Part II
Thermoanalytical studies

Chapter 4

Nimmy Kuriakose “Physicochemical, thermoanalytical, electrochemical and antitumour studies of transition metal complexes of schiff bases derived from heterocyclic carbonyl compounds” Thesis. Department of Chemistry, St. Thomas College, University of Calicut, 2015

CHAPTER 4

THERMAL DECOMPOSITION KINETICS OF Ni(II) COMPLEXES OF T2YMABA, PHMT2YBA, CTHMT2YBA, CTHMF2YBA AND I3YT2YMAPA

Thermogravimetry and differential thermal analysis methods were carried out to study the thermal behavior of Ni(II) complexes of (E)-3-[thiophen-2-ylmethyleneamino] benzoic acid (T2YMABA), (E)-4-(5-[(2-phenylhydrazono)methyl) thiophen-2-yl]benzoic acid (PHMT2YBA), (E)-4-(5-[(2-carbamothioylhydrazono)methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA), (E)-4-(5-[(2-carbamothioyl hydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA) and 3-(1H-indol-3-yl)-2-[(E)-(thiophen-2-ylmethylidene)amino] propanoic acid (I3YT2YMAPA). These complexes were synthesized by refluxing the ligands with the metal acetate in ethanolic medium and were characterized by different techniques. The detailed procedures are given in Part I. The thermal behaviors of all these chelates are described in detail here using Coats-Redfern method and nine mechanistic equations. The thermodynamic and kinetic parameters like activation energy, change in entropy and Arrhenius frequency factor were calculated and the non-isothermal methods were employed for the evaluation of reaction mechanism as suggested by Satava.

Figures 2.5 to 2.9 represent the structures and instrumental TGA/DTA curves of Ni(II) complexes with five different ligands. The thermal decomposition data of these compounds are given in Tables 2.12 and 2.13.

The decomposition pattern of $[NiL^1Ac(H_2O)_3]$ (L^1= T2YMABA) comprises of two stages. The first stage represents the loss of all the three coordinated water molecules from the complex in the temperature range 117-243^{0}C The loss of ligand and acetate group is assigned in the second stage at 429^{0}C. The overall mass loss according to the TG

curve and the theoretical mass loss for the conversion of the complex into corresponding oxide are 81.15% and 81.34% respectively. The mass loss from pyrolysis is also found to be 81.41% which is in good agreement with the theoretical value.

The complex $[NiL^2{}_2Ac_2(H_2O)_2]$ (where L^2=PHMT2YBA) has two stages of decomposition reaction. The first one is due to the loss of two coordinated water molecules and two carboxyphenyl moieties of ligand from the complex. The second stage corresponds to the loss of two acetate groups and the rest of both ligands at around 401^0C. Overall mass loss from TG curve (91.62%) and the same from theoretical calculations (91.28%) are found to be in good agreement with the mass loss of 91.48% in pyrolytic studies.

The decomposition of Ni(II) complex of CTHMT2YBA, $[NiL^3{}_2(H_2O)_2]$ also resulted with a definite three stage pattern. The first stage ($65\text{-}130^0$C) is assigned to the loss of two water molecules. The second stage is further divided into three substages. In the first substage two COOH groups are lost. Then two NH_2 groups and two phenyl groups are removed in the second and third substages respectively. The third stage corresponds to the loss of rest of both the ligands at 364^0C. The percentage mass loss according to the TG curve is 88.89% which is in good agreement with the theoretical value (89.37%). The mass loss from the pyrolysis is found to be 88.19%.

Ni(II) complex of the ligand CTHMF2YBA, $[NiL^4{}_2(H_2O)_2]$ also underwent a three stage decomposition pattern. Loss of two water molecules are observed at $65\text{-}130^0$C in the initial stage. Here also as in the case of previous chelate, the second stage consists of three substages. Two COOH groups, two NH_2 molecules and two phenyl rings are lost at around 235^0C, 259^0C and 319^0C respectively in each of these substages. In the third

stage of decomposition the rest of both the ligands are lost. 88.12% mass loss is observed from the thermogravimetric curves. The theoretical and pyrolytic mass loss percentages are 88.85% and 87.67% respectively.

Thermogravimetric curves of $[NiL^5Ac(H_2O)_3]$ (where L^5= I3YT2YMAPA) gave a three stage decomposition pattern. The first stage comprises of two substages in the temperature range 60-120^{0}C and 120-305^{0}C. The first substage of the curve represents the loss of a water molecule from the chelate molecule, which confirmed the presence of coordinated water molecules in the complex. The remaining two water molecules and the acetate group are lost in the next substage. The second stage represents the loss of tryptophan moiety from the ligand. The removal of rest of the ligand is assigned in the third stage. The overall mass loss according to the TG curve is 84.20%. The theoretical mass loss for the conversion of the complex into metal oxide is 84.08%. The mass loss according to the pyrolytic data is also found to be 83.16%.

Kinetics of decomposition

The kinetic parameters such as energy of activation E, pre-exponential factor A and entropy of activation ΔS calculated for the various stages of decomposition of the complexes using mechanistic and non mechanistic kinetic equations are summarized in Tables 2.14 to 2.17. The mechanisms of decomposition of various stages as well as the order of reactions of all the various decomposition stages of the complexes are given in Tables 2.18 to 2.21.

In the decomposition of $[NiL^1Ac(H_2O)_3]$ and $[NiL^2{}_2Ac_2(H_2O)_2]$ complexes (where L^1= T2YMABA and L^2= PHMT2YBA), first order kinetics was found to be followed by all the decomposition stages. Since the parameters E, A and ΔS values obtained from the

Coats-Redfern method with n=1 are in close agreement with those obtained from the Mampel equation, it can be concluded that the rate controlling process of the reaction is random nucleation with the formation of one nucleus in each particle.

