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Synthesis, Characterization and Morphology Behaviour of Mn (II), Co (II), Ni (II) and Cu (II) Chelate Polymer Compounds Based on Chelating Ligand

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ABSTRACT

A series of chelate polymer compounds having formulae $[MnL(H_2O)_2]_n(1)$, $\{[CoL(H_2O)_2]2H_2O\}_n(2)$, $\{[NiL(H_2O)_2]2H_2O\}_n(3)$ and $\{[CuL(H_2O)_2]H_2O\}_n(4)$ were synthesized based on chelating ligand *i.e.* terphthaoyl-*bis* (paramethoxyphenylcarbamide) (L). The authenticity of four divalent transition metal chelate polymers were characterized by elemental analysis, infrared, diffuse reflectance spectroscopy, magnetic measurements, X-ray diffraction, thermal and SEM techniques. The infrared spectroscopy supports interaction through nitrogen and oxygen atom of ligand with metal ion. Diffuse reflectance spectral studies suggest an octahedral geometry for Mn (II), Co (II), Ni (II) and Cu (II) chelate polymers, which was further supported by other instrumental technique in present work. Furthermore, solid state electrical conductivity of all chelate polymers have been measured in compressed pellet form over 311 K by two probe method. The morphology behaviour of all polymer compounds was identified by SEM and XRD techniques. The crystalline and amorphous nature of chelate polymer compounds were determined by X-RD technique, while SEM images reveals that, the particle sizes of chelate polymers were found to be between 100-985nm.

Key Words: Chelating ligand, chelate polymer compounds, infrared, diffuse reflectance spectroscopy, morphology.

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INTRODUCTION

The most interesting topics in current chemical science and crystal engineering are organometallic chelate polymers commonly known as coordination polymer or chelate polymer compounds. This organometallic chelate polymer is derived from collaboration of organic moieties and metal ion sometimes called as metal-organic frameworks (MOFs). Chemistry of MOFs is arising from coordination of organic ligand having electron donating property with central metal ion. The coordination chemistry of nitrogen donor ligand is an active area of research in solid state chemistry. The nitrogen donor ligand in organic moiety is conveniently used in medicine. The valuable attention has been paid in area of a organometallic chelate polymers formed by divalent transition metal ions with thioamide, which act as bidentate ligand and interaction takes place through nitrogen and sulphur donor atoms [1-3]. The metal complexation in polymer-supported ligand is also interested topic for analytical reagents, pollution control, catalyst [4] antibiological properties [5], separation of toxic and carcinogenic metal ions [6]. Nowadays also special consideration has been paid to designing organicinorganic magnetic molecular conductor characterized by different physicochemical properties within the crystal lattice [7]. Research in field of divalent transition metal chelate polymer compounds have been evoke attention due to the promise of generating material with specific physical properties based on the chosen building blocks. Such metal-organic polymers provide an opportunity for expansion of fundamental knowledge, development of new material assisting in the advancement of technology and stimulating the thought of what might if organic and inorganic chemistry are combined in polymer science [8]. Over the past few decades, great efforts have been made for the synthesis and investigation of new thermally stable organometallic chelate polymers. The synthesis and characterization of chelate polymers have attracted much attention due to their high stability and intricate interweaving of multiple networks [9]. The numerous chelate polymers can be used as sensor, catalyst and adsorbent [10].

In the present paper, we have reported synthesis and structural elucidation of divalent transition metal chelate polymers by various techniques. Beside, examinations of spectral study, solid state conductivity and morphological behaviour of chelate polymers were carried out by scanning electron microscopy (SEM) and XRD. SEM images significantly suggest that, particle size of metal chelate polymers were found to be in the range 100-985 nm. SEM image of chelate polymers shows the cauliflower, globule, rod type, beads, flat rod and needle shape structure.

MATERIALS AND METHODS

Materials, method and measurements

The chemicals used for synthesis of a chelating ligand and its metal chelate polymer compounds were of analytical grade. Solvents were double distilled before used.

