

Research Article

Condensation Polymers of Terephthalic Acid and 1,4-Diaminobutane and Their Schiff Base Complexes

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Amino-terminated oligomeric poly(tetramethylene terephthalamide) (PTTA) was prepared by condensation of terephthalic acid and 1,4-diaminobutane using phosphorylation technique. Schiff base complexes of this polyamide were synthesized with salicylaldehyde and 2-hydroxy-1-naphthaldehyde complexes of Co(II), Ni(II), and Cu(II). The polyamide as well as Schiff base complexes were characterized by elemental analysis, IR spectroscopy, and magnetic susceptibility measurements. Thermal stabilities of ligand and its various complexes were compared by thermogravimetric analysis.

1. Introduction

Polyamides, the condensation polymers of dicarboxylic acids and diamines, are frequently referred to as nylons, an important group of polymers which can be synthesized using phosphorylation technique [1]. Oligomers based on these polyamides having reactive terminals are of great importance in order to yield materials with novel properties. Most of the polyamides do not withstand elevated temperature for a longer time. We have tried to get thermally resistant polyamide-metal complexes by inserting metal ions in ligands through the formation of Schiff's base complexes. We have reported Schiff base complexes with oligomeric poly(methylene diphenylene terephthalamide) [2]. In the present communication we are reporting Schiff base complexes of amino-terminated low molecular weight poly(tetramethylene terephthalamide), PTTA, with salicylaldehyde and 2-hydroxy-1-naphthaldehyde complexes of Co(II), Ni(II), and Cu(II).

Various Schiff bases involving aldehydes with aromatic diamines are extensively studied by numerous workers and are critically reviewed and reported for their biological properties, such as antibacterial and antifungal activities [3–5]. Few polymeric complexes with Schiff's base structures have

been synthesized from aromatic amines and phenolic aldehydes. These metal complexes have been widely studied because they have anticancer and herbicidal applications [6–8].

2. Materials and Methods

2.1. Materials. The materials of analytical quality or equivalent grades were used. Salicylaldehyde was from S. Merck, India, and 2-hydroxy-1-naphthaldehyde (AG) was from Fluka. 1,4-diaminobutane of AR grade was obtained from E. Merck, India, and was used without further purification. Dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), and pyridine were GR grade products of Qualigens, Glaxo, India, and were distilled before use. Acetates of cobalt(II), nickel(II), and copper(II) (all of AR grade from E. Merck, India) were used as such.

2.2. Synthesis of Amino-Terminated Oligomeric Polyamide (PTTA). The amino terminated oligomeric polyamide ligands were prepared by a known procedure. Terephthalic acid (0.1 mol) was treated with 0.12 mol of 1,4-diaminobutane, which was finely powdered in the presence of triphenyl phosphite. A mixture of DMF (150 mL) and pyridine (30 mL) was taken as solvent. The resulting mixture was maintained

at 80°C for 1.5 hrs under nitrogen atmosphere. The amino group terminated oligomer thus formed was separated out by precipitating out from the reaction mixture by addition of excess of distilled methanol. The precipitated products were washed several times with methanol, filtered under suction, and then dried in air oven at 80°C for 20 hrs (see Scheme 1).

The PTTA oligomer was characterized by IR spectroscopy and elemental analysis. The mass average molecular mass \overline{M}_w was calculated by viscometry using the following equation given by Aoki et al. [9]:

$$[\eta] = 9.9 \times 10^{-4} \overline{M}_w^{0.8} \quad (1)$$

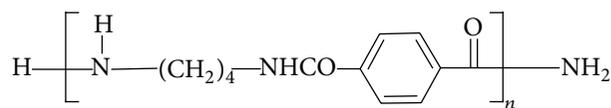
2.3. Synthesis of Metal-Aldehyde Complexes. The metal-aldehyde complexes were prepared by mixing aqueous solutions of acetates of cobalt(II), nickel(II), and copper(II) with ethanolic solutions of salicylaldehyde or 2-hydroxy-1-naphthaldehyde in respective preparations (see Schemes 2 and 3). The reaction mixture was refluxed with continuous stirring for 2-3 hrs. The coloured solid complexes were filtered, washed with ethanol followed by ether, and then dried in an oven at 60°C. The complexes were characterized by elemental analysis and IR spectroscopy (see Tables 1 and 2).

