Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2011, 3 (4):314-322
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Antimicrobial activity and thermal properties of copolymer resin derived from 2, 2'-dihydroxybiphenyl, dithiooxamide and formaldehyde

Sanjiokumar S. Rahangdale[a] and Wasudeo B. Gurnule[b *]

[a]*Department of Chemistry, Jagat Arts, Commerce and Indiraben Hariharbhai Patel Science College, Goregaon, Maharashtra, India*
[b]*Department of Chemistry, Kamla Nehru Mahavidyalaya, Sakkardara Square, Nagpur, Maharashtra, India*

ABSTRACT

The copolymer (2, 2'-HBDF) synthesized by the condensation of 2, 2'-dihydroxybiphenyl (2, 2'-HB) and dithiooxamide (D) with formaldehyde (F) in the presence of acid catalyst and using 1:1:2 molar proportions of the reacting monomers. The copolymer possesses antimicrobial activity for certain bacteria such as Staphylococcus aureus, Escherichia coli, and fungi Aspergillus niger, Candida albicans. The thermogravimetric analysis of copolymer resin prepared in present study has been carried out by non-isothermal thermogravimetric analysis technique in which sample is subjected to condition of continuous increase in temperature at linear rate. Thermal study of the resin was carried out to determine its mode of decomposition and relative thermal stabilities. The Freeman-Carroll and Sharp-Wentworth methods have been used in the present investigation to calculate thermal activation energy and different kinetic parameter of the copolymer resins. The advantage of Freeman-Carroll method is to calculate both the order of reaction (n) and energy of activation in one single stage by keeping heating rate constant. By using data of thermogravimetric analysis, various thermogravimetric parameters like frequency factor (Z), entropy change (ΔS), free energy change (ΔF) and apparent entropy (S) have been determined using Freeman-Carroll method.*

Keywords: Antimicrobial screening; Polycondensation; Synthesis; Thermal degradation.

INTRODUCTION

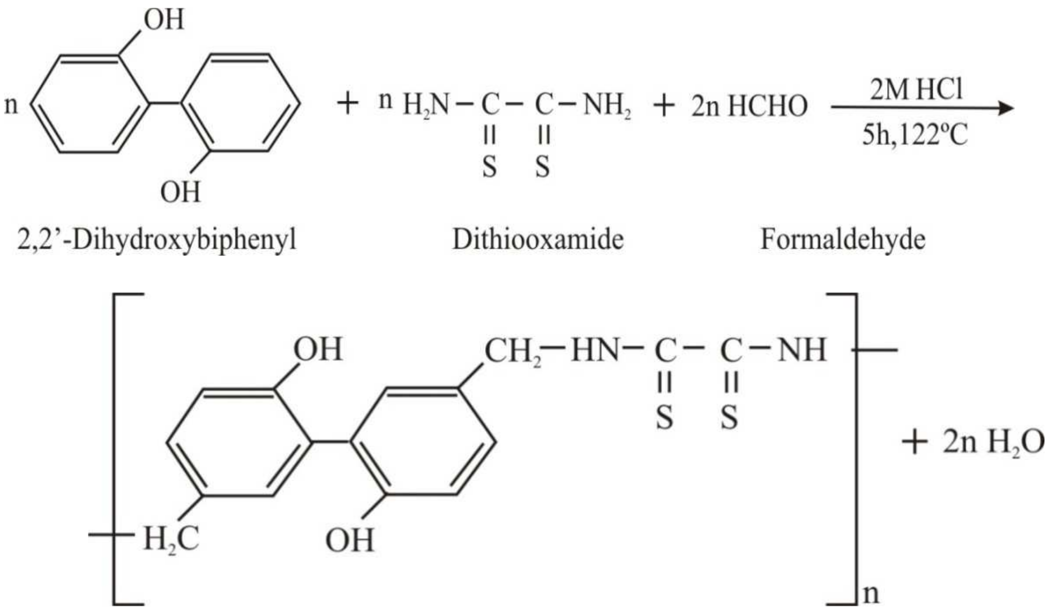
The thermal degradation study of copolymers has become a subject of interest. Study of thermal behaviour of copolymers in air at different temperature provides information about the nature of species produced at various temperatures due to degradation. Copolymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. In this laboratory, extensive work on the thermal degradation of copolymers has been undertaken [1-3]. Copolymers occupy an intermediate position between organic and inorganic compounds and it is hoped that the study of copolymer will lead to the production of polymer, which are both thermally stable and useful as fabricating materials. Patel et al. [4] studied the thermal properties of copolymers. Zeman and Tokarova [5] prepared urea–formaldehyde terpolymers and studied their TGA and DTA data. Literature survey reveals the chelating ion-exchange properties of 2-hydroxyacetophenone-formaldehyde resin [6], and oximes of 2-hydroxyacetophenone-substituted benzoic acid-formaldehyde resin [7] for different metal ions. Copolymer resins having good thermal stability have enhanced the scope for development of some polymeric materials. The study of the thermal degradation of terpolymer resins have recently become a subject of interest. Zhao Hong et. al. studied the thermal decomposition behavior of phosphorous containing co polyester [8]. In an earlier communication [9-12] from this department number of studies on such copolymers has been reported. However, the literature studies have revealed that no copolymer has been synthesized using the monomer 2, 2'-dihydrobiphenyl, dithiooxamide and formaldehyde. Therefore, in the present communication we report the synthesis, thermal degradation and antimicrobial studies of 2, 2'-HBDF-I copolymer. After treating the thermal degradation data with Sharp-Wentworth (SW) and Freeman-Carroll (FC) methods, activation energy and kinetic parameters such as ΔS, z, S^* and n (order of reaction) have been evaluated [13]. A copolymer involving 2, 4-dichlorophenylmethacrylate and vinyl acetate was reported as a significant inhibitor for the growth of microorganisms [14].