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IR studies of chelate polymer compounds were recorded by using KBr pellets in the range 4000 - 400 cm⁻¹ on a Shimandzu FT-IR-8101A spectrophotometer at Sophisticated Instrumental Facility, Indian Institute of Science (IISc), Bangalore (India). Solid reflectance spectral analyses were recorded in the range 200 – 600 nm at STIC Cochin University, Kerala, India. The magnetic moment measurements of polymer complexes were carried out at room temperature by Gouys method at Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University Nagpur. X-ray diffraction analyses of polymer complexes were carried out in solid powder form at Sophisticated Instrumental Facility, Department of Chemistry, Indian Institute of Science (IISc), Bangalore (India). Electrical conductivity of chelate polymers was carried out in pellet form of solid powder and found an average range of conductivity. This study were carried out in compressed pellet form over 311 *K* by two probe method. SEM studies of chelate polymer compounds were carried out on scanning electron microscope machine at STIC Cochin University, Kerala, India. A remarkable good appearance with high resolution was obtained. This study noteworthy suggests distinct morphology for chelating ligand and chelate polymer compound.

General method for synthesis of chelate polymers compounds (1-4)

The *bis* (bidentate) chelating ligand terphthaoyl-*bis* (paramethoxyphenylcarbamide) (TBPMPC) was synthesized by method reported earlier [11]. The condensation method [12-13] was used for synthesis of metal chelate polymer compounds from TBPMPC (0.01 mol) with metal acetate (0.01 mol) by using high temperature reaction technique (Scheme 1). The coloured chelate polymers appeared after 20-24 *h*, were filtered, washed with hot DMF, DMSO. Finally, resulting products were dried in an oven. The resulting products were insoluble in almost all organic solvents. The yields of chelate polymers were found to be in range of 50%-65%. The analytical and physiochemical data of chelate polymer compounds have been reported in Table 1.

M(CH₃COO)₂ + TBPMPC (L)
Metal acetate Ligand

$$\frac{DMF + Alcohol, 150 \ ^{0}C}{Reflux, 20-24h \text{ in an oil bath}} \rightarrow \{[M L(H2O)n] xH2O\}n$$
Chelate polymer compounds

Where M= Mn(II), Co(II), Ni(II) and Cu(II)

Scheme1. Synthesis of divalent transition metal chelate polymer compounds

2.1a. [MnL(H₂O)₂]_n(1). Yield: 65.4 %. Colour: Off-white; mp 355 $^{\circ}$ C(DTG); Elemental Analysis: Calcd for C₂₄H₂₂N₄O₈Mn (*FW* 550.93): C, 52.2%; H, 4.4%; N, 10.2%; Mn, 9.9%. Found: C, 52.0%; H, 4.1%; N, 10.1%; Mn, 9.8%. FT-IR (KBr, cm¹): 754(coordinated water), 3318(-NH), 1639(-C-O in polymer), 1515 (C-N), 2953(-CH₃), 1600(C=C), 1412(aromatic ring), 557(M-O), 649(M-N); Conductivity ($\Omega \ cm^{-1}$): 4.6 × 10⁻⁵; Diffuse reflectance ($\lambda_{max} \ cm^{-1}$):18668, 23992; Magnetic moment, μ_{eff} : 5.41.

2.1b. {[CoL(H₂O)₂] 2H₂O}_n(**2**). Yield: 62.1%; Colour: Purple; mp 812 ^oC (DTG); Elemental analysis: calcd for C₂₄H₂₈N₄O₁₀Co (*FW* 590.93): C, 48.7%; H, 4.7%; N, 9.5%; Co, 9.9%. Found: C, 48.2%; H,

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4.5%; N, 9.3%; Co, 9.3%. FT-IR (KBr, cm⁻¹): 3415(lattice water), 732(coordinated water), 3258(-NH), 1639(C-O in polymer), 1514(C=N), 2943(-CH₃), 1611(C=C), 1431(aromatic ring), 553(M-O), 615(M-N); Conductivity ($\Omega \ cm^1$): 5.3 × 10⁻⁵; Diffuse reflectance (λ_{max} / cm^{-1}): 16431, 19120; Magnetic moment, μ_{eff} : 3.58.