2.4. Synthesis of Polyamide-Metal Complexes. Equimolar solutions of metal aldehyde and the amino-terminated oligomer PTTA in 50 mL hot DMF were mixed in respective preparations and refluxed on a heating mantle for 6–8 hrs to obtain solid coordination polymers. The coloured precipitates were filtered, washed repeatedly with hot DMF and alcohol, and then dried. The polyamide PTTA-metal complexes were coloured, powdery solids insoluble in water and common organic solvent. The reaction scheme for the synthesis of amide-metal complexes is given in Figure 1.

2.5. Characterization. Elemental analysis of polyamide ligand (PTTA) and its coordination polymers was carried out on Perkin Elmer Elemental Analyzer model 2400. The metal contents were determined by complexometric titration with EDTA after decomposing the coordination polymers with fuming nitric acid. Molecular weights of the coordination polymers could not be determined due to their insoluble nature. IR spectra of the ligand and the coordination polymers were recorded on a Perkin Elmer Infrared Spectrophotometer Model 1430 using CsI pellets in 4000–200 cm^{-1} range. The magnetic susceptibility measurements were done at room temperature with a guoy's balance using $\text{HgCo}(\text{NCS})_4$ as a calibrant. Thermogravimetric analysis was performed on a Perkin-Elmer Thermal Analyzer TGA 7 with professional computer 7700 in an inert atmosphere at a heating rate of 20°C/min.

3. Results and Discussion

The analytical data for the ligand and their metal complexes are presented in Table 1. The compositions and theoretical analytical results are based on assumed structures. In case of PTTA the number of repeated units (n) is taken as 8 to 9 for the theoretical calculations. The average of molecular masses



PTTA

SCHEME 1

TABLE I: Analytical data of PTTA and its metal complexes.

No.	Compound	Elemental analysis*			
		%C	%H	%N	%M
1	PTTA	63.40	5.96	13.20	—
		64.70	6.50	14.10	—
2	PTTA-Co(II)-Sal'	60.36	6.19	9.69	3.00
		62.40	5.90	11.80	2.80
3	PTTA-Ni(II)-Sal'	59.86	4.97	9.22	3.22
		62.40	5.9	11.8	2.79
4	PTTA-Cu(II)-Sal'	60.14	5.02	10.04	3.78
		62.20	5.88	11.79	3.00
5	PTTA-Co(II)-Naphthal'	62.25	4.97	9.98	3.28
		64.60	5.77	11.03	2.68
6	PTTA-Ni(II)-Naphthal'	63.98	4.88	10.12	4.00
		64.62	5.77	11.03	2.66
7	PTTA-Cu(II)-Naphthal'	62.46	5.16	10.06	4.58
		64.41	5.76	10.99	2.88

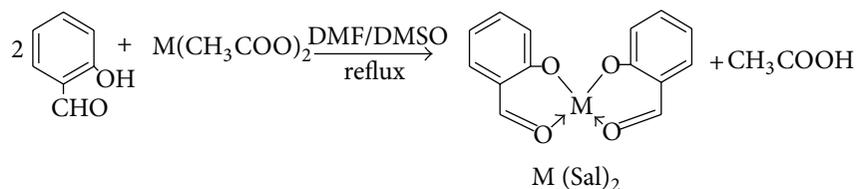
* In every case the upper value represents the observed results, and the lower value represents the theoretically calculated values.

calculated on the basis of $n = 8$ is $\overline{M}_w = 1750$ which is close to the experimentally found value that is 1758.

It was observed that the deviations of the experimental values of elemental analysis from the theoretical ones were beyond experimental error. This discrepancy between the calculated and observed results may be due to the strong moisture pickup tendency of polyamide [10].