MATERIALS AND METHODS

The important chemicals (starting materials) like 2, 2'-dihydroxybiphenyl, dithiooxamide and formaldehyde used in the preparation of various new 2, 2'-HBDF copolymer resins were procured from the market and were of chemically pure grade, and wherever necessary the purity was tested and confirmed by thin layer chromatography.

Synthesis of 2, 2'-HBDF -I copolymer resin

The 2, 2'-HBDF-I copolymer resin was prepared by condensing 2, 2'-HBDF (1.86 gm, 0.1mol) and dithiooxamide (1.20 gm, 0.1mol) with formaldehyde (7.5 mL of 37 %, 0.2 mol) in the presence of 2M HCl (200 mL) as a catalyst at 122 ^{0}C in an oil bath for 5 h with occasional shaking to ensure thorough mixing[15-18].



Scheme 1: Proposed reaction for 2, 2'-HBDF-I copolymer resin

The solid resinous product obtained was removed immediately from the flask. It was washed with cold water, dried and powdered. The powder was repeatedly washed with hot water to remove unreacted monomers. Then it was extracted with diethyl ether to remove excess of 2, 2'-dihydroxybiphenyl-formaldehyde copolymer which might be present along with 2, 2'-HBDF copolymer resin. The purified copolymer resin was finely ground and kept in a vacuum over silica gel. The yield of the copolymer resin was found to be 70 %.

Characterization

Instrumentation

The non-isothermal thermogravimetric analysis was performed in air atmosphere with heating rate of 100 ^{0}Cmin^{-1} using 5 - 6 mg of samples in platinum crucible from temperature of 400 ^{0}C to 800 ^{0}C and thermograms are recorded for 2, 2'-HBDF-I sample at SICART, Vallabhvidyanagar, Gujrat. With the help of thermogravimetric data the thermal activation energies (*Ea*) and order of reaction (*n*) calculated. Also other thermodynamic parameters such as entropy change (ΔS), apparent entropy change (S^*) and frequency factor (z) are determined and reported in the Table 1.

Theoretical considerations

To provide further evidence regarding the degradation system of analyzed compounds, we derived the TG curves by applying an analytical method proposed by Sharp-Wentworth and Freeman- Carroll.

Freeman-Carroll method

The straight-line equation derived by Freeman and Carroll [19], which is in the form of n

$$[\Delta \log (dw / dt)] / \Delta \log Wr = (-E / 2.303R) . \Delta (1/ T) / \Delta \log Wr + n \text{ -----------------(1)}$$

Where,

dw/dt = rate of change of weight with time.

