR, 8(9) 174-180.

22. Sanjiokumar S. Rahangdale, Santosh P. Chakole, Jyotsna V. Khobragade, And W. B. Gurnule (2021), Thermal Degradation Studies of 2,2'-Dihydroxybiphenyl-Ethylenediamine-Formaldehyde Copolymer. RJPBCS, 12(6) 1-12.

23. Silva ME, Dutra ER, Mano V, Machado JC (2000). Preparation and thermal study of polymers derived from acrylamide. Polym. DEGRAD. Stab., 67, 491-495.

24. Ullah S, Bustam MA, Nadeem M, Naz MY, Tan WL, Shariff AM (2014). Synthesis and thermal degradation studies of melamine formaldehyde resin. The Scientific World J. Article ID 940502, 1-6.

25. Yeole MM, Shrivastava S, Gurnule WB (2015). Synthesis and characterization of copolymer resin derived from 4-methyl acetophenone, phenyl hydrazine and formaldehyde. Der Pharm. Chem., 7(5), 124-129.

26. Rathod YU, Zanje SB, Gurnule WB (2021). Hydroxyquinoline copolymer synthesis, characterization and thermal degradation. Journal of Physics Conf. Series, 1913 (1) 012061.

27. Mishra PA, Rathod YU, Pandit VU, Gurnule WB (2022). Thermal degradation studies of 2-hydroxy-4-methoxy acetophenone, guanidine and formaldehyde copolymer, Mat. Today Prco. 53, 86-90.

28. Mahant RD, Gurnule WB (2019). Synthesis and thermal degradation studies of aromatic based epoxy resins bearing salicylaldehyde and epichorohydrin group. RJPBCS, 10(1) 1643-1649.

29. Kohod CG, Gurnule WB (2019). Synthesis and thermal degradation studies of p-toluidine, ethylenediamine and formaldehyde. Int. J. Curr. Eng. Sci. Res., 6, 503-512.

30. Gupta PM, Rathod YU, Pandit VU, Gupta RH, Gurnule WB (2022). Non isothermal decomposition study of copolymer derived from 2-amino-6-nitro benzothiozole, melamine and formaldehyde, Mat. Today Proc., 53, 101-106.