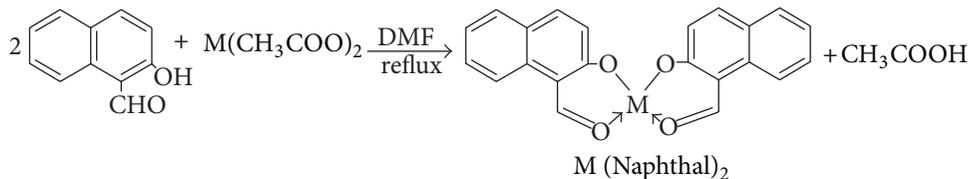
Puffer and Sebenda [11] have described sorption and desorption isotherms of water for several crystalline as well as amorphous polyamides and the model amides. They have shown that, in nylon 6, three molecules of water are sorbed on two neighbouring amide groups. The first molecule is firmly bound between the CO groups, and the other two molecules form H-bonds between the CO and the NH groups (loosely bound water). In nylons, two to six water molecules are sorbed on two amide groups, probably as firmly bound water. Nylon 7 stands somewhere between the two groups.

In our report on poly(methylene diphenylene terphthalamide) and its coordination polymers, we have also observed the moisture pickup by the polyamide as well as its coordination polymers. The number of water molecules sorbed to the amide groups has been considered as 1.5 per CONH group excluding the capillary condensation. Because of the polymeric nature, the possibility of structural defects is always there. Further, the exact amount of adsorbed and capillary condensation water cannot be calculated.



where M = Co(II), Cu(II), or Ni(II) and
Sal = salicylaldehyde

SCHEME 2



where M = Co(II), Cu(II), or Ni(II) and
Naphthal = 2-hydroxy-1-naphthaldehyde

SCHEME 3

3.1. IR Spectral Studies. The structurally important infrared spectral bands for the amino terminated oligomeric ligands and their metal complexes are depicted in Table 2. The assignments are based on the available literature [12, 13]. In the spectrum of PTTA ligand, there is a sharp and strong band at 3305 cm^{-1} attributed to C=O of amide group of polyamide chain. The band at 1630 cm^{-1} is attributed to carbonyl frequency of amide I. The absorption due to NH deformation appears at 1545 cm^{-1} or amide II. Another band due to C–N appears at 1285 cm^{-1} ; p-substituted benzene ring vibration appears at 855 cm^{-1} . A band at 1470 cm^{-1} is assigned to $-\text{CH}_2$ bending mode of polyamide chain of PTTA.

The spectra of all the complexes show a strong and sharp band at 3305 cm^{-1} due to the NH of polyamide chain of PTTA. Appearance of bands in the region $1550\text{--}1555\text{ cm}^{-1}$, as a result of splitting of amide or NH deformation in the spectra of all the complexes, indicates involvement of amino group in the complexation. Therefore, one band is ascribed to C=N–M while the other may be due to amide or NH deformation of amide group of PTTA ligand.

The appearance of new bands in the lower frequency region due to M–O at $560\text{--}520\text{ cm}^{-1}$ and due to M–N in the region of $480\text{--}420\text{ cm}^{-1}$ further supports and confirms the involvement of nitrogen and oxygen atoms in complex formation.

The other bands of the ligands appear uninfluenced upon coordination suggesting noninvolvement of amide groups of polyamide in coordination. The characteristic absorptions due to acetate group could not be observed in the IR spectra of metal complexes thereby suggesting absence of acetate ions. This observation supports the suggested formula without acetate ions on the basis of elemental analysis data. The appearance of new bands in the far IR region attributed to

M–O and M–N further confirms the complexation through nitrogen and oxygen.

3.2. Magnetic Susceptibility Measurements. The diamagnetic behaviour of Ni(II) complexes indicates their square-planar geometry [14]. The square-planar geometry of Cu(II) complexes is indicated by the magnetic moment values in the range of 1.69–1.85 BM [15, 16].