For the complex $[NiL^3{}_2(H_2O)_2]$ (L^3=CTHMT2YBA), first stage and the three substages of second stage decomposition process are assigned first order. For the last stage, R_3 mechanism and hence order of the reaction 2/3 can be assigned. In the case of $[NiL^4{}_2(H_2O)_2]$ complex, order 1/3 is suggested for the stage IIc in which two phenyl rings are lost and for all other stages first order kinetics is assigned.

In the case of thermal decomposition of the Ni(II) complex of 3-(1H-indol-3-yl)-2-[(E)-(thiophen-2-ylmethylidene)amino]propanoic acid (I3YT2YMAPA), i.e. $[NiL^5Ac(H_2O)_3]$ for the stages Ia, Ib and III, the kinetic parameters derived using the non mechanistic equation with n=1 are in good agreement with those values obtained from the equation V (Mampel equation) of mechanistic equations. Whereas for stage II, in which the tryptophan moiety is lost from the molecule, R_3 mechanism based on phase boundary reaction with spherical symmetry is assigned since the kinetic parameters of integral method matched with those obtained from equation IX. Hence the order would be 2/3 for this stage.

Initial decomposition temperatures, inflection temperatures, peak temperatures and the activation energy of decomposition reactions can be used to determine the thermal stability of the metal complexes. In the case of Ni(II) complexes, the relative thermal stabilities can be given as $[NiL^4{}_2(H_2O)_2] < [NiL^5Ac(H_2O)_3] < [NiL^3{}_2(H_2O)_2] < [NiL^1Ac(H_2O)_3] < [NiL^2{}_2Ac_2(H_2O)_2]$.

