Non Isothermal Kinetic Study of Some Novel Coordination Polymers

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ABSTRACT

Thermal decomposition behaviour of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) coordination polymers with glutaryl-bis nicotinamide (GBNA) has been investigated by thermogravimetric analysis (TGA) at different (5 ^{0}C, 10 ^{0}C ,15 ^{0}C min^{-1}) heating rates. The thermogravimetric analysis of these coordination polymers has been carried out by dynamic or non-isothermal thermogravimetric analysis technique. The decomposition temperature of all the coordination polymers was determined by half decomposition temperature curve technique. The Freeman-Carroll, Sharp-Wentworth and Broido methods have been used in the present investigation to calculate thermal activation energy and different thermodynamic parameters of the coordination polymers. By using data of thermogravimetric analysis, various thermodynamic parameters like frequency factor (Z), entropy change (ΔS), free energy change (ΔF) and apparent entropy (S*) have been determined using Freeman-Carroll method. The novelty of this study is that the coordination polymers under study have thermal stability at elevated temperature so they can be used as powder coating materials.. Scanning electron microscope images of some coordination polymers were revealed that particle sizes of coordination polymers were of nanomaterial level therefore, resulting coordination polymers might be called as nanomaterial.

Keywords: Coordination polymers, Thermal studies, Kinetic parameters, Glutaryl-bis nicotinamide.

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INTRODUCTION

Coordination polymers present a tempting perspective in the aspects of selective catalysis, molecular recognition, enantiomer split, nonlinear optic materials, magnetic materials and superconducting materials [1-3]. Coordination polymers with good thermal stability have enhanced the development of polymeric materials. Recently, great efforts have been taken for the synthesis and investigation of new thermally stable polymeric materials, as such materials have found wide applications in number of areas like coating, photo resist, laminate, thermal properties and electrically conductive [4]. Literature survey revealed that, in recent years, many transition metal coordination polymers by using transition metal ions and various bidentate ligands have been synthesized and investigated. The thermal degradation pattern and kinetic parameters study of a series of coordination polymers $\{[M(BDC)(azoles)(H_2O)_m].xH_2O\}_n$ (where M = Co(II), Ni(II), and Cu(II); BDC = 1,4-benzenedicarboxylate; azoles = 2aminobenzothiazole, 2-aminothiazole, and 2-amino-4-methyl-thiazole) has been reported [5]. A novel zinc (II) coordination polymer, $[(pipzH_2)[Zn(pyzdc)_2].6H_2O]_n$ (H_2pyzdc and pipz are pyrazine-2,3- dicarboxylic acid and piperazine respectively), has been synthesized for exhibiting good thermal stability [6]. Coordination polymers of first transition series metal ions of a novel bis(oxine) bidentate ligand N,N'-di(8-hydroxyquinolinolyl-5-methyl)-N,N'-diethyl-1,3-propane diamine (QEPD) have been synthesized and characterized by magnetic susceptibilities, elemental, spectral and thermal analysis [7]. The thermal stabilities and kinetic parameters studies of coordination polymers of pimeloyl bis-2-aminobenzothiazole with transition metal ions have been reported [8]. The thermal degradation pattern and spectroscopic studies of four novel mixed-ligand complexes of Co(II), Ni(II), Cu(II) and Zn(II) with m-hydroxybenzoate(m-Hba) and N,N-diethylnicotinamide (Dena) have been reported [9]. Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) polymers with terphthaoyl-bis(p-methoxyphenylcarbamide) have been synthesized and characterized. The thermal degradation behaviour of these polymers has been investigated by thermogravimetry (TG), method. These coordination polymers were coloured, insoluble in almost all organic solvents and were found to be thermally stable [10]. Polymers containing metallic elements offer a wider range of novel characteristics and provide potential access to new processible functional polymeric materials and thus, study on the synthesis and prospective applications of metallopolymers have become an area of interest to polymer chemists. As a part of research on chemistry of transition metal coordination polymers the present work deals with the thermal and kinetic parameters studies of coordination polymers of ligand glutaryl bis-nicotinamide (GBNA) with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) metal ions. The ligand type attachment around transition metal ion was found identical in all the coordination polymers, while, the difference was observed in their thermal decomposition pattern.

EXPERIMENTAL

Synthesis of ligand and coordination polymers

Ligand, i.e. GBNA was synthesized and published elsewhere [11]. The coordination polymers (Fig.1) were synthesized by condensation method [12, 13]. Coordination polymers were characterized by elemental analysis, IR spectroscopy, XRD technique, electronic spectral and magnetic moment studies to assign the geometry of coordination polymers.