Wr = Wc-W

Wc = weight loss at completion of reaction.
W = fraction of weight loss at time t.
Ea = energy of activation.
n = order of reaction.

The plot between the terms $[\Delta \log (dw/dt)] / \Delta \log Wr$ Vs $\Delta (1/T) / \Delta \log Wr$ gives a straight line from which slope we obtained energy of activation (*Ea*) and intercept on Y-axis as order of reaction (*n*). The change in entropy (ΔS), frequency factor (z), apparent entropy (S^*) can also be calculated by further calculations.

(i) Entopy Change:

$$\text{Intercept} = [\log KR/h\phi E] + \Delta S / 2.303 R \text{ ------------------- (2)}$$

Where,

K = 1.3806 x 10^{-16} erg/deg/mole
R = 1.987 Cal/deg/mole

$h = 6.625 \times 10^{-27}$ erg sec.
$\phi = 0.166$
ΔS = Change in entropy
E = Activation energy from graph.

(ii) Free Energy Change:

$$\Delta F = \Delta H - T\Delta S \qquad \text{------------------------------------}(3)$$

ΔH = Enthalpy Change = activation energy
T = Temperature in K
ΔS = Entropy change from (i) used.

(iii) Frequency Factor:

$$B_n = \text{Log } ZEa \,/\, \phi R \text{ ----------------------------------}(4)$$

$$B_1 = \log [\,\ln 1/1\text{-}\alpha\,] - \log P(x) \text{ -------------------}(5)$$

Z = frequency factor
B = calculated from equation (5)
Log P(x) = calculated from Doyle’s table corresponding to activation energy.

(iv) Apparent Entropy Change:

$$S^* = 2.303 \log Zh \,/\, KT^* \qquad \text{-------------------------}\ (6)$$

Z = from relation (4)
T* = temperature at which half of the compound is decomposed from it total loss.

Sharp -Wentworth method:
Using the equation derived by Sharp and Wentworth [1],

$$\log [(dc/dT)/\,(1-c)] = \log (A/\beta) - [Ea/2.303R].\ 1/T \quad \ldots\ldots\ldots\ldots.(7)$$

Where,

dc/dT = rate of change of fraction of weight with change in temperature
β = linear heating rate *dT/dt*.

By plotting the graph between log dc/dt/ (1-c) vs 1/T we obtained the straight line which give energy of activation (*Ea*) from its slope. Where β is the conversion at time *t*, *R* is the gas constant (8.314 $\text{Jmol}^{-1}\text{K}^{-1}$) and *T* is the absolute temperature. The plots (figure 2) give the activation energies at different stages of degradation reaction take place. This isoconversional (model-free) kinetic methods use to check the variation of the apparent activation energy values with degree of degradation. This kinetic analysis should be a starting point for obtain the useful information on the behaviour of the sample (Table 1).

Antimicrobial Screening

Biological assay depends upon a comparison of the inhibition of growth of microorganism by measuring the concentration of the sample to be examined with the known concentration of standard antibiotic. For the antimicrobial analysis the in vitro disc diffusion method has been employed. In this study the ligand and their chelates were tested for their effect on certain human pathogenic bacteria such as Gram-positive (*Aspergillus niger and Candida albicans*).

The nutrient agar medium was boiled and sterilized by autoclaving at 7 kg pressure (120 ^{0}C) for 20 min for the study of antibacterial activity. 20 mL media was poured into the sterilized Petri plates and kept at room temperature for a few minutes, and allowed to solidify in plates. It was then incubated for 12 h and inoculated with microorganism using sterile swabs. All of these manipulations were carried out with utmost care under aseptic conditions. The test solution prepared by dissolving the compound in DMSO was filled with the media using a micropipette and incubated at 35 ^{0}C for 48 h. The same procedure was adopted for the antifungal studies in which potato dextrose agar was the medium.

During the course of time, the test solution diffuses and the growth of the inoculated microorganisms such as Staphylococcus aureus, Escherichia coli, Aspergillus niger, and Candida albicans were found to be affected. The activity developed on the plate was measured by measuring the diameter of the inhibited zone in millimetres. The drug ciprofloxacin was used as the standard for bacteria and nystatin for fungi.