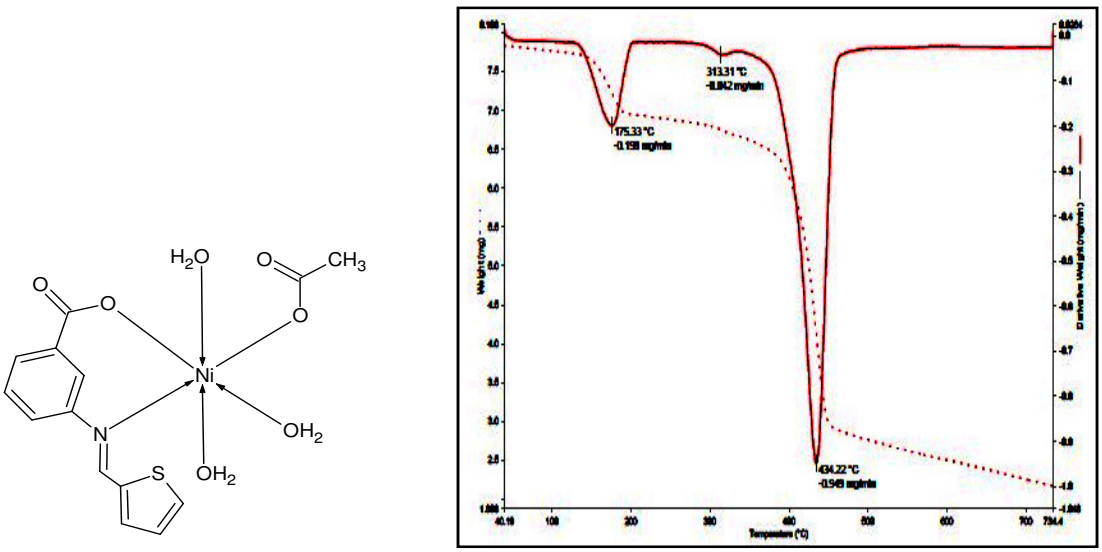

Fig. 2.5 Structure, TGA and DTA curves of $[NiL^{1}Ac(H_2O)_3]$

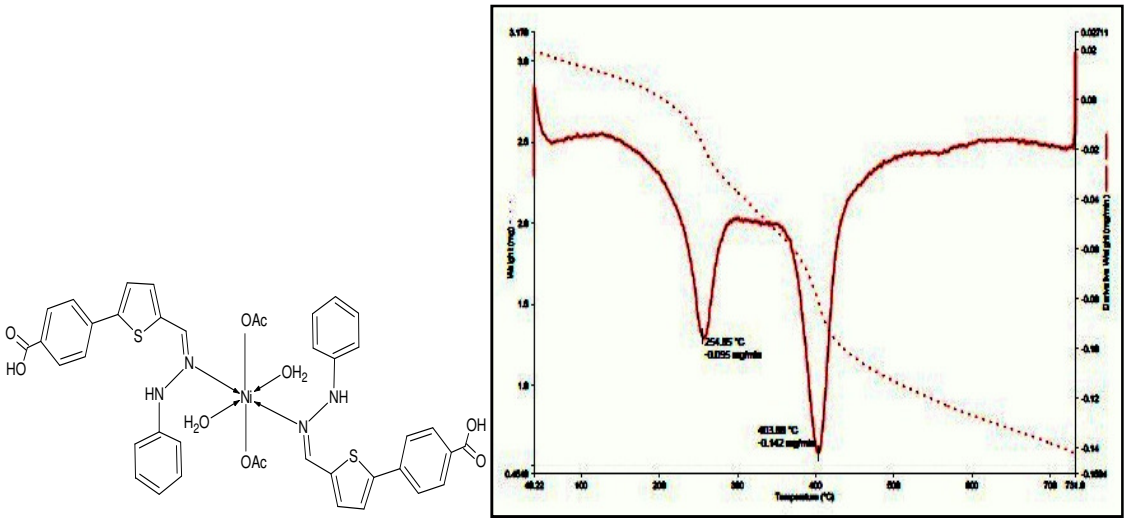

Fig. 2.6 Structure, TGA and DTA curves of $[NiL^{2}{}_2Ac_2(H_2O)_2]$

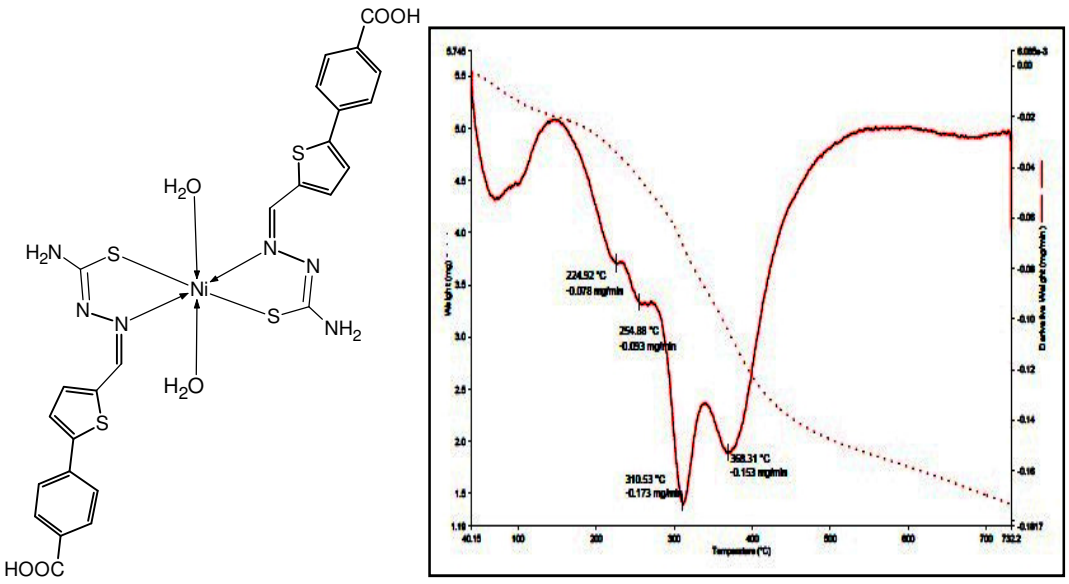

Fig. 2.7 Structure, TGA and DTA curves of $[NiL^{3}{}_{2}(H_2O)_2]$

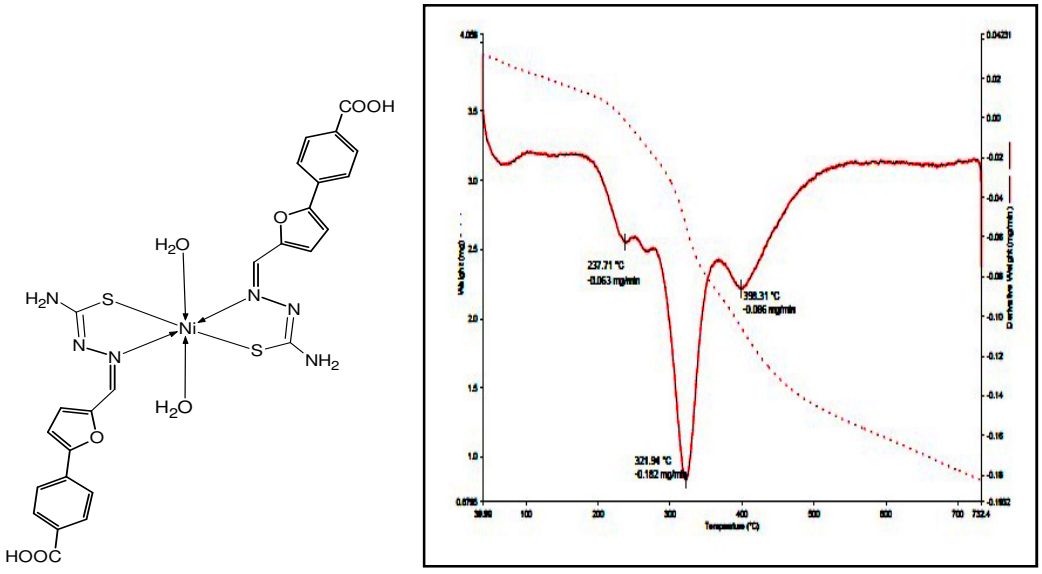

Fig. 2.8 Structure, TGA and DTA curves of $[NiL^{4}{}_{2}(H_2O)_2]$

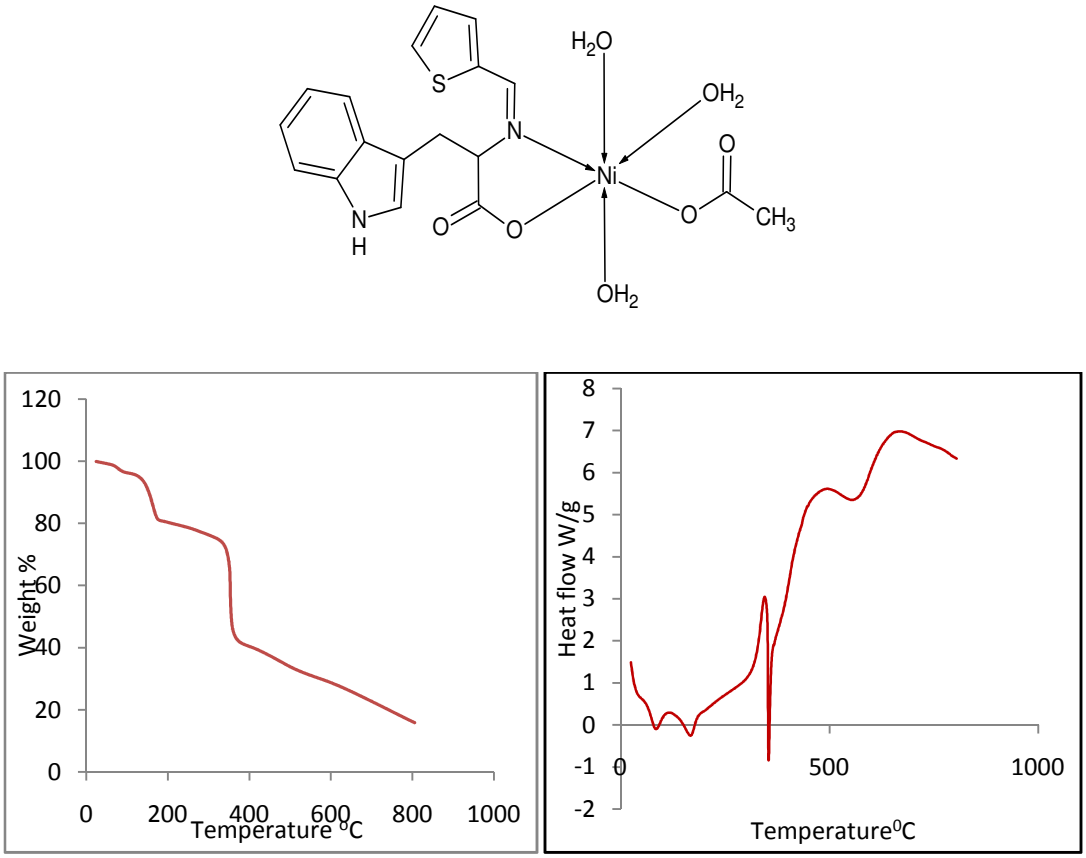

Fig. 2.9 Structure, TGA and DTA curves of $[NiL^5Ac(H_2O)_3]$

Table 2.12 Thermal decomposition data of Ni(II) complexes of (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA), (E)-4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid (PHMT2YBA) and (E)-4-(5-[(2-carbamothioylhydrazono)methyl] thiophen-2-yl)benzoic acid (CTHMT2YBA)

Complex	Stage	Temp range in TG (^{0}C)	Peak temp in TG (^{0}C)	Peak temp in DTA (^{0}C)	Loss of mass %			Probable assignment
					From TG	Cald.	From Pyrolysis	
$[NiL^1Ac(H_2O)_3]$	I	117-243	172	175	13.28	13.43	-	Loss of 3 H_2O
	II	243-734	429	434	67.87	67.91	-	Loss of ligand and acetate group
					81.15	81.34	81.41	
$[NiL^2{}_2Ac_2(H_2O)_2]$	I	70-342	253	255	33.10	32.44	-	Loss of two H_2O and two carboxyphenyl moieties of ligand
	II	373-734	401	404	58.52	58.84	-	Loss of 2 acetate groups and rest of both ligands
					91.62	91.28	91.48	
$[NiL^3{}_2(H_2O)_2]$	I	60-156	89	91	5.48	5.12	-	Loss of 2 H_2O
	IIa	156-237	221	225	12.92	12.80	-	Loss of 2 COOH groups
	IIb	237-276	252	255	4.04	4.55		Loss of 2 NH_2 groups
	IIc	276-338	309	311	20.91	20.05	-	Loss of 2 phenyl groups
	III	338-732	364	369	45.54	45.85	-	Loss of rest of both ligands
					88.89	89.37	88.19	

L^1 = T2YMABA, L^2= PHMT2YBA, L^3= CTHMT2YBA

Table 2.13 Thermal decomposition data of Ni(II) complexes of (E)-4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA) and 3-(1H-indol-3-yl)-2-[(E)-(thiophen-2-ylmethylidene)amino]propanoic acid (I3YT2YMAPA)

Complex	Stage	Temp range in TG (^{0}C)	Peak temp in TG (^{0}C)	Peak temp in DTA (^{0}C)	Loss of mass %			Probable assignment
					From TG	Cald.	From Pyrolysis	
$[NiL^4_2 (H_2O)_2]$	I	65-130	78	84	5.68	5.36	-	Loss of 2 H_2O