SEM images revealed nanomaterial characteristic for some coordination polymer compounds.

Thermal studies of coordination polymers

The thermogravimetric analysis (TG) was carried out in range at room temperature to 1,200 ^{0}C on Perkin Elmer, Diamond TG/DTA Analyzer in SAIF Cochin University, Kerala, in air atmosphere at three different heating rates (5 ^{0}C, 10 ^{0}C and 15 ^{0}C min^{-1}). The thermal stabilities of coordination polymers were evaluated by dynamic or non isothermal thermogravimetric analysis in which sample is subjected to condition of continuous increase in temperature at linear rate to determine their mode of decomposition and relative thermal stabilities. The Freeman-Carroll [14], Sharp-Wentworth [15] and Broido [16] methods have been used in the present investigation to calculate thermal activation energy and different thermodynamic parameters of the coordination polymers. It was observed that the sequence of degradation that takes place in coordination polymers started with lattice water, further it was followed by coordinated water and finally fragment of organic moieties (i.e. bis(bidentate) ligand) attached to metal ion. The thermal decomposition data of all the coordination polymers at 5, 10 and 15 ^{0}C min^{-1} has been given in Table **1**. The data obtained by thermal analysis was in good agreement with the elemental and IR analysis and also clearly support proposed structure of metal coordination polymers. The decomposition temperatures of polymers were determined by half decomposition curve technique. 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 thermodynamic parameters like frequency factor (Z), entropy change (ΔS), free energy change (ΔF) and apparent entropy (S*) have been determined using Freeman-Carroll method.

Table 1. Thermal decomposition data of coordination polymers at 5, 10 and 15 ^{0}C min^{-1}

Coordination polymers	% loss due to lattice water			% loss due to co-ordinated water			Decomposition Temp. (^{0}C)		
	5^{0}C	10^{0}C	15^{0}C	5^{0}C	10^{0}C	15^{0}C	5^{0}C	10^{0}C	15^{0}C
{[Mn(II)(GBNA)(H$_2$O)$_2$]H$_2$O}$_n$	4.2	4.1	4.7	8.4	8.4	8.3	415	405	415
{[Co(II)(GBNA)(H$_2$O)$_2$]H$_2$O}$_n$	4.1	4.1	4.4	7.4	7.9	7.4	425	415	425
{[Ni(II)(GBNA)(H$_2$O)$_2$]H$_2$O}$_n$	4.3	4.1	4.4	7.9	7.8	7.6	455	445	445
{[Cu(II)(GBNA)(H$_2$O)$_2$]H$_2$O}$_n$	4.5	4.4	4.4	7.3	7.9	7.6	395	385	375
{[Zn(II)(GBNA)]H$_2$O}$_n$	4.7	4.2	4.1	-	-	-	435	425	435

Freeman–Carroll method

In this method, the following expression was used to evaluate various kinetic parameters:

$$\frac{\Delta \log dW/dt}{\Delta \log Wr} = (-Ea/2.303R) \ \frac{\Delta(1/T)}{\Delta \log Wr} + n \tag{1}$$

where dW/dt is the rate of change of weight with time, Wr = Wc - W, where Wc is the weight loss at completion of reaction and W is fraction of weight loss at time t, T is temperature, R is gas constant, and n is the order of reaction.

Hence, by plotting

$$\frac{\Delta \log dW/dt}{\Delta \log Wr} \quad \text{versus} \quad \frac{\Delta(1/T)}{\Delta \log Wr}$$

n was obtained as an intercept on former axis and Ea is the slope of the line. The change in entropy (ΔS), frequency factor (z), apparent entropy (S*) can also be calculated by further calculations.

i) Entropy change

Intercept = log(KR/hØE) + ΔS/2.303R

$$\therefore \text{ Intercept} = \log(R^2/ \text{NhØE}) + \Delta S/2.303R \tag{2}$$

Where constant

$N = 6.023 \times 10^{23}$
R = 8.314J/K.mol
$h = 6.625 \times 10^{-34}$ J.sec
Ø = 0.166
ΔS = change in entropy
E = Activation energy from graph

ii) Free energy change
$$\Delta F = \Delta H - T\Delta S \tag{3}$$

ΔH = Enthalpy change = Activation Energy
ΔS = Entropy change (from (i) used)
T = Temperature in K (at the start of reaction)

iii) Frequency Factor

$$B_n = [\log Z \times Ea] / R\Phi] \tag{4}$$
$$B_n = \log \ln (1/ (1-\alpha) \times \log p(x) \tag{5}$$

Z = Frequency factor
B = Calculated from equation (5)

Log p(x) = calculated from Doyel's table corresponding to activation energy.

iv) Apparent entropy change

$$S* = 2.303 \log (Zh/KT*) \tag{6}$$

Z = from relation (4)
T* = Temperature at which half of coordination polymer decomposes from its total loss.