2.1c. {[NiL(H₂O)₂]2H₂O}_n(**3**). Yield: 63.4 %; Colour: Cement; mp 835 °C(DTG);. Elemental calcd for C₂₄H₂₈N₄O₁₀Ni (*FW* 590.69): C, 48.8%; H, 4.7%; N, 9.5%; Ni, 9.9%. Found: C, 48.9%; H, 4.6%; N, 9.4%; Ni, 9.7%. FT-IR (KBr, cm⁻¹): 3414(lattice water),732(coordinated water), 3318(-NH), 1638(-C-O in polymer), 1515(C=N), 3049(-CH₃), 1600(C=C), 1412(aromatic ring), 525(M-O), 616(M-N); Conductivity (Ω cm¹): 4.8 ×10⁻⁵; Diffuse reflectance (λ_{max} /cm⁻¹): 16528, 26315; Magnetic moment, μ_{eff} : 2.89.

2.1d. {[CuL(H₂O)₂]H₂O}_n(**4**) Yield: 64.1%; Colour: Black; mp 1000 °C (DTG); Elemental analysis: calcd for C₂₄H₂₆N₄O₉Cu (*FW* 577.54): C, 49.9%; H, 4.5%; N, 9.7%; Cu, 11.0%. Found: C, 49.9%; H, 4.7%; N, 9.6%; Cu, 10.6%. FT-IR (KBr, cm⁻¹): 3704(lattice water), 822(coordinated water), 3429(-NH), 1638(-C-O in polymer), 1513(C=N), 2980(-CH₃), 1601(C=C), 1462, 1417(aromatic ring), 444(M-O), 589(M-N); Conductivity ($\Omega \ cm^1$): 1.6 × 10⁻⁵; reflectance ($\lambda_{max} / \ cm^{-1}$): 16260, 17421; Magnetic moment, μ_{eff} : 1.99.

RESULTS AND DISCUSSION

The chelate polymer compounds of divalent transition metal were synthesized from chelating ligand and structurally characterized. The presence of hydration water whether inside the sphere of attraction of central metal ion or outside the sphere was determined on the basis of thermal analysis. Finally, the structure of chelate polymer compounds has been deduced by spectral, elemental, diffuse reflectance, magnetic moment measurement, thermal, X-ray diffraction and display in Figure **1**. The thermal study of metal chelate polymer compounds still have not discuss in this article because of previously published [13].

Synthesis and characterization

The infrared spectra of *bis* (bidentate) ligand exhibits strong sharp band [14-15] in region of 3323 cm⁻¹ which may be due to the N-H group (Table 2). Infrared spectra of polymer compounds **1** and **3** are shown in Figure **2**. However in chelate polymer compounds, this band shifted toward the lower frequencies [16] which may be due to the decreasing the electron density of nitrogen atom, due to donation of the lone pair of electron of to the central metal ions. A broad stretching frequency in chelate polymer **1** found at 3318cm⁻¹ and 3377cm⁻¹ may be due to N-H group and lattice water [17-18] respectively, while in other chelate polymers also show stretching frequency in the range of 3318-3282 cm⁻¹. The strong band appeared at 1668 cm⁻¹ which may be due to the C=O bond [19] in ligand, whereas in metal chelate polymer compounds **1-4**.