	IIa	130-245	235	238	13.11	13.41	-	Loss of 2 COOH groups
	IIb	245-278	259	262	4.82	4.76	-	Loss of two NH_2 molecules
	IIc	278-366	319	322	22.50	22.65	-	Loss of two phenyl rings
	III	366-732	396	399	42.01	42.67	-	Loss of rest of both ligands
					88.12	88.85	87.67	
$[NiL^5Ac (H_2O)_3]$	Ia	60-120	85	89	3.80	3.84	-	Loss of one H_2O
	Ib	120-305	165	168	20.08	20.26	-	Loss of one acetate group and two H_2O molecules
	II	305-412	355	359	36.92	37.10	-	Loss of tryptophan moiety
	III	412-800	559	564	23.40	23.45	-	Loss of rest of the ligand
					84.20	84.08	83.16	

L^4 = CTHMF2YBA, L^5= I3YT2YMAPA

Table 2.14 Kinetic parameters of the decomposition of Ni(II) complexes of (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA) and (E)-4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid (PHMT2YBA) from TG using mechanistic equations

Complex	Parameter*	Mechanistic equations								
		1	2	3	4	5	6	7	8	9
$[NiL^1Ac(H_2O)_3]$	E	129.62	141.08	158.70	146.67	86.21	39.38	23.77	71.25	75.62
	A	1.1×10^{12}	1.78×10^{13}	7.7×10^{14}	2.1×10^{13}	4.58×10^{7}	105.09	1.08	2.4×10^{5}	$6. \times 10^{5}$
Stage I	ΔS	-17.63	5.44	36.77	6.86	-101.58	-209.54	-247.55	-145.23	-137.47
	r	0.9007	0.9169	0.9398	0.9249	0.9565	0.9476	0.9360	0.9221	0.9338
Stage II	E	162.08	162.65	163.22	162.84	77.10	33.76	19.31	76.68	76.82
	A	1.49×10^{9}	8.5×10^{8}	2.16×10^{8}	1.97×10^{8}	808.60	0.3117	0.017	364.99	251.76
	ΔS	-76.42	-81.09	-92.49	-93.23	-196.36	-261.72	-285.86	-202.98	-206.07
	r	0.9287	0.9292	0.9298	0.9294	0.9221	0.9008	0.8706	0.9211	0.9214
$[NiL^2{}_2Ac_2(H_2O)_2]$	E	103.82	114.94	130.19	119.88	70.61	32.20	19.39	58.23	61.99
	A	7.26×10^{11}	1.84×10^{13}	8.5×10^{14}	2.31×10^{13}	4.5×10^{7}	113.28	1.20	2.72×10^{5}	6.9×10^{5}
Stage I	ΔS	-22.57	4.29	36.18	6.20	-103.12	-210.31	-248.07	-145.59	-137.75
	r	0.8811	0.9046	0.9303	0.9140	0.9445	0.9339	0.9205	0.9109	0.9237
Stage II	E	419.75	450.46	490.53	463.524	261.99	125.56	80.09	229.94	239.83
	A	4.4×10^{30}	8.02×10^{30}	3.82×10^{35}	2.2×10^{33}	3.6×10^{18}	3.7×10^{7}	6614.3	3.7×10^{15}	1.6×10^{16}
	ΔS	334.93	378.22	429.48	386.51	103.68	-106.72	-178.55	46.41	58.96
	r	0.9275	0.9406	0.9536	0.9454	0.9608	0.95749	0.9538	0.9455	0.9516