RESULTS AND DISCUSSION

Thermogravimetric analysis of the copolymer

The thermal stability of copolymer is evaluated by dynamic thermogravimetric analysis in air atmosphere with heating rate of 10 ^{0}C min^{-1} to economize the space the thermal data of only the representative sample 2, 2'-HBDF-I has been given. Thermogram of 2, 2'-HBDF-I copolymer is shown in Figure 1. Examination of thermogram and TG data of 2, 2'-HBDF copolymer resin showed that this polymer has resistance to elevated temperatures. Thermogram of 2, 2'-HBDF-I copolymer exhibited two stages of decomposition after loss of water molecule. It is observed from TG data of these copolymer resins that the sample lost 4.0 to 7.0 % of its weight when the temperature was raised to 160 ^{0}C. This initial weight loss may be attributed to solvent or moisture entrapped in the copolymer samples. First decomposition step in 2, 2'-HBDF copolymer resin represents degradation of both phenolic hydroxyl groups. Second decomposition step in case of 2, 2'-HBDF-I copolymer resin shows the complete degradation of aromatic biphenyl nucleus and side chain attached to aromatic biphenyl ring.

Thermo-analytical data

A plot of percentage mass loss versus temperature is shown in the Fig. 1 for a representative 2, 2'-HBDF-I copolymer. To obtain the relative thermal stability of the copolymer, the method described by Sharp-Wentworth and Freeman-Carroll adopted. The thermal stability of copolymer, based on the initial decomposition temperature, has also been used here to define their relative thermal stability, neglecting the degree of decomposition. From the TG curves, the thermoanalytical data and the decomposition temperatures were determined for different stages as given in figure 1. By using thermal decomposition data and then applying above methods the activation energy (Ea) is calculated which are not perfectly in agreement with each other. But the 'average *Ea*' calculated by Freeman-Carroll (17.97 KJ/mole) and 'average *Ea*' by Sharp-Wentworth (18.02 KJ/mole) is nearly same.