Fig. 1. Structure of divalent transition metal chelate polymer compounds of terephthaloyl *bis* (paramethoxyphenylcarbamide); where M= Mn (II), Co (II), Ni (II), and Cu (II) ions

Ligand/	Empirical	Color	MP/DT	Found(Calc)%			
polymers	formula		(°C)	С	н	N	М
L	C24H22N4O6	Light yellow	355	61.9	4.4	12.4	
				(62.2)	(4.7)	(12.1)	()
Mn(II)	In(II) C24H24N4O8M Off white		812	52.0	4.1	10.1	9.8
	n			(52.2)	(4.4)	(10.2)	(9.9)
Co(II)	C24H28N4O10C	Purple	900	48.2	4.5	9.3	9.3
	0			(48.7)	(4.7)	(9.5)	(9.9)
Ni(II)	C24H28N4O10N	Cement	835	48.9	4.6	9.4	9.7
	i			(48.8)	(4.7)	(9.5)	(9.9)
Cu(II)	C24H26N4O9Cu	Black	1000	49.9	4.7	9.6	10.6
				(49.9)	(4.5)	(9.7)	(11.0)

MP= melting point, DT = decomposition temperature

Table 2. Infrared data of ligand and its chelate polymer compounds

Ligand/ polymers	v(NH)	v(C=O)	v(C-N)	v(HOH)	ν(M-N)	v(M-O)
L	3323	1668	1508	,		
Mn(II)	3318	1639	1515	,754	649	557
Co(II)	3258	1639	1514	3415,732	615	553
Ni(II)	3318	1638	1515	3414,732	616	525
Cu(II)	3429	1638	1513	3704,822	589	444



Chelate polymers	Conductivity (Ω cm1)	Magnetic µeff (B.M.)	Reflectance data (cm-1)	Assignments	Geometry
Mn(II)	4.6 × 10-5	5.41	18668	6A1g →4T2g(G	Octahedral
Co(II)	5.3 × 10-5	3.58	19120	4T1g →4T1g(P)	Octahedral
Ni(II)	4.8 × 10-5	2.89	26315	3A2g →3T1g(P)	Octahedral
Cu(II)	1.6× 10-5	1.99	17421	2B1g →2A1g	Octahedral

Table 3. Conductivity, n	nagnetic moments a	ind reflectance da	ta of chelate polymers
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Fig. 2. Infrared spectra of chelate polymer compounds (a) Mn (II) and (b) Ni (II)

Table 4.	Solubility	of ligand and	d chelate	polymer	compounds in	various solve	ents

Ligand/polymo		Solvents								
	DMF	DMSO	CHCl₃	CCl ₄	C ₆ H ₆	DMAc	DCE	C₂H₅OH	H_2SO_4	HCI
L	++	++	-	-	-	+	±h	+	+	+
Mn(II)	-	-	-	-	-	-	-	-	+	±h
Co(II)	-	-	-	-	-	-	-	-	+	±h
Ni(II)	-	-	-	-	-	-	-	-	±h	±h
Cu(II)	-	-	-	-	-	-	-	-	+h	+h

+, Soluble at room temperature,; +h, soluble on heating; -, insoluble; ± h, partially soluble on heating

Band shift to lower frequency at range 1639-1637 cm⁻¹ because the bond strength is reduced, while C-N bond is shifted from 1508 cm⁻¹ to 1511-1521 cm⁻¹ due the strengthened the C=N bond as result of chelate formation (polymerization). It may be due to the disappearance of C=O bond and appearances of C=N bond in chelate polymers (chelation). It indicates ligand undergoes keto-enol tautomerism during coordination in chelate polymers. The shift of these bands in chelate polymers **1-4** suggests the coordination of nitrogen and oxygen from ligand to central metal ion. Significantly similar strong band observed in ligand and metal chelate polymers **1-4** at 1491-1510 cm⁻¹ which may be attributed to the C=C group frequency of aromatic ring. The investigation of -OCH₃ group in ligand and chelate polymers **1-4** in



the range 400-560 cm⁻¹ which may be due the formation of O-M bond [21] and second new band [22] in the range 550-750 cm⁻¹ due to the metal–nitrogen (M \leftarrow N coordination bond). The broad band of free H-OH stretching vibration is exhibited at 3445-3510 cm⁻¹ and 732-792 cm⁻¹ due the lattice water and coordinated water [23] respectively.