Sharp–Wentworth method

The following expression was used to evaluate activation energy:

$$\log\left?\frac{dC/dT}{1-C}\right? = \log(A/?) - (Ea/2.303R) \times 1/T \qquad (7)$$

where ? is the linear heating rate, dT/dt. Therefore, a linear plot of

$$\log\left?\frac{dC/dT}{1-C}\right? \text{ versus } 1/T$$

was obtained whose slope gives the value of Ea.

Broido method

This is a simple and sensitive graphical method of treating TGA data. The following equation was used to evaluate activation energy:

$$\ln\left?\ln\frac{1}{y}\right? = \frac{-Ea}{R}\ \frac{1}{T} + \left?\frac{R}{Ea}\ \frac{A}{\beta}\ T^2 \max\right? \qquad (8)$$

Where, y is fraction of initial molecules not yet decomposed, $y = (w_t - w_\alpha) / (w_o - w_\alpha)$, w_o is the initial weight of the material and w_α is the weight of the residue at the end of the degradation. T_{max} is the temperature of maximum reaction velocity. A plot of $\ln(\ln 1/y)$ versus 1/T yields a straight line. The slope is equal $-E/2.303R$.

Surface morphology

The surface morphology of metal coordination polymers was investigated by scanning electron microscopy. SEM images were recorded at energy of 20 kV with magnification X 10,000. The micrograph of ligand (Figure 2) is totally different from the micrograph of metal coordination polymers (Figure 3); hence it is the evidence of formation of new product. The micrograph of ligand at 1µm found to be irregular shaped gravels of rock like structure while the micrograph of Cu-coordination polymer at 1µm shows fine sharp needle shape structure having diameter size 335.26nm, 252.98nm and 156.20nm which appeared like the bundle of needles generated from a particular point. It was remarkably noted that each needle does vary in diameter and length. The significant differences in morphology behaviour of ligand and coordination polymers signify the formation of polymers.
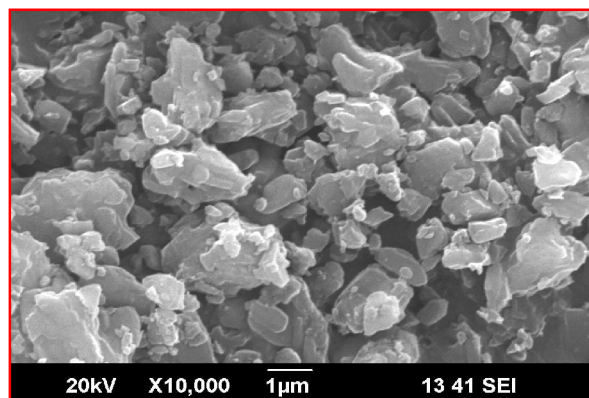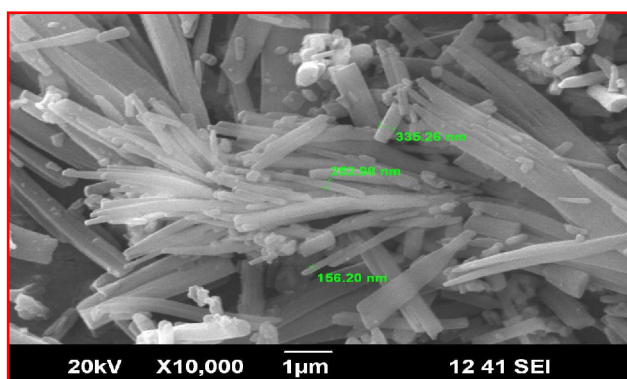
Fig. 2. SEM image of GBNA ligand