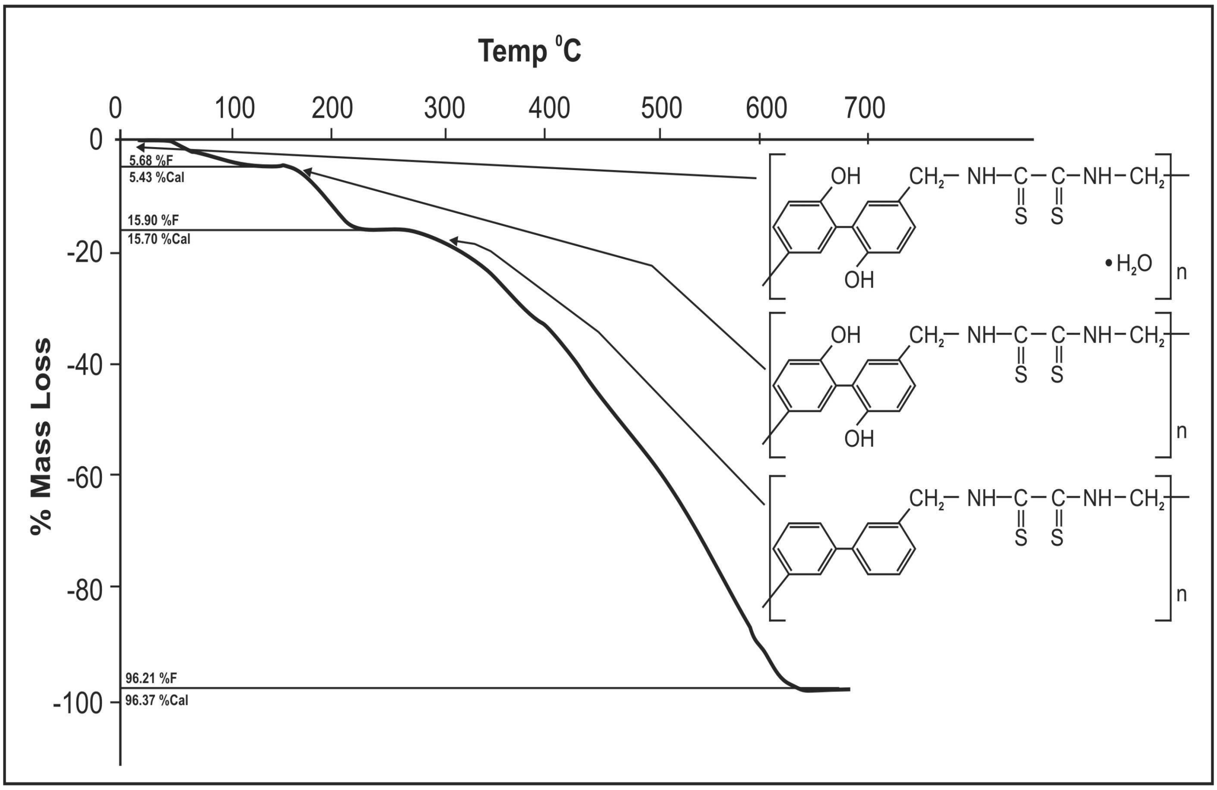


Fig. 1 : TG plot of 2, 2'- HBDF-I copolymer

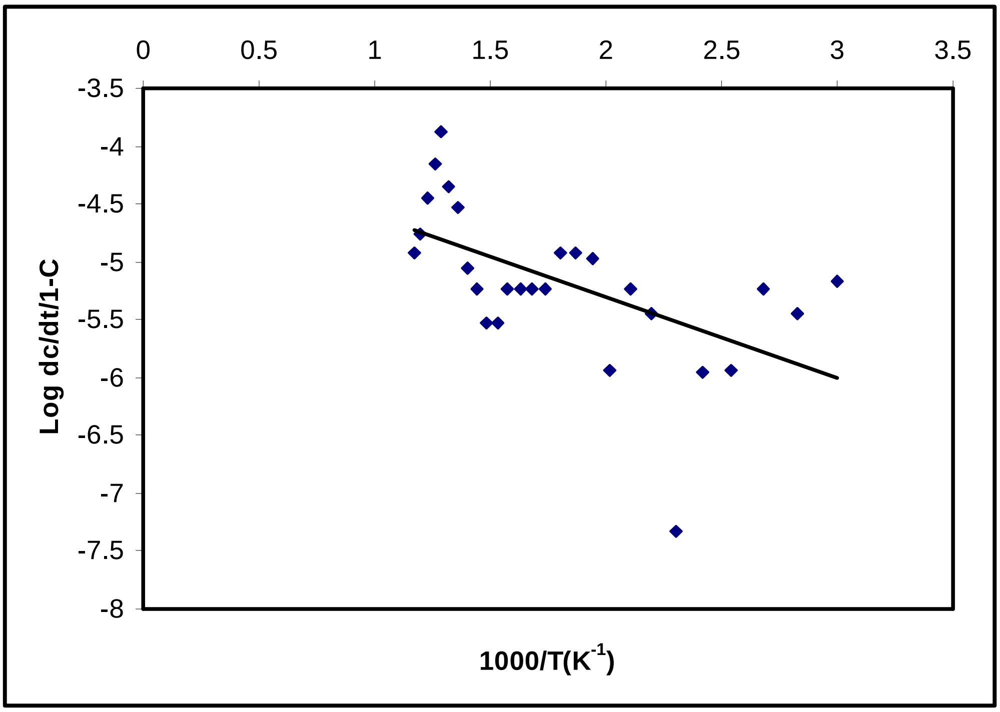


Fig. 2: Sharp-Wentworth plot of 2, 2'-HBDF-I copolymer

However the error in activation energies obtained from the Sharp-Wentworth isoconvensional method is significant and largely increases as far as conversion increases. On the other hand, it has been considered of interest to analyze the behavior of the process constitute by two competitive reactions that would lead to an apparent dependence between Ea and A when analyzed by isoconvensional method, in spite such dependence is not real [20-24]. A representative thermal activation energy plot of Sharp-Wentworth (Fig. 2) and Freeman-Carroll (Fig. 3-4) method for the copolymer has been shown.