Reflectance and magnetic moment studies depict the geometry of chelate polymers. Herein we tabulated electronic transition data and diffuse reflectance spectra in Table 3 and Figure 3-4 respectively. The reflectance spectra of chelate polymer 1 shows bands at 15,898 cm-1, 18668 cm-1 and 23,992 cm-1 may be assigned $6A1g \rightarrow 4T1g(4G)$, $6A1g \rightarrow 4T2g(G)$, and $6A1g \rightarrow 4E(G)$ transition [24] respectively and magnetic moment value obtained 5.41 B.M. which suggesting octahedral geometry [25]. The polymer (2) exhibits two bands (Figure 2) at 16431 cm-1 and 19120 cm-1 which pertaining to $4T1g(F) \rightarrow 4T1g(P)$ and $4T1g \rightarrow 4T1g(P)$ transitions [26, 21] respectively and magnetic moment 3.58 B.M. hence it suggested octahedral geometry [27]. Chelate polymer 3 shows two bands at 16528 cm-1 and 26315 cm-1 due to $3A2g(P) \rightarrow 3T1g(F)$ and $3A2g \rightarrow 3T1g(P)$ transition [28] respectively and obtained magnetic susceptibility value 2.89 B.M. The diffuse reflectance spectra of polymer 4 display in Figure 3, showed band around at 16260 cm-1 and 17421cm-1. 2Eg and T2g state of octahedral polymer 4 split under the influence of the tetrahedral distortion and peak seen at range 22471-26500 cm-1 is due to ligand to metal charge transfer transition [29]. Polymer 4 exhibits magnetic moment value 1.99 B.M. expected to be octahedral geometry [30].

Physicochemical properties

The physiochemical properties of chelating ligand and polymer compounds 1-4 were definably manner. discussed and interpreted in well The crude product of paramethoxyphenylcarbamide was dark brown in color, however after recrystallization in water medium it gave pale brownish fine crystal with 86% yield. The chelating ligand was found light orange in color. The ligand was recrystallized from dimethylformamide-alcohol medium and obtained amorphous powder with yield 73 %, whereas the percent yield of crude ligand was higher as compare to recrystalized ligand. The chelate polymer compounds 1-4 were obtained at different time intervals (20 h and 24 h). Polymers compounds 1-4 were found distinct color. Polymer 1 found off white with yield 65.4%, 2 purple with yield 62.1%, 3 cement with yield 63.4% and 4 was found black color with yield 64.1%. The polymers 1-2 were found amorphous form, whereas 3-4 obtained crystalline form.





The solubility of chelate polymers were investigated with 0.01 g in 2 ml of solvent and tabulated in Table 4. The solubility of all the chelate polymers were found to be insoluble in organic protic and aprotic solvents, however polymer 4 could be partially dissolved in organic polar solvents in hot condition such as dimethyl sulphoxide (DMSO) and N, N dimethyl acetamide (DMAc). However, the ligand showed high solubility in dimethyl formamide, dimethylformamide-alcohol and dimethylsulphoxide at room temperature and found out its antimicrobial activity and molar conductivity. The paramethoxyphenylcarbamide was soluble in hot water and organic polar solvents. It was also noticed that the solubility of ligand increases suddenly when increase the temperature and partially soluble at 25 °C, however it get dissolved in higher temperature. The solubility of ligand was decreases as bulkiness of ligand increases. The melting points of paramethoxyphenylcarbamide and ligand were carried out on melting point apparatus at room temperature for powder form and observed 168 °C and 355 °C respectively. The melting point of paramethoxyphenylcarbamide was found to be totally different from ligand and 1-4. The high insolubility and high thermal stabilities showed by 1-4 as compared to ligand. Hence, it was probably revealed that the chelate compounds 1-4 must have high molecular weight, 6-member heterocyclic ring and polymerization. The melting point of polymer compounds 1-4 could not be measured on melting point apparatus because of its

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highly thermally stable, hence its thermal degradation were measured by thermal analysis (TG/DTG/DTA) techniques. Because of high thermal stability of polymer compounds **1-4**, these can be used as thermally resistance material.