Fig. 3. SEM image of Cu(II) coordination polymer

RESULTS AND DISCUSSION

The ligand and its coordination polymers were synthesized and characterized by elemental analysis, IR spectroscopy and ^{1}H NMR studies and published elsewhere [11]. The presences of lattice and coordinated water in coordination polymers were determined on the basis of elemental analysis, thermal and infrared spectroscopy. The proposed molecular structure (Figure 1) of resulting coordination polymers has been deduced by spectral, elemental, electronic, magnetic susceptibility measurement, XRD and thermal analysis. The surface morphology studies point towards the polymer formation. The thermal degradation behaviour of all coordination polymers were keenly interpreted and discussed. The newly synthesized coordination polymers were found to be highly thermally stable as compared with their bis(bidentate) ligand. The high thermal stability of metal coordination polymers were due to its chelating effects which are formed by heterocyclic ring formation. The aromatic or heterocyclic rings as backbone in metal coordination compounds greatly enhance the thermal stability of coordination polymers [17, 18].
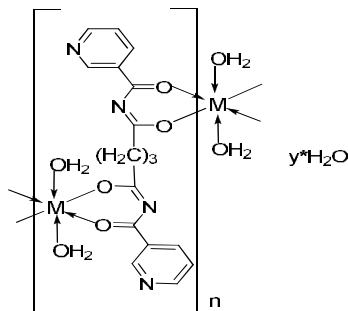
Fig 1. Proposed Structure for GBNA Coordination Polymers

M = metal ion, Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). y* H_2O ——lattice water.
*H_2O is present in all the coordination polymers and coordinated H_2O is absent in Zn(II) polymer. y = 1 for all coordination polymers.

The evaluation of thermogravimetric data revealed that after the loss of lattice or coordinated water molecules, the coordinated polymers gradually degrades, the first step of degradation was found to be fast as compared to second step of degradation. This may be due to the fact that non-coordinated part of ligand decomposed first, while actually coordinated part decomposed later [19]. The degradation process continues till the formation of stable metal oxide. The thermal decomposition data of all the coordination polymers at different heating rates (5^0C min^{-1}, 10^0C min^{-1} and $15\ ^0$C min^{-1}) has been given in Table 1. This data clearly specify that the order of thermal stability of all the coordination polymers remain same in different heating rates. The decomposition temperatures of nickel and zinc coordination polymers were found to be higher than cobalt, manganese and copper coordination polymers. The coordination polymers slowly degrade with three major steps of decomposition. First step shows loss of lattice water, second step was loss of coordinated water and third was due to loss of ligand attached to metal ion. The presence of lattice water and coordinated water is also confirmed by elemental analysis and infrared spectral studies. In FTIR spectra band appeared at range of 3404.8– 3568.7 cm^{-1} may be due to lattice water and a range of 819.5–822.1 cm^{-1} may be due to coordinated water [20, 21]. The representative TG curves of {[Ni(II)(GBNA)(H_2O)$_2$]H_2O}$_n$ at heating rates 5^0C min^{-1}, $10\ ^0$C min^{-1} and 15^0C min^{-1} have been shown in Figure 4-6. The thermograms of{[Ni(II)(GBNA)(H_2O)$_2$]H_2O}$_n$ at heating rates 5^0C min^{-1}, $10\ ^0$C min^{-1} and 15^0C min^{-1} shows mass loss upto 135 ^{0}C due to loss of one lattice water molecule. The thermograms later shows mass loss upto 235 ^{0}C at 5^0C min^{-1} and $10\ ^0$C min^{-1} and mass loss upto 255^{0}C at 15^0C min^{-1} heating rate which may be due to the loss of two coordinated water molecules. Then a gradual mass loss was observed in the region of 700 ^{0}C due to the decomposition of ligand attached to the metal ion. Further, it was supported by elemental analysis (C, obs. 45.11, cal. 45.07, H, obs. 4.92, cal. 4.89, N, obs. 12.39, cal. 12.36) and IR value at 822.1cm^{-1} which may be due to the coordinated water (H-O-H). The peak at 3520.6 cm^{-1} in the IR spectra of Ni(II) GBNA coordination polymer indicate presence of lattice water. Thermodynamic parameters have been calculated on the basis of thermal activation energy data at different heating rates have been tabulated in Tables **2**, **3**, and **4**. From the given data, it can be observed that the energy of activation evaluated from the Freeman-Carroll, Sharp-Wentworth method and Broido method were found to be nearly equal and the thermodynamic parameters obtained from Freeman-Carroll method were found to be

similar, indicating the common reaction mode [22-24]. In order to economize the space only representative thermal activation energy plots of Sharp-Wentworth (Figure 7), Freeman-Carroll (Figure 8-9) and Broido (Figure 10) method for the $\{[Ni(II)(GBNA)(H_2O)_2]H_2O\}_n$ coordination polymer at heating rate 15^0C min^{-1} has been shown. The linear relationship confirmed that assumed order (n = 1) was correct. Fairly straight line plots were obtained using the three methods. However, it was observed that all the points did not fall on the straight line. These types of deviation of points is expected, since, the decomposition of all the coordination polymers of glutaryl bis-nicotinamide ligand(GBNA) with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) is not obeying the first order kinetics perfectly [25, 26]. The negative values of ΔS and S* for the decomposition stages indicate that the activated polymer has more ordered structure than the reactants and the reactions are slower than normal [27]. This is further supported by low Z values. From abnormally low values of frequency factor (Z), it may be concluded that the decomposition reaction of coordination polymers can be classed as a slow reaction [28]. There seems to be no other obvious reason. The end products obtained by the thermal studies and classical oxide method were found to be nearly same [29-30].