*E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$

Table 2.15 Kinetic parameters of the decomposition of Ni(II) complex of (E)-4-(5-[(2-carbamothioylhydrazono)methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA) from TG using mechanistic equations

Complex	Mechanistic equations									
	Parameter*	1	2	3	4	5	6	7	8	9
$[NiL^3{}_2(H_2O)_2]$ Stage I	E	60.84	68.89	80.49	72.62	43.79	18.75	10.40	34.24	37.10
	A	4.1×10^5	4.0×10^6	6.11×10^7	3.5×10^7	5097.26	0.8785	0.03599	71.465	140.4
	ΔS	-138.90	-119.95	-97.46	-121.16	-175.55	-247.59	-274.16	-211.03	-205.41
	r	0.8458	0.8778	0.9145	0.8912	0.9335	0.9112	0.8772	0.8814	0.9009
Stage IIa	E	170.50	182.54	198.23	187.66	103.911	48.07	29.45	91.36	95.23
	A	9.7×10^{15}	1.3×10^{17}	2.32×10^{18}	1.25×10^{17}	1.24×10^9	584.4*	3.60	1.8×10^7	3.6×10^7
	ΔS	56.94	78.97	102.49	78.22	-75.015	-196.14	-238.45	-110.09	-104.39
	r	0.8458	0.8778	0.9145	0.8912	0.9335	-0.9112	0.8772	0.8814	0.9009
Stage IIb	E	337.95	373.77	423.09	389.74	235.01	113.10	72.47	194.98	207.15
	A	8.03×10^{30}	1.9×10^{34}	4.8×10^{38}	1.8×10^{35}	1.56×10^{21}	9.05×10^8	61806.7	5.7×10^{16}	6.9×10^{17}
	ΔS	342.02	406.81	491.03	425.66	156.08	-78.15	-157.89	71.18	91.91
	r	0.8854	0.9078	0.9328	0.9169	0.9497	0.9459	0.9418	0.9186	0.9302
Stage IIc	E	247.91	276.44	317.05	289.52	177.05	83.71	52.59	143.69	153.7
	A	5.5×10^{19}	1.5×10^{22}	2.46×10^{25}	5.9×10^{22}	6.4×10^{13}	1.4×10^5	150.8	1.96×10^{10}	1.2×10^{11}
	ΔS	127.52	174.11	235.59	185.47	13.83	-151.78	-208.77	-53.44	-38.27
	r	0.8727	0.8985	0.9279	0.9092	0.9471	0.9413	0.9344	0.9098	0.9238
Stage III	E	254.16	281.93	321.12	294.57	177.59	83.39	51.99	145.48	155.15
	A	4.5×10^{17}	5.52×10^{19}	2.7×10^{22}	1.47×10^{20}	9.34×10^{11}	1.5×10^4	31.18	7.82×10^8	3.6×10^9
	ΔS	86.79	126.71	178.19	134.87	-22.06	-171.10	-222.62	-80.97	-68.28
	r	0.9726	0.9859	0.9961	0.9909	0.9944	0.9935	0.9923	0.9921	0.9957

*E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$

Table 2.16 Kinetic parameters of the decomposition of Ni(II) complex of (E)-4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA) from TG using mechanistic equations

		Mechanistic equations								
complex	Parameter*	1	2	3	4	5	6	7	8	9
$[NiL^4_2 (H_2O)_2]$ Stage I	E	91.51	101.62	115.56	106.14	62.59	28.23	16.78	51.28	54.71
	A	1.87×10^{10}	3.6×10^{11}	1.16×10^{13}	4.02×10^{11}	4.07×10^{6}	32.11	0.49489	32821.9	77198.2
	ΔS	-49.62	-25.04	3.83	-24.12	-119.72	-217.42	-252.11	-159.81	-152.699
	r	0.9007	0.9169	0.9398	0.9249	0.9565	0.9476	0.9361	0.9221	0.9338
Stage IIa	E	144.36	158.73	178.12	165.04	96.29	44.55	27.29	80.68	85.46
	A	5.20×10^{14}	1.95×10^{16}	1.41×10^{18}	2.85×10^{16}	2.3×10^{9}	827.27	4.66	1.0×10^{7}	2.8×10^{7}
	ΔS	32.39	62.539	98.09	65.67	-70.12	-193.49	-236.54	-115.24	-106.52
	r	0.90066	0.9169	0.9398	0.9249	0.9565	0.9476	0.9360	0.9221	0.9338
Stage IIb	E	425.48	467.89	525.78	486.65	141.03	141.03	91.05	244.15	258.42
	A	1.4×10^{39}	1.4×10^{43}	2.1×10^{48}	2.5×10^{44}	4.44×10^{11}	4.4×10^{11}	4.1×10^{6}	2.7×10^{21}	5.1×10^{22}
	ΔS	500.61	576.93	675.97	600.63	-26.37	-26.37	-122.66	161.1	185.38
	r	0.8957	0.9163	0.9387	0.9245	0.9538	0.9510	0.9479	0.9264	0.9367
Stage IIc	E	345.47	372.83	409.65	384.77	220.67	105.51	67.12	190.91	199.99
	A	1.64×10^{39}	3.1×10^{30}	1.98×10^{33}	9.15×10^{30}	3.4×10^{17}	1.1×10^{7}	3111.3	2.56×10^{14}	1.2×10^{15}
	ΔS	289.51	333.12	386.82	342.10	85.02	-115.27	-183.74	25.21	38.38
	r	0.9279	0.9425	0.9580	0.9482	0.9677	0.9647	0.9614	0.9488	0.9561
Stage III	E	81.19	91.21	105.66	95.86	57.16	24.55	13.69	45.23	81.19
	A	$6. \times 10^{5}$	6.1×10^{6}	8.1×10^{7}	5.1×10^{6}	4942.95	0.7744	0.0308	76.36	6.85×10^{5}
	ΔS	-139.9	-121.67	-100.17	-123.21	-180.91	-253.75	-280.55	-215.58	-139.9
	r	0.8496	0.8801	0.9154	0.8929	0.9339	0.9122	0.8793	0.8834	0.8496