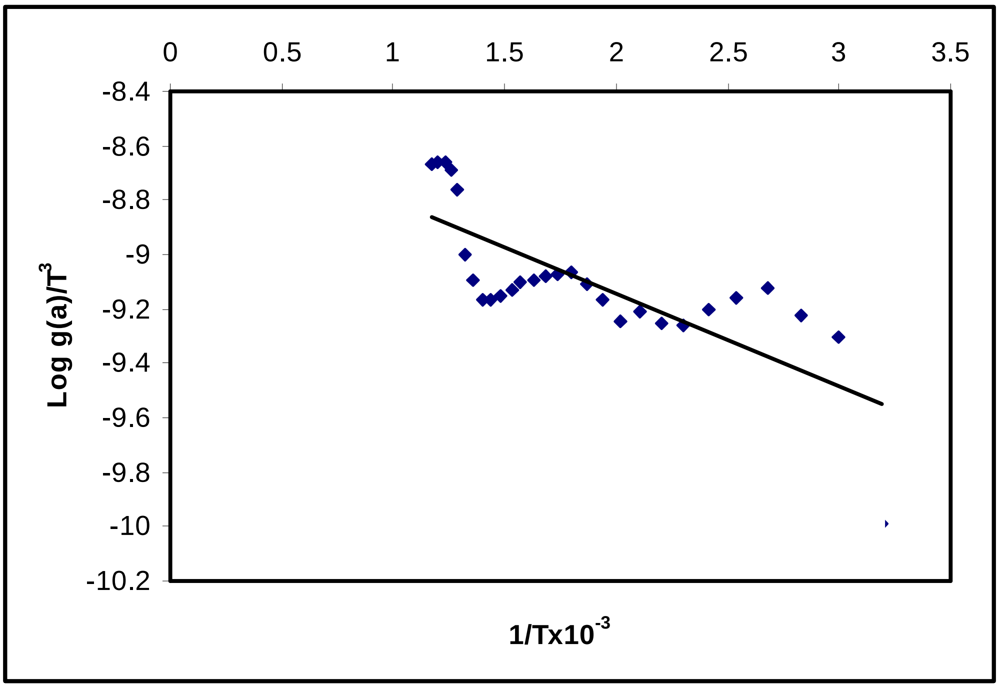


Fig. 3: Freeman-Carroll plot of 2, 2'-HBDF-I copolymer

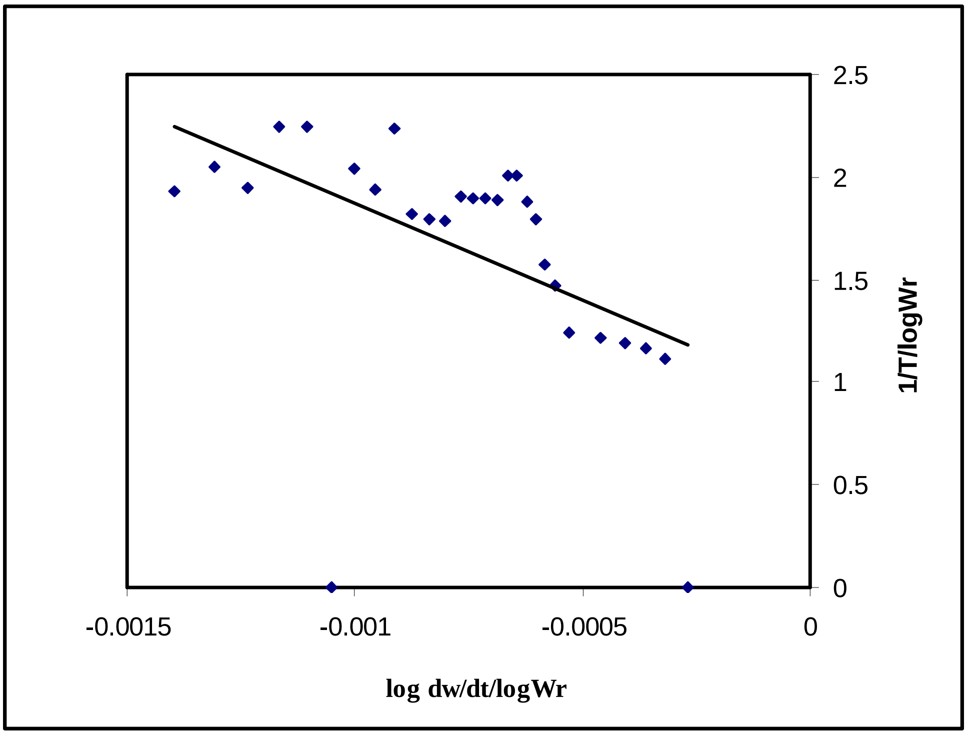


Fig. 4: Thermal activation energy plot of 2, 2'-HBDF-I copolymer

Thermodynamic parameters such as entropy change (*ΔS*), frequency factor (*z*), apparent entropy change (*S**) calculated on the basis of thermal activation energy (*Ea*) using equations (3), (4), (5). These values are given in (Table 1).

Table 1Kinetic Parameters of 2, 2' – HBDF-I copolymers

Copolymer	Entropy change	Free energy change	Frequency factor	Apparent entropy change	Order of reaction
	ΔS(J)	**ΔF(KJ)**	**$Z(s^{-1})$**	**S* (KJ)**	**n**
2, 2'-HBDF -I	-8.4675	13.872	26	-26.42	0.92

The abnormally low value of frequency factor, it may be concluded that decomposition reaction of 2, 2'-HBDF copolymer can be classed as a 'slow' reaction. There is no other obvious reason [24-26]. Fairly good straight-line plots are obtained using the two methods. This is expected since the decomposition of copolymer is known not to obey first order kinetic perfectly [27].

Antimicrobial Screening

The microbial screening results of 2, 2'-HBDF copolymer ligand show (Table 2) higher activity is due to the donor atoms of the ligand and the π-electrons delocalization. This effect increases the lipophilic character, which favours the permeation through the lipoid layer of the bacterial and fungal membranes [16]. The higher activity may also be due to the presence of - OH and the aromatic ring [28]. It is perceived that the factors such as solubility, conductivity, dipole moment and cell permeability mechanism may be alternative reasons