Table 2. Kinetic Parameters of GBNA Coordination Polymers

(Heating rate = 5 ^{0}C min^{-1})

Coordination polymers	Activation energy (Ea)/ kJ mo^{-1}			Entropy change Δ(S)/J	Free energy Change Δ(F)/kJ	Frequency factor (Z)/S^{-1}	Apparent entropy change (S*)/KJ	Order of Reaction (n)
	SW	FC	BR					
$\{[Mn(II)(GBNA)(H_2O)_2]H_2O\}_n$	20.41	19.12	21.54	-222.90	136.81	557.33	-199.32	0.88
$\{[Co(II)(GBNA)(H_2O)_2]H_2O\}_n$	19.45	19.33	20.65	-225.55	142.94	571.94	-199.23	0.91
$\{[Ni(II)(GBNA)(H_2O)_2]H_2O\}_n$	22.76	19.66	23.37	-220.54	136.25	389.22	-202.78	0.94
$\{[Cu(II)(GBNA)(H_2O)_2]H_2O\}_n$	19.24	16.21	19.35	-224.59	134.80	308.15	-204.00	0.97
$\{[Zn(II)(GBNA)]H_2O\}_n$	17.27	16.57	17.73	-226.23	145.07	285.06	-205.14	1.05

(Keys: FC=Freeman-Carroll, SW=Sharp-Wentworth, BR=Broido)

**Table 3. Kinetic Parameters of GBNA Coordination Polymers**

(Heating rate = 10 ^{0}C min^{-1})

Coordination polymers	Activation energy (Ea)/ kJ mo^{-1}			Entropy change Δ(S)/J	Free energy Change Δ(F)/kJ	Frequency factor (Z)/S^{-1}	Apparent entropy change (S*)/KJ	Order of Reaction (n)
	SW	FC	BR					
$\{[Mn(II)(GBNA)(H_2O)_2]H_2O\}_n$	21.55	18.27	20.67	-222.44	140.16	403.26	-201.89	0.92
$\{[Co(II)(GBNA)(H_2O)_2]H_2O\}_n$	22.53	20.52	21.96	-224.17	143.37	799.88	-196.32	0.87
$\{[Ni(II)(GBNA)(H_2O)_2]H_2O\}_n$	20.10	19.24	22.03	-220.42	135.62	568.49	-199.51	1.03
$\{[Cu(II)(GBNA)(H_2O)_2]H_2O\}_n$	20.29	18.15	19.81	-221.74	130.80	422.50	-201.25	0.95
$\{[Zn(II)(GBNA)]H_2O\}_n$	18.66	16.79	20.56	-225.94	140.60	284.48	-205.03	1.02

Table 4. Kinetic Parameters of GBNA Coordination Polymers

(Heating rate = 15 ^{0}C min^{-1})