*E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$

Table 2.17 Kinetic parameters of the decomposition of Ni(II) complex of 3-(1H-indol-3-yl)-2-[(E)-(thiophen-2-ylmethylidene)amino]propanoic acid (I3YT2YMAPA) from TG using mechanistic equations

Complex	Parameter*	Mechanistic equations								
		1	2	3	4	5	6	7	8	9
$[NiL^5Ac(H_2O)_3]$	E	106.46	118.19	134.37	123.44	73.26	33.624	20.41	60.19	64.18
	A	$6.66x10^{12}$	$2.43 x10^{14}$	$1.9 x10^{16}$	$3.6 x10^{14}$	$2.95 x10^{8}$	307.16	2.45	$1.19 x10^{6}$	$3.4 x10^{6}$
Stage Ia	ΔS	-0.9406	28.97	65.224	32.33	-84.27	-198.81	-238.98	-130.12	-121.21
	r	0.85222	0.8780	0.9093	0.8885	0.9254	0.9126	0.8967	0.8844	0.8988
Stage Ib	E	52.95	59.46	69.09	62.55	36.19	14.13	6.78	28.20	30.58
	A	682.04	2805.43	12894.03	1654.87	26.88	0.0418	0.0031	0.9750	1.434
	ΔS	-193.91	-182.16	-169.42	-186.49	-220.74	-274.49	-295.92	-248.32	-245.11
	r	0.7262	0.7588	0.8031	0.7741	0.8147	0.7351	0.6106	0.7387	0.7644
Stage II	E	346.49	375.08	419.86	389.21	231.91	110.72	70.33	193.58	204.69
	A	$4.9 x10^{25}$	$8.72 x10^{27}$	$1.78 x10^{31}$	$3.5 x10^{28}$	$8.9 x10^{16}$	$5.66 x10^{6}$	1840.3	$1.7 x10^{123}$	$1.1 x10^{14}$
	ΔS	240.84	283.78	347.15	295.25	73.36	-121.82	-188.6	2.020	17.72
	r	0.9194	0.9289	0.9443	0.9342	0.9572	0.9531	0.9485	0.9340	0.9416
Stage III	E	82.60	91.52	103.55	95.43	51.37	18.55	7.61	41.67	44.64
	A	29.06	70.25	124.68	30.74	0.9560	0.0048	0.0005	0.0806	0.0933
	ΔS	-225.43	-218.09	-213.32	-224.96	-253.82	-297.79	-317.04	-274.37	-273.16
	r	0.8741	0.8997	0.9255	0.9093	0.9263	0.8675	0.7253	0.8853	0.9015

*E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$

Table 2.18 Kinetic parameters of the decomposition of Ni(II) complexes of (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA) and (E)-4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid (PHMT2YBA) from TG using non mechanistic equation (Coats-Redfern) and its correlation with mechanistic equation

Complex (stage)	Non-mechanistic/ mechanistic equation	Kinetic parameters*				Order of reaction (n)	Mechanism of decomposition
		E	A	ΔS	r		
$[NiL^1Ac(H_2O)_3]$ Stage I	Coats-Redfern	86.21	$4.58x10^7$	-101.58	0.9565	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	86.21	$4.58x10^7$	-101.58	0.9565		
Stage II	Coats-Redfern	77.10	808.60	-196.36	0.9221	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	77.10	808.60	-196.36	0.9221		
$[NiL^2{}_2Ac_2(H_2O)_2]$ Stage I	Coats-Redfern	70.61	$4.5x10^7$	-103.12	0.9445	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	70.61	$4.5x10^7$	-103.12	0.9445		
Stage II	Coats-Redfern	261.99	$3.6x10^{18}$	-103.68	0.9608	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	261.99	$3.6x10^{18}$	-103.68	0.9608		

*E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$

Table 2.19 Kinetic parameters of the decomposition of Ni(II) complex of (E)-4-(5-[(2-carbamothioylhydrazono)methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA) and its correlation with mechanistic equation

Complex (stage)	Non-mechanistic/ mechanistic equation	Kinetic parameters*				Order of reaction (n)	Mechanism of decomposition
		E	A	ΔS	r		
$[NiL^3_2(H_2O)_2]$ Stage I	Coats-Redfern	43.79	5097.26	-175.55	0.9335	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	43.79	5097.26	-175.55	0.9335		
Stage IIa	Coats-Redfern	103.91	$1.24x10^9$	-75.02	0.9335	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	103.91	$1.24x10^9$	-75.02	0.9335		
Stage IIb	Coats-Redfern	235.01	$1.56x10^{21}$	-156.08	0.9497	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	235.01	$1.56x10^{21}$	-156.08	0.9497		
Stage IIc	Coats-Redfern	177.05	$6.4x10^{13}$	13.83	0.9471	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	177.05	$6.4x10^{13}$	13.83	0.9471		
Stage III	Coats-Redfern	153.39	$1.9x10^6$	-68.74	0.9957	2/3	R_3 mechanism. Phase boundary reaction. Spherical symmetry
	Equation IX	155.15	$3.6x10^9$	-68.28	0.9957		