Furthermore, the electrical conductivities measured over 311 K for chelate polymers by two probe method. The electrical conductivity data are presented in table **3**. The values obtained an average range of $5.12 \times 10^{-11} - 1.6 \times 10^{-5} \Omega$ cm⁻¹ which indicates moderate semiconductor nature. The low conductivities were shown by polymers **1-2** however, high order of conductivity shown by polymers **3-4**.

X-ray diffraction studies

The X-ray analysis of chelate polymers 1-2 do not shows any sharp defined peaks, which indicates the amorphous nature, whereas chelate polymer compounds 3-4 displayed some fine peaks due to semi-crystalline nature. The XRD pattern of polymer compounds is display in Figure 5. The XRD curves without crystalline peaks and dark micrograph indicate amorphous characters of polymers have been investigated [31]. X-RD pattern for chelate polymers 3 and 4 exhibit some long broadening of peaks hence, it shows the hallow pattern [32] in the region 2¢ = 10-500 this indicate that polymers 3 and 4 are semi-crystalline in nature.



Fig. 5. XRD pattern of chelate polymers compounds (a) Mn(II), (b) Co(II), (c) Ni(II) and (d) Cu(II)

Surface morphology

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Scanning electron microscopy studies determine the surface morphology of chelate polymer compounds **1-4**. SEM images of polymers **1-4** were recorded at energy of 20 kV with magnification X 5000. SEM micrograph of ligand was totally different from chelate polymers **1-4**, hence it was the conspicuous of formation of new product. Also it was found that, morphology of individual chelate polymers significantly different from other chelate polymers at magnification X 5000. SEM images have shown in Figure 6-7.

The SEM images of chelate polymers 1-4 were found different morphology, yet it was synthesized from a particular ligand. The SEM image (Figure 6) of chelate polymer 1 found cauliflower structure which is formed due to the aggregation of small globule like droplet particle, while polymer 2 (Figure 6) observed like sharp flat rod plane structure having diameter size 756.04 nm and 985 nm with cracks at tip [33]. The diameter and length of each flat rod is different.

SEM image (Figure 7) of polymer **3** seen droplet structure and small irregular shape particle entrapped on bigger size particle that indicate the accumulation of number of polymers [34]. The micrograph of polymer **4** (Figure 7) shows fine sharp needle shape structure which appeared like the bundle of needles shape crystal generated from single point. The diameter of single needle shape was found to be 100.0 nm. It is interesting to note that the needle does vary in length from top to bottom. The tip of the needle does not develop very well. The lengths that, the needle are varying from bunch of needles. SEM of polymers **1-4** was reveals particle size at nanoparticles levels. The significant different of morphological were observed in chelate polymers **1-4** and ligand, hence it indicate the formation of polymers.



Fig. 6. SEM image of polymer compounds (a) Mn (II) and (b) Co (II)





Fig. 7. SEM image of chelate polymer compounds (a) Ni (II) and (b) Cu (II)

CONCLUSIONS

In summary, we have described the synthesis, structural characterization, physicochemical properties and morphological behaviour of chelate polymer compounds. The presences of lattice and coordinated water were identified by CHN, and infrared spectroscopy. Finally, on the basis of elemental data, spectroscopic studies, diffuse reflectance, magnetic susceptibility measurements and X-ray-diffraction studies have been suggested an octahedral geometry for all chelate polymer compounds (Figure 1). Morphology behaviour of all compounds reveals polymer formation with distinct shapes.