Coordination polymers	Activation energy (Ea)/ kJ mo^{-1}			Entropy change Δ(S)/J	Free energy Change Δ(F)/kJ	Frequency factor (Z)/S^{-1}	Apparent entropy change (S*)/KJ	Order of Reaction (n)
	SW	FC	BR					
{[Mn(II)(GBNA)(H$_2$O)$_2$]H$_2$O}$_n$	18.80	17.75	19.37	-221.74	139.26	408.17	-201.91	0.93
{[Co(II)(GBNA)(H$_2$O)$_2$]H$_2$O}$_n$	17.00	16.29	18.66	-227.79	136.54	301.45	-204.55	1.01
{[Ni(II)(GBNA)(H$_2$O)$_2$]H$_2$O}$_n$	22.03	19.79	22.17	-220.13	140.43	823.74	-196.43	0.90
{[Cu(II)(GBNA)(H$_2$O)$_2$]H$_2$O}$_n$	18.18	15.60	19.05	-222.79	137.69	311.76	-201.30	0.99
{[Zn(II)(GBNA)]H$_2$O}$_n$	17.38	16.55	19.77	-225.29	135.51	284.53	-205.15	1.05
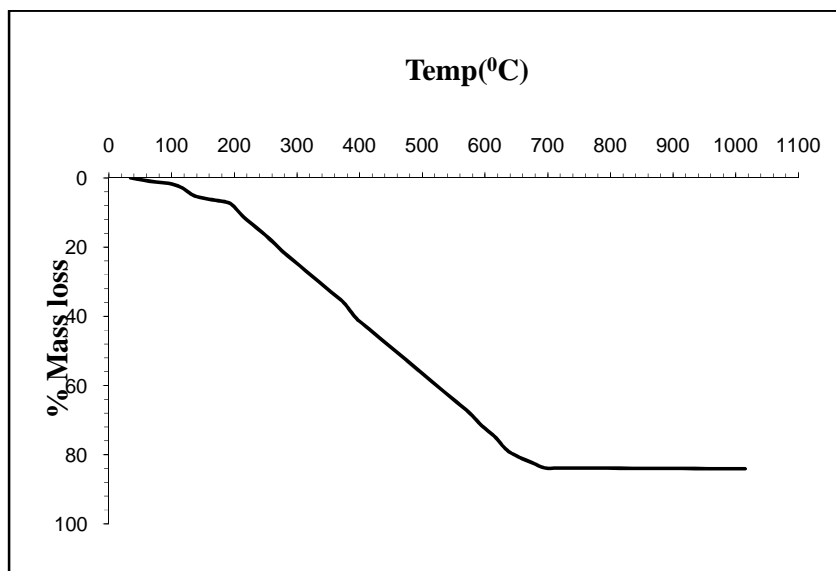