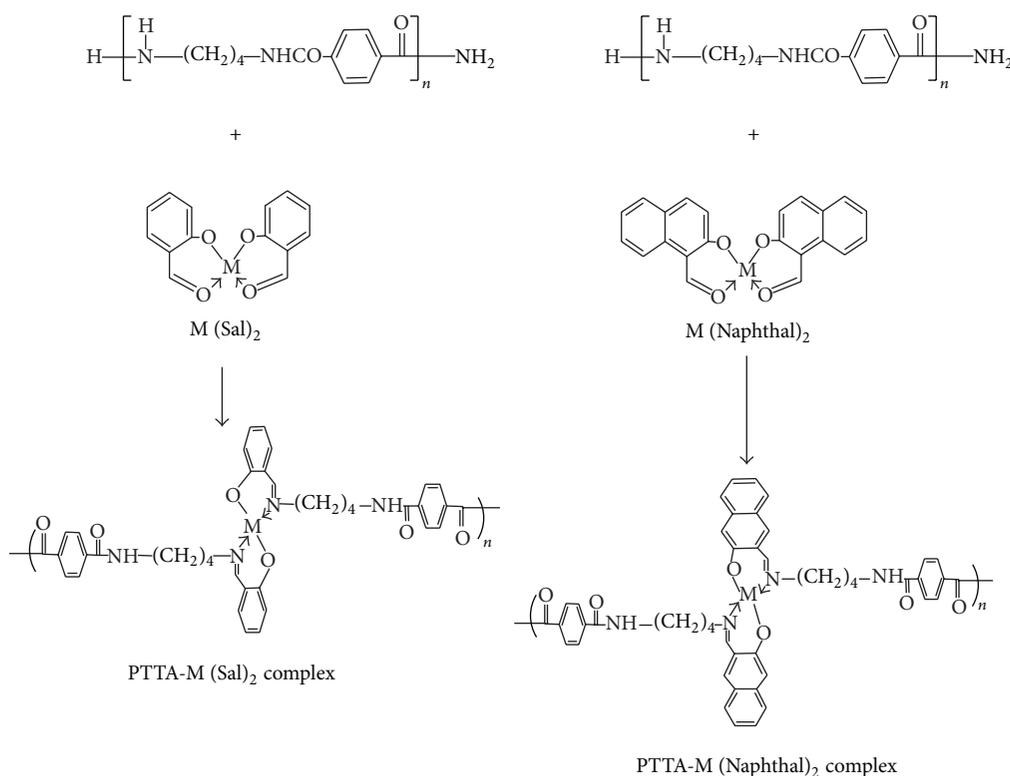
Tetrahedral geometry of Co(II) complexes is inferred from the magnetic moment values of 4.59 and 4.44 for PTTA-Co(II)-Sal and PTTA-Co(II)-Naphthal, respectively. Diamagnetic behaviour of Ni(II) complexes indicates their square-planar behaviour. PTTA-Cu(II)-Sal and PTTA-Cu(II)-Naphthal complexes have magnetic moment values of 1.72 and 1.78, respectively, which were in the range predicted for square-planar complexes of Cu(II).

On the basis of all the aforementioned studies, a tentative structure as shown in Figure 1 can be proposed for the complexes. Magnetic moment values of amide-metal complexes are summarized in Table 3.

3.3. Thermogravimetric Analysis. Thermogravimetric data of polyamide ligand PTTA and its metal complexes are presented in Table 4. The TG curves of ligand PTTA and its complexes were compared in order to determine the influence of metal ion on the thermal stability. Thermal stabilities have been compared on the basis of initial decomposition temperature, residual percentage by weight at a particular temperature, and energy of activation (E) calculated by Fuoss method [17]. PTTA and its complexes with Ni(II)-Sal and Cu(II)-Sal show stepwise degradation whereas PTTA-Co(II)-Sal complex exhibits continuous degradation above 250°C , and the weight becomes constant above 550°C in all the cases. Residual percentage weights at 600°C for the complexes are

TABLE 2: IR spectral assignments of amides and their metal complexes.