for the increased activity of the metal complexes [29]. The ligand has good inhibition against the growth of Gram-negative bacteria which induces tumour. Hence the copolymer ligand may possess antitumor activity. The Gram-positive bacteria are both pathogenic and invasive. The copolymer has good inhibition characteristics against the growth of this pathogen. *Aspergillus niger* cause aspergillosis, the growth of the fungus is controlled by the copolymer chelates to some extent. The *Candida albicans* can penetrate into the intestinal walls and cause diseases. From the findings, the growth of *Candida albicans* is inhibited by the addition of 2, 2'-HBDF copolymer resin.

Table 2. Antimicrobial activities of 2, 2'-HBDF copolymer resin

Copolymer	Diameter of zone of inhibition (mm)			
	S. Aureus	***E. Coli***	***A. Niger***	***C. Albicans***
2, 2'-HBDF-1	14	15	16	14
Solvent (DMSO)	--	--	--	--

CONCLUSION

1) The 2, 2'-HBDF-I copolymer based on the condensation polymerization of o-aminophenol and urea with formaldehyde in the presence of acid catalyst has been prepared.

2) In TG the energy of activation evaluated from the Freeman-Carroll and Sharp-Wentworth methods are found to be nearly equal and the thermodynamic parameters obtained from Freeman-Carroll method are found to similar, indicating the common reaction mode.

3) Low values of frequency factor (Z) may be concluded that the decomposition reaction of 2, 2'-dihydroxybiphenyl-dithiooxamide-formaldehyde copolymer can be classified as 'slow reaction'.

Acknowledgements
The authors gratefully acknowledge financial supports from the University Grant Commissions, New Delhi.