Fig. 4. Thermogram of {[Ni(II)(GBNA)(H$_2$O)$_2$]H$_2$O}$_n$ at heating rate 5^{0}C/min
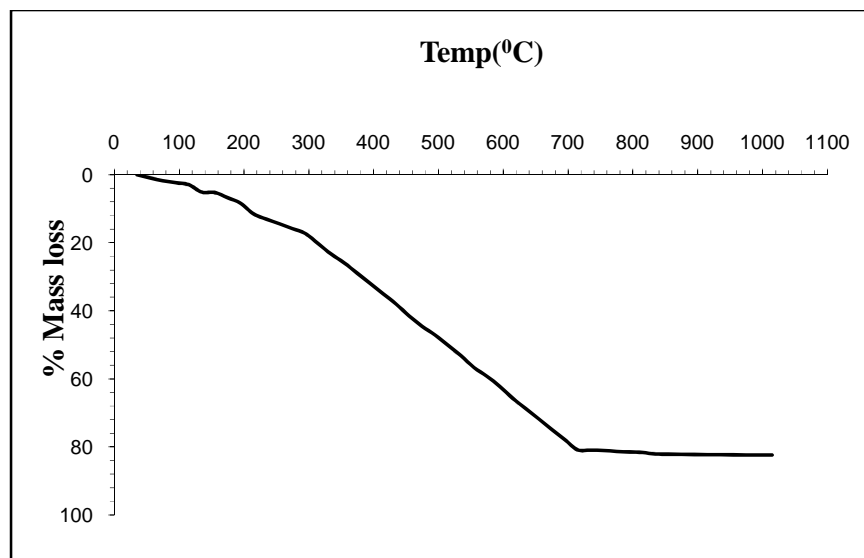
Fig. 5. Thermogram of {[Ni(II)(GBNA)(H$_2$O)$_2$]H$_2$O}$_n$ at heating rate 10^{0}C/min
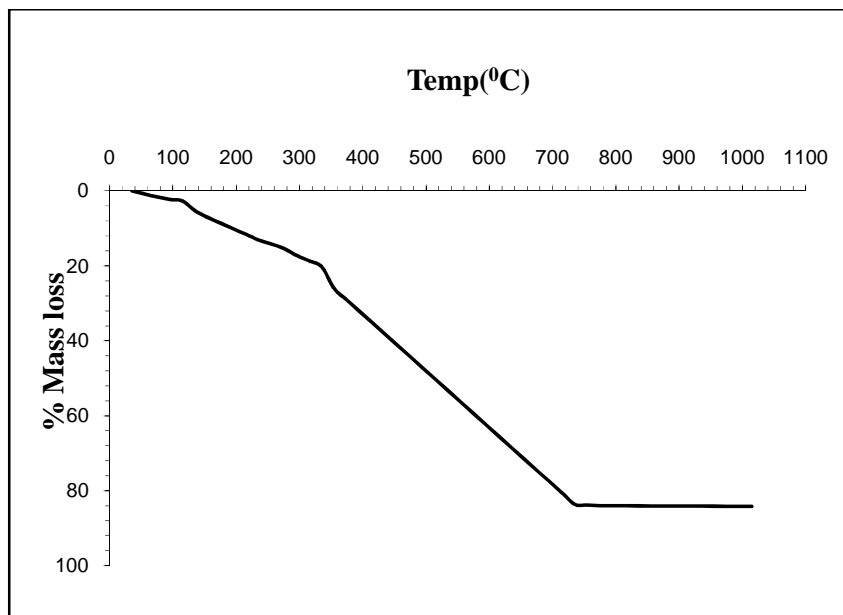
Fig. 6. Thermogram of {[Ni(II)(GBNA)(H$_2$O)$_2$]H$_2$O}$_n$ at heating rate 15^{0}C/min
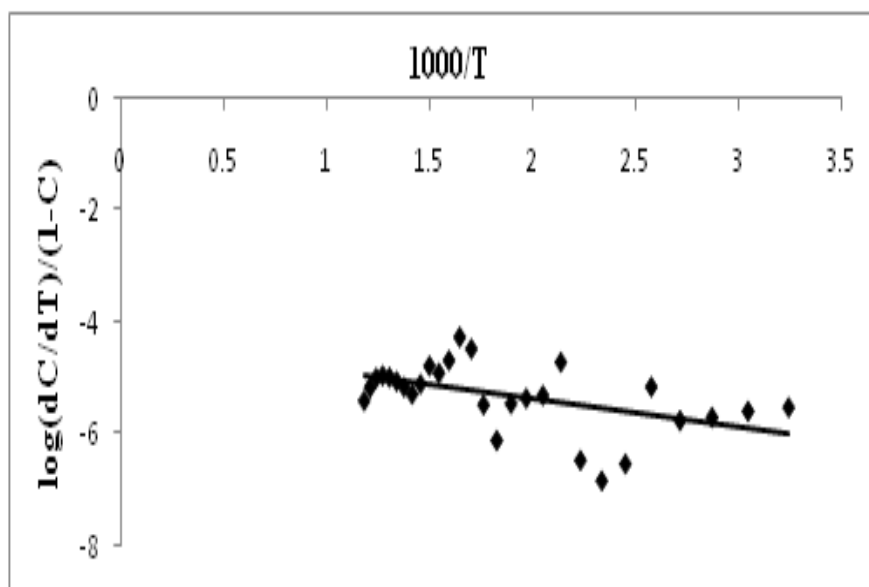
Fig. 7. Sharp-Wentworth plot for Activation Energy of {[Ni(II)(GBNA)(H$_2$O)$_2$]H$_2$O}$_n$ at heating rate 10^{0}C/min
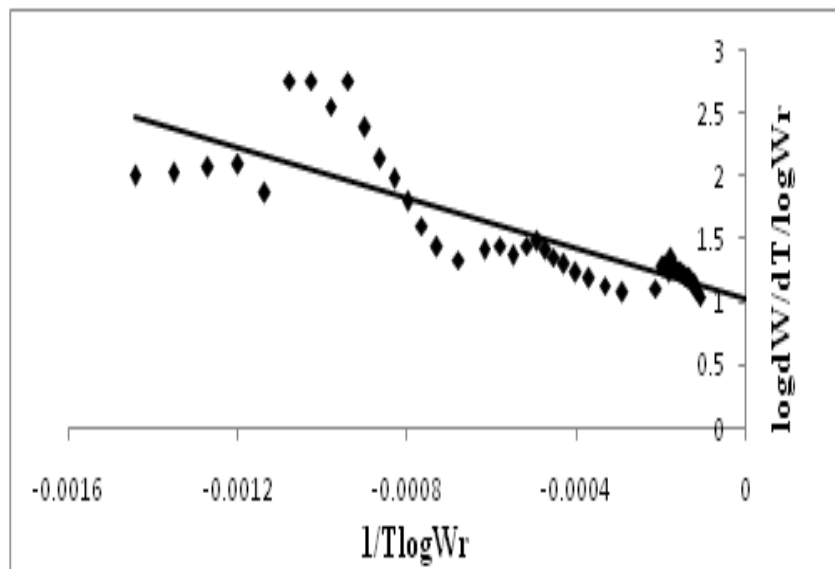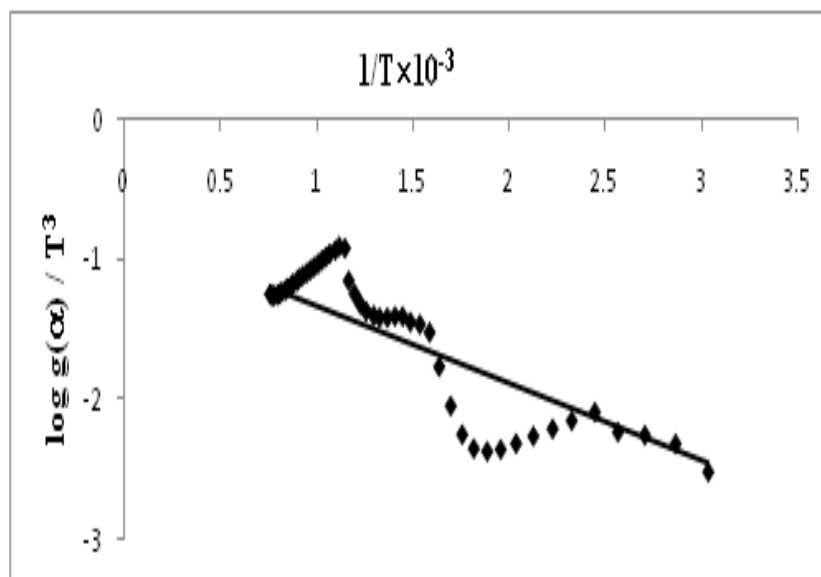
Fig. 8. Freeman Carroll plot 1 for Activation Energy of $\{[Ni(II)(GBNA)(H_2O)_2]H_2O\}_n$ at heating rate 10^0C/min