*E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$

Table 2.20 Kinetic parameters of the decomposition of Ni(II) complex of (E)-4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA) from TG using non mechanistic equation (Coats-Redfern) and its correlation with mechanistic equation

Complex (stage)	Non-mechanistic/ mechanistic equation	Kinetic parameters*				Order of reaction (n)	Mechanism of decomposition
		E	A	ΔS	r		
$[NiL^4_2 (H_2O)_2]$ Stage I	Coats-Redfern	62.59	4.07×10^6	-119.72	0.9565	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	62.59	4.07×10^6	-119.72	0.9565		
Stage IIa	Coats-Redfern	96.29	2.3×10^9	-70.12	0.9565	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	96.29	2.3×10^9	-70.12	0.9565		
Stage IIb	Coats-Redfern	141.03	4.44×10^{11}	-26.37	0.9538	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	141.03	4.44×10^{11}	-26.37	0.9538		
Stage IIc	Coats-Redfern	182.57	8.23×10^{13}	-15.78	0.9409	1/3	R_2 mechanism. Phase boundary reaction. Cylindrical symmetry
	Equation VIII	190.90	2.56×10^{14}	25.21	0.9487		
Stage III	Coats-Redfern	48.80	145.42	-210.23	0.9022	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	57.16	4942.9	-180.91	0.9339		

*E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$

Table 2.21 Kinetic parameters of the decomposition of Ni(II) complex of 3-(1H-indol-3-yl)-2-[(E)-(thiophen-2-ylmethylidene)amino] propanoic acid (I3YT2YMAPA) from TG using non mechanistic equation (Coats-Redfern) and its correlation with mechanistic equation

Complex (stage)	Non-mechanistic/ mechanistic equation	Kinetic parameters*				Order of reaction (n)	Mechanism of decomposition
		E	A	ΔS	r		
$[NiL^5Ac(H_2O)_3]$ Stage Ia	Coats-Redfern	73.26	$2.95x10^8$	-84.27	0.9254	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	73.26	$2.95x10^8$	-84.27	0.9254		
Stage Ib	Coats-Redfern	36.19	26.88	-220.49.	0.7351	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	36.19	26.88	-220.49	0.7351		
Stage II	Coats-Redfern	204.65	$3.28x10^{14}$	26.77	0.9415	2/3	R_3 mechanism. Phase boundary reaction. Spherical symmetry
	Equation IX	204.69	$1.1x10^{14}$	17.72	0.9416		
Stage III	Coats-Redfern	51.37	0.9560	-253.82	0.9263	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	51.37	09560	-253.82	0.9263		

*E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$

SUMMARY

Thermogravimetric studies of Cr(III) and Ni(II) complexes of novel Schiff base ligands such as I3YT2YMAPA, T2YMABA, CTHMT2YBA, PHMT2YBA and CTHMF2YBA were conducted. The regions of thermal stability and the temperature of decomposition were noted from the data. Also the temperatures of maximum rate of decomposition of each complex were assigned from the thermograms. The thermogravimetric data of all the complexes were subjected to kinetic studies. Mechanistic and non mechanistic equations were employed for the analysis of different stages of thermograms. Kinetic parameters like Arrhenius frequency factor, energy of activation and entropy of activation of all the stages were calculated. The mechanism of decomposition reaction in each stage and hence the order of decomposition reactions also were determined. The thermal stabilities of the chelates were compared with the aid of energy of activation, initial/final decomposition temperature, inflection temperature and peak temperature from the TG and DTA data.

In order to ascertain the order of the decomposition reactions, nine mechanistic equations and an integral equation formulated by Coats and Redfern, which is a non mechanistic equation, were employed and the kinetic parameters were calculated. Comparing the correlation between the kinetic parameters obtained from these mechanistic equations and the Coats-Redfern method, reaction mechanisms and orders of different decomposition stages were ascertained.

Thermal decomposition studies on Cr(III) complexes with four different heterocyclic Schiff bases, 3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA), 4-(5-[(2-carbamothioylhydrazono)methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA),

4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid (PHMT2YBA) and 4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA) are discussed in Chapter 3. The complexes of Cr(III) with T2YMABA and CTHMF2YBA exhibited four stage decomposition pattern in which the coordinated water molecules were lost during the first stage decomposition and acetate groups, CO_2 molecules and bridged acetate groups were lost in subsequent stages. Whereas the other two complexes with PHMT2YBA and CTHMT2YBA ligands, exhibited three stages of decomposition in the TGA/DTA curves. The kinetic parameters also were calculated. The thermal stabilities of these complexes were found to be increasing in the order $[CrL^3Ac_2(H_2O)]_2$<$[CrL^4Ac_2(H_2O)]_2$<$[CrL^1Ac_2(H_2O)]_2$< $[CrL^2Ac_3(H_2O)_2]$.

Chapter 4 explains the thermal decomposition studies of the complexes of Ni(II) with the novel Schiff bases synthesized. The Ni(II) complexes 3-[thiophen-2-ylmethyleneamino)benzoic acid (T2YMABA) and 4-(5-[(2-carbamothioylhydrazono) methyl]hiophen-2-yl)benzoic acid (CTHMT2YBA) showed two stage decomposition process. Well defined three stage decomposition pattern, with certain definite substages was exhibited by the nickel chelates of PHMT2YBA, CTHMF2YBA and I3YT2YMAPA. Kinetic parameters such as E, A, ΔS along with the correlation coefficient of each stages of decomposition were calculated. Attempts were made to derive the order of reaction of thermal decomposition processes of these complexes. Generally it is noticed that the orders of various disintegration steps involved during the thermal studies of the present compounds follows the order 1, 1/3 and 2/3. The relative thermal stabilities was found to be in the order $[NiL^4{}_2(H_2O)_2]$<$[NiL^5Ac(H_2O)_3]$< $[NiL^3{}_2(H_2O)_2]$< $[NiL^1Ac(H_2O)_3]$ < $[NiL^2{}_2Ac_2(H_2O)_2]$.