Abbreviation
2, 2'-HBDF = 2, 2'-dihydroxybiphenyl-dithiooxamide-formaldehyde
FC= Freeman-Carroll
SW=Sharp-Wentworth
TGA= Thermogravimetric Analysis
TG= Thermogravimetric

REFERENCES

[1] R. N. Singru, A. B. Zade, W. B. Gurnule, *Iran. Polym. J.*, **2010**, 19 (3), 169.
[2] M. V. Tarase, A. B. Zade, W. B. Gurnule , *J. Ultra. Sci.*, **2007**, 3, 41.
[3] W. B. Gurnule, H. D. Juneja, , L. J. Paliwal, *Orient. J. Chem.*, **1999**, 15, 283.
[4] R. Patel, K. Patel, *J. Ind. Chem. Soc.*, **1984**, 54.
[5] S. Zeman, L. A. Tokarova, *Thermochim. Acta.*, **1992**, 712, 181.
[6] D. K. Rath , P. L. Nayak, S. Lenka, *J. Appl. Polym.Sci.*, **1994**, 52, 1679.
[7] U. K. Samal, P. L. Nayak, S. Lenka, *J. Appl. Polym. Sci.*, **1993**, 47, 1315.
[8] Zhao Hong, Wang Yu-Zhang, Wang Xui-Li and Yang Ke-Ke, *Polym. Deg. Stab.*, **2002**, 80, 135.
[9] W. B. Gurnule, H. D. Juneja, L. J. Paliwal, R. B. Kharat, *J. Appl. Polym Sci.*, **2003**, 89, 886.
[10] W. B. Gurnule, H. D. Juneja, L. J. Paliwal, *React. Funct. Polym.*, **2003**, 55, 255.
[11] R. N. Singru, A. B. Zade, W. B. Gurnule, *J. Appl. Polym. Sci.*, **2008**, 109, 859.
[12] P. E. P. Michel, J. N. Barbe, H. D. Juneja, L. J. Paliwal, *Europ. Polym. J.*, **2007**, 43, 4995.
[13] P. E. P. Michael, P. S. Lingala, H. D. Juneja, L. J. Paliwal, *App. Polym. Sc.*, **2004**, 92, 2278.
[14] M. B. Patel, S. A. Patel, A. Ray, R. M. Patel, *J. Appl. Polym. Sci.*, **2003**, 89, 895.
[15] B. A. Shah, A. V. Shah, R. R. Bhatt, *Iran. Polym. J.*, **2007**, 16 (3), 173.
[16] M. M. Patel, M. A. Kapadia, G. P. Patel, J. D. Joshi, *J. Appl. Polym. Sci.*, **2007**,106 (2), 1307.
[17] D. T. Masram, K. P. Karia, N. S. Bhave, Arch. Appl. Sci. Res., **2010**, 2(2), 153.
[18] W. B. Gurnule, D. B. Patle, *Arch. Appl. Sci. Res.*, **2010**, 2(1), 161.
[19] P. K. Rahangdale, W. B. Gurnule, H. D. Juneja, L. J. Paliwal, *Synth. React. Inorg. Met. Org. Chem.*, **2003**, 33, 1187.
[20] A. I. Vogal, *Textbook of Practical Organic Chemistry, Longman Scientific and Technical, UK*, **1989**.
[21] W. Kemp, *Organic Spectroscopy, Macmillan, Hong Kong*, **1975**.
[22] Jang Bok Nam, Costache Marious, A. Charles, *Polymer*, **2005**, 46, 10678.
[23] J. M. Criado, P. E. Sanchez-Jimenez, L. A. Perez-Maqueda, *J. Them. Anal. Cal.*, 2008, 92, 199.
[24] H. Chen, N. Liu, W. Fang, *Polym. Degrad. Stab.*, **2006**, 91, 1726.
[25] T. Vlase, G. Vlase, N. Birta, N. Doca, *J. Therm. Anal. Cal.*, **2007**, 88, 631.
[26] A. Khawam, D. R. Flanagan, *Thermichim. Acta.*, **2005**, 429, 93.
[27] A. A. Joraid, *Themochim. Acta.*, **2007**, 456, 1.
[28] N. Singh, S. Gupta, G. Nath, *Central National De La Recherche Scientifique (CAT. INIST)*, **2000**, 14, 484.
[29] G. B. Bagihalli, S. A. Patil, P. S. Badami, *J. Iran. Chem. Soc.*, **2009**, 6 (2), 259.