Fig. 9. Freeman-Carroll plot 2 for Activation Energy of $\{[Ni(II)(GBNA)(H_2O)_2]H_2O\}_n$ at heating rate 10^0C/min
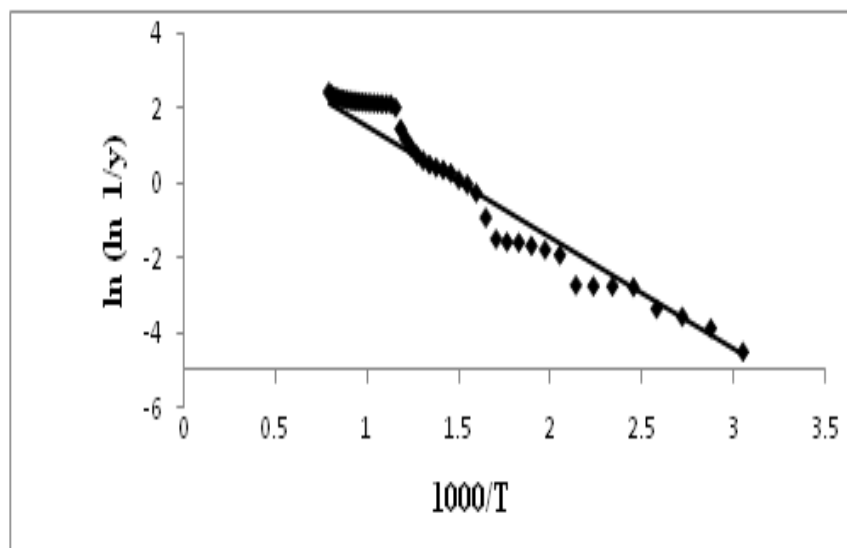
Fig. 10. Broido plot for Activation Energy of $\{[Ni(II)(GBNA)(H_2O)_2]H_2O\}_n$ at heating rate 10^0C/min

CONCLUSION

The newly synthesized coordination polymers were found to be thermally stable at elevated temperature. Significant difference in morphology behaviour supports polymer formation. The presence of lattice and coordinated water were confirmed by TG analysis which is supported by the CHN and IR spectroscopy studies. On the basis of decomposition temperature the thermal stability of coordination polymers follows the order Ni(II)> Zn(II)> Co(II)>Mn(II)> Cu(II). The values of activation energy calculated by Sharp-Wentworth, Freeman-Carroll and Broido methods were in good agreement with each other and the thermodynamic parameters obtained from Freeman-Carroll method were found to be similar, indicating the common reaction mode. The negative values of ΔS and S* for the decomposition stages indicate that the activated polymer has more ordered structure than the reactants. Low values of frequency factor (Z) may be concluded that the decomposition of all the coordination polymers can be classified as 'slow reaction'. Since these coordination polymers have high thermal stability and high insolubility they can be used as powder coating materials.

ACKNOWLEDGEMENTS

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