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REFERENCES

- Muresan V, Sbirna L S, Sbirna S, Lepadatu C I and Muresan N. Acta Chim Slov 2001; 48: 439.
- [2] Kriza A, Reiss A, Muresan V and Florea S. J Ind Chem Soc 1999; 76: 406.
- [3] Muresan V and Muresan N. Polish J Chem 1995; 69:385.
- [4] Radi S, Ramdani A, Lekchiri Y, Morcellet M, Crini G, Morcellet J and Janus L . Eropean Polym J 2000; 36: 1885.
- [5] Bankova M, Petrova T, Manolova N and Rashkov I. Eur Polym J 1996; 32: 325.
- [6] Beauvais RA and Alexandratos SD. React & Funct Polym 1998; 36: 113.
- [7] Styczen E, Waranke Z, Wyrozekowasky D, Klak J, Mrozinski J and Sikorski A. Struct Chem 2010: 269.
- [8] Rahimi A. Iranian Polym J 2004; 13: 149.



- [9] Fua F, Chen R and Xiong Y. Sep Puriff Technol 2006; 52: 388.
- [10] Padole Gaikwad GS and Juneja HD. J Therm Anal Calorim 2010; 100: 645.
- [11] Chaudhary RG, Gharpure MP and Juneja HD. Int J Appl Biol Pharm Technol 2012; 3: 88.
- Bonde AD, Juneja HD, Ukey VV, Ghubde RS and Husain R. J Mat Sci and Eng B 2006; 132: 16.
- [13] Chaudhary RG, Juneja HD and Gharphure MP. J Therm Anal Calorim 2013; 112(2): 637-647.
- [14] Asundariya ST, Patel PR and Patel KC. Int J Polym Mater 2009; 58: 692.
- [15] Bharani M, Karpagam T, Varalakshi B, Gayathiri G and Lakshmi P. Int J Appl Biol Pharm Technol 2012; 3: 58.
- [16] Sonar S, Sadapal S, Pawar S and Shinghate M. Chin Chem Lett 2009; 20: 557.
- [17] Dolaz M and Tumer M. Transition Met Chem 2004; 29: 516.
- [18] Shrinivasan BR, Naik AR, Dhuri SN, Nather C and Bensch WJ. Chem Sci 2011; 123: 55.
- [19] Syamal A, Singh MM and Kumar D. React & Funct Polym 1999; 39: 27.
- [20] Kaya I and Koca S. Iranian Polym J 2009; 18: 25.
- [21] Kaya I, Bilici A and Sacak M. J Inorg Organomet Polym 2009; 19: 443.
- [22] Gaballa AS. J Spectrochim Acta A 2010; 75: 146.
- [23] Favier I, Gomez M, Muller G, Picurelli P, Nowicki A and Roucoux A. J Appl Polm Sci 2007; 105: 2772.
- [24] Bansod AD and Aswar AS. J Saudi Chem Soc 2007; 11: 243.
- [25] Gudasi K, Patil M, Vadavi R, Shenoy R and Patil S. J Serb Chem Soc 2007; 72: 357.
- [26] Chandra S, Gautam A and Tyagi M. Trans Met Chem 2007; 32: 1079.
- [27] Cotton FA, Wilkinson G, Murillo CA and Bochman M. 1999 Advance inorganic chemistry, New York, USA: Interscience,
- [28] Drago RS. Physical method in inorganic chemistry, New York, USA: Rein Hold, 1965.
- [29] Manonmani J, Tirunubn R, Kndaswami M, Kuppaee M and Ponuswammy HK. Polyhedron 2000; 1980: 2011.
- [30] Mujumdar A, Pilet G, Rodriguez MTG and Mitra S. Polyhedron 2006; 25: 2550.
- [31] Uma T, Mahalingam T and Stimming UJ. Mater Sci 2004; 39: 2901.
- [32] Ahamed IS, Ghonaim AK, Abdel Hakim AA, Moustafa MM and Kamal El-Din AH. J Appl Sci Res 2008; 4: 1946.
- [33] Bruni G, Berbenni V, Milanese C, Girella A and Marini A. J Therm Anal Calorim 2010; 102: 193.
- [34] Sadek SA, Solyman S, Abdel-Samd H and Hasan S. Int J Polym Mater 2010; 59; 353.