Compounds	Assignments cm^{-1}					
	ν_{NH}	Amide (I)	Amide (II)	$\nu_{\text{C=N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$
PTTA	3305 s	1630 s	1545 s	—	—	—
PTTA-Co(II)-Sal'	3305 s	1630 s	1545 s	1550 s	560 s	480 m
PTTA-Co(II)-Naphthal'	3305 s	1630 s	1540 s	1550 s	560 s	485 w
PTTA-Ni(II)-Sal'	3305 s	1630 s	1540 s	1550 sh	540 s	485 s
PTTA-Ni(II)-Naphthal'	3305 s	1630 s	1535 s	1550 s	570 s	470 m
PTTA-Cu(II)-Sal'	3305 s	1630 s	1530 s	1555 s	520 s	490 s
PTTA-Cu(II)-Naphthal'	3305 s	1630 s	1535 s	1560 s	560 m	480 s



where M = Co(II), Cu(II), or Ni(II),
 Sal = salicylaldehyde,
 and Naphthal = 2-hydroxy-1-naphthaldehyde

FIGURE 1

TABLE 3: Magnetic moment values for polyamide-metal complexes.

Compounds	Magnetic moment μ B.M.	Geometry proposed
PTTA-Co(II)-Sal'	4.59	Tetrahedral
PTTA-Co(II)-Naphthal'	4.44	Tetrahedral
PTTA-Ni(II)-Sal'	Diamagnetic	Square planar
PTTA-Ni(II)-Naphthal'	Diamagnetic	Square planar
PTTA-Cu(II)-Sal'	1.72	Square planar
PTTA-Cu(II)-Naphthal'	1.78	Square planar

slightly greater than the residual weight for the ligand. The order of stability on the basis of residual weights can be given as

$$\text{PTTA-Ni(II)-Sal}' > \text{PTTA-Co(II)-Sal}' > \text{PTTA-Cu(II)-Sal}' > \text{PTTA}. \quad (2)$$

On the basis of energy of activation calculated by Fuoss method, the following order of thermal stability was observed:

$$\text{PTTA-Cu(II)-Sal}' > \text{PTTA-Ni(II)-Sal}' > \text{PTTA-Co(II)-Sal}' > \text{PTTA}. \quad (3)$$

TABLE 4: TGA data of PTTA and its metal complexes.

Compounds	Temperature in °C							
	100	200	300	400	500	600	650	700
PTTA	1.0	5.0	10.0	50.0	80.0	98.0	—	—
PTTA-Co(II)-Sal'	0.0	0.0	0.0	19.0	72.0	92.0	93.0	94.0
PTTA-Co(II)-Naphthal'	2.0	3.0	7.0	25.0	91.0	92.0	92.0	92.0
PTTA-Ni(II)-Sal'	0.0	2.0	8.0	42.0	85.0	90.0	91.0	92.0
PTTA-Ni(II)-Naphthal'	4.0	7.0	10.0	22.0	69.0	76.5	78.0	79.0
PTTA-Cu(II)-Sal'	0.0	2.0	9.0	39.0	77.0	94.0	94.0	94.5
PTTA-Cu(II)-Naphthal'	0.0	7.0	13.2	37.5	78.0	90.0	94.0	—

The expected enhancement in the stabilities could not be obtained in the present case contrary to our previous observation [18, 19]. It may be due to the fact that sometimes the metal ion catalyses the degradation of the polymeric ligand. It is also possible that slight changes in polymeric environment influence the thermal degradation phenomenon to a large extent. The ligands which show two-step decomposition indicate the formation of intermediate products during thermal degradation process due to the rupture of polyamide chain. The degradation of amide takes place through the random scission of polymer chain into low molecular weight organic compounds and various volatile gaseous products like CO₂, NH₃, and water are evolved. Therefore it is expected that the different chain environments may be responsible for the different degradation mechanisms. Sazanov et al. [20] in their comparative thermal analysis (CTA) studies with thermally stable polyimides and model compounds have shown that the process of thermooxidation is of successive character; that is, the defective fragments are “burned out” before the main structure is oxidized.

4. Conclusion

Introduction of metal ion in polyamide chain through terminal groups generally results in increase in thermal stability of resulting polymer complexes. Further, this work can be extended to prepare similar kinds of polyamides, and, technique may also be used for increasing the thermal stability of fibres, films, sheets this and blocks of amino group containing polyamides.

Slight lowering in the initial decomposition of few complexes than the ligand PTTA may be due to the catalytic effect of metal ion on thermal degradation process.

Another application of these polyamide complexes may be as antimicrobial agents because of Schiff base moiety.

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