REFERENCES

1. C. Daval, *Inorganic Thermogravimetric Analysis*, Elsevier, New York, 2nd Ed. (1963).
2. A. K. Srivastava, P.C. Jain, *Instrumental Approach to Chemical Analysis*, (2009).
3. W. J. Smoothers, M. S. Yaochiang, *Handbook of Differential Thermal Analysis,* Chemical Publising Co., New York (1966).
4. D. Schulze, *Differential Thermoanalyser*, VEB Verlangder Wissanchften, Berlin (1966).
5. K. D. W. van , H. C. van , F. Huntjens, *J. Fuel*, 30 (1951) 253.
6. C. D. Doyle, *J. App. Polymer Sci.*, 5 (1961) 285.
7. H. H. Horowitz, G. Metzger, *Anal. Chem.*, 35 (1963) 1464.
8. W. W. Wendlandt, *Thermal Methods of Analysis*, John Wiley, New York, 2nd Ed. (1974).
9. E. S. Freeman, B. Carroll, *J. Phys. Chem.*, 62 (1958) 394.
10. J. Sestak, V. Satava, W. W. Wendlandt, *Thermochim. Acta,* 7 (1973) 333.
11. J. Sestak, *Talanta,* 13 (1966) 567.
12. Varhegy, *J. Anal. Appl. Pyrol*, 79 (2007) 278.
13. A. W. Coats, J. P. Redfern, *Analyst*, 88 (1963) 2938.
14. J. Sestak, *Silikaty*, 11 (1967) 153.
15. B. Carroll, E. P. Manche, *Thermochim. Acta,* 2 (1972) 449.
16. J. G. Santos, M. M. Conceicao, M.M. Trinade, *J. Therm. Anal. Calorim.,* 75 (2004) 591.

17. A. G. Souza, M. M. Oliveira, I. M. G Santos, M. M. Conceicao, *J. Therm. Anal. Calorim.,* 67 (2002) 359.

18. G. M. Luckaszewski, J. P. Redfern, *Lab. Pr.,* 10 (1961) 721.

19. D. Rainville, *Special Functions*, Mac Millan, New York, 44 (1960).

20. J. Sestak, G. Berggren, *Thermochim. Acta*, 3 (1971)1.

21. V. Satava, *Thermochim. Acta*, 2 (1971) 243.

22. V. M. Gorbachev, *J. Therm. Anal.,* 8 (1975) 349.

23. M. D. Jaddo, M. T. Pope, *J. Therm. Anal.,* 4 (1972) 37.

24. V. P. Ivanov, *Zap. Uses. Miner. Obschch.,* 90 (1961) 50.

25. C. G. Scency, J. F. Smith, J. O. Hill, R. J. Magee, *J. Therm. Anal.,* 9 (1976) 415.

26. M. Lehtinen, K. Maire, *Acta Pharma. Farn.,* 90 (1981) 187.

27. N. Kavitha, P.V. A. Lakshmi, *J. Saudi Chem. Soc.*, doi:10.1016/j.jscs.2015.01.003 (2015).

28. A. Azza, Abu-Hussen, *J. Coord. Chem*., 59 (2) (2006) 157.

29. K. Singh, M. S. Barwa, P. Tyagi, *European J. Med. Chem*., 42 (3) (2007) 394.

30. M. Sharaby, *Spectrochim. Acta*, 66(4) (2007) 1271.

31. S. A. Abdel Latif, H. B. Hassib, Y.M. Issa, *Spectrochim. Acta*, 67 (3) (2007) 950.

32. M. Sonmez, M. Sekerci, *Polish J. Chem*., 76 (2002) 907.

33. E. Canpolat, M. Kaya, *J. Coord. Chem*.**,** 57(14) (2004) 1217.

34. G. G. Mohamed, M. M. Omar, A. M. Hindy, *Turk J. Chem*., 30 (2006) 361.

35. A. M. Khedr, H. M. Marwani, *Int. J. Electrochem. Sci*., 7 (2012) 10074.

36. L. Pardeshi, R. A. Bhobe, *Acta Cienc. Indica,* 9 (1983) 18.

37. A. K. Galwey, M. E. Brown, *Hand Book in Thermal Analysis*, (1998) 147.

38. Brown M.E., Maciejewski M., Vyazovkin S., Nomen R., Sempere J., *Thermochim. Acta*, 355 (2000) 125.

39. L. Pardeshi, R. A. Bhobe, *Acta Cienc. Indica,* 8 (1982) 178.

40. K. N. Johri, B. S. Arora, *Thermochim. Acta,* 54 (1982) 237.

41. C. Reverte, J. L. Dirion, M. Cabassud, *J. Anal. Appl. Pyrol.*, 79 (2007) 297.

42. B. Sleema, G. Parameswaran, *Asian J. Chem.,* 13-2 (2001) 709.

43. P.V. Marykutty, G. Parameswaran, *Asian J. Chem.,* 13-3 (2001) 905.

44. R. Seshadri Naidu, Raghava Naidu, *Indian J. Chem.,* 15A (1977) 652.

45. A. P. Mishra, M. Khare, *J. Indian Chem. Soc.,* 77 (2000) 367.

46. K. J. Thomas, G. Parmeswaran, *J. Therm. Anal.,* 45-6 (1996) 1491.

47. Joby Thomas, Geetha Parameswaran, *Asian J. Chem.,* 14-3 (2002) 1370.

48. S. Volker, T. Rieckmann, *J. Appl. Polym. Sci*., 62 (2002) 165.

49. J. H. Tassel van , W. W. Wendlandt, *J. Amer. Chem. Soc.*, 81 (1959) 813.

50. G. M. Lukaszewski, J. P. Redfern, *J. Chem. Soc.*, (1962) 4802.

51. M. S. Masoud, S. A. Abon, H. M. Kamel, *Indian J. Chem.,* 41A (2002) 297.