

# Synthesis and Characterization of Coordination Polymers of Polyesters with Pendant Amino Groups

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**ABSTRACT:** Oligomeric polyester, namely, poly(tetramethylene aspartate) (PTMA), was synthesized from D,L-aspartic acid and 1,4-butanediol by a melt-condensation technique. Polyester-metal complexes were synthesized by the reaction of PTMA with hydrated acetates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Mg(II), Ca(II), Pb(II), and Ce(IV) in DMSO. The polyester-metal complexes were characterized by elemental analysis, IR spectral studies, magnetic susceptibility measurements, and thermogravimetry. The metal ions were found to be six-coordinated with two water molecules as additional ligands besides oxygen and nitrogen atoms of polyester repeating units. Thermogravimetric analysis (TGA) showed that coordination polymers are thermally more stable than is polyester. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 751–759, 1998

**Key words:** melt condensation; poly(tetramethylene aspartate); polyester-metal complexes; thermogravimetric analysis; coordination polymers

## INTRODUCTION

The interest in metal-containing polymers has increased since the decade of the 1960s as they show many potential uses as functional materials with desirable chemical and physical properties. Polymer-supported metal complex catalysts, biological agents such as models for various metalloenzymes or biomedical control release agents, solid-state materials such as semiconducting substances, and heat-resistant materials for aerospace requirements were further studied. Sheats presented the history of organometallic polymers.<sup>1</sup> Some extensive reviews have appeared on metal-containing polymers.<sup>2–6</sup>

In polymer-metal complexes, the central metal ions are surrounded by polymeric ligands. The polymer-metal complexes can show interesting characteristics, especially with reference to catalytic activities differing from the corresponding ordinary metal complexes of low molecular weight. The synthesis of coordination polymers is usually achieved by one of the following procedures: (1) a metal complex may yield a polymeric material during its formation, due to favorable donor groups present in the ligand<sup>7–8</sup>; (2) the ligand itself may be a preformed organic polymer to which metal ion may suitably be coordinated<sup>9–12</sup>; and (3) a metal ion may be coordinated with a ligand and the monomeric metal complex may react with another organic compound to form a polymeric complex.<sup>13–16</sup>

The complexing ability of polyesters has been of particular interest as they abound in polar groups and are able to coordinate and/or associate with metal ions. A few research groups have been ac-

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computer 7700 in an inert atmosphere at the rate of 20°C/min.

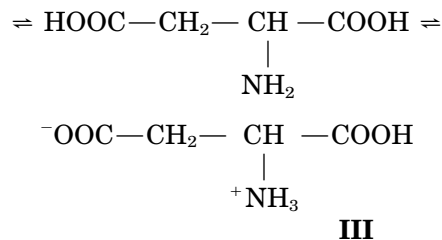
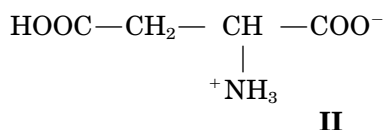
## RESULTS AND DISCUSSION

The degree of polymerization for the polyester PTMA is kept low so that it can be dissolved easily for further reaction with metal acetates for the formation of metal complexes. The polyester cannot be easily purified by crystallization or distillation; therefore, we have used the excess of one reactant (1,4-butanediol) to achieve maximum conversion. Winter et al.<sup>31</sup> in their synthesis of  $\alpha,\omega$ -ethyl maleate-functionalized poly(propylene glycol)s developed a route with 100% chemoselectivity and directed reactions toward 100% conversion by using an excess of the appropriate reagents. The excess chemicals were removed by simple procedures like extraction or filtration.

### Chemoselective Polycondensation

Under this reaction condition, the formation of polyamide is not expected.  $\alpha$ -Amino acids undergo dehydration on heating (200°C) to give diketopiperazines (cyclic diamides).  $\beta$ -Amino acids lose ammonia on heating to form  $\alpha,\beta$ -unsaturated acids. Treatment of acids with amines does not directly give amides. In peptide synthesis, the use of coupling agents such as dicyclohexylcarbodiimide facilitates the reaction to proceed in good yield.<sup>32</sup>

To attack the carboxylic carbon atom of aspartic acid, two competing nucleophiles are the hydroxyl groups of 1,4-butanediol and the amino group of aspartic acid itself. In nucleophiles with similar structures where the attacking atom is nitrogen or oxygen, the order of nucleophilicity is N > O. However, the hydroxyl groups of 1,4-butanediol are better nucleophiles than are the amino group of aspartic acid. Amino acids exist as dipolar ions or zwitterions. Aspartic acid, being an acidic amino acid, exists in two zwitterionic forms, II and III; therefore, it has a greater contribution from the weakly acidic  $-\text{NH}_3^+$  group rather than from the basic  $-\text{NH}_2$  group<sup>33</sup>:



Actually, in the neutral condition, the basic group in amino acids is  $-\text{COO}^-$ , not  $-\text{NH}_2$ .

Further, the strong absorption near 1550  $\text{cm}^{-1}$ , which is very characteristic of *N*-monosubstituted amide, is not observed in the IR spectrum of PTMA. The out-of-plane NH wag which absorbs broadly near 700  $\text{cm}^{-1}$  is also absent from the IR spectrum of PTMA.<sup>34</sup> Therefore, it is concluded that the possibility of the formation of polyamide, if any, is very scarce.

### Composition

Although the results of elemental analysis for polymeric compounds do not have much significance, we can get some indication about the number of metal atoms attached to the polymeric chains. The elemental analysis of ligand and polyester-metal complexes are summarized in Table I with the theoretical compositions based on assumed structures. The number-average molecular mass ( $M_n$ ) was found to be 1750 and this closely resembles the theoretical value of 1773 calculated for  $n = 9$  in formula A. Therefore, for calculation of the theoretical compositions, we used formula I with nine repeat units. For polyester-metal complexes, the observed analytical values are in the best agreement with the ones calculated for the six metal ions per oligomer. The deviation of the observed analysis data from the theoretical values may be attributed to the polymeric nature. The complexes may have a broad molecular weight distribution including low molecular weight (e.g., DP < 9) oligomers, bound to metal ions. Further, in one case, a metal ion may be complexed to only one polymer molecule, and in another, two or three polymers (oligomers) may be attached as ligands to the metal.

### IR Spectral Studies

The important IR bands of PTMA and its metal complexes are listed in Table II(a,b). In the IR spectrum of polyester, a very broad and strong band is observed in the region 3500–3200  $\text{cm}^{-1}$ .

**Table I Analytical Data of PTMA and Its Metal Complexes**

Sample No.	Compounds	Elemental Analysis <sup>a</sup>			
		%C	%H	%N	%M
1	PTMA	51.4	7.2	7.1	—
	C <sub>76</sub> H <sub>127</sub> N <sub>9</sub> O <sub>38</sub>	48.9	5.6	6.7	
2	PTMA–Mn(II)	39.4	6.2	5.4	14.2
	C <sub>76</sub> H <sub>127</sub> N <sub>9</sub> O <sub>38</sub> · Mn <sub>6</sub> · 12H <sub>2</sub> O	40.2	5.2	5.6	12.5
3	PTMA–Co(II)	39.0	6.2	5.4	15.1
	C <sub>76</sub> H <sub>127</sub> N <sub>9</sub> O <sub>38</sub> · Co <sub>6</sub> · 12H <sub>2</sub> O	39.6	5.2	5.3	14.2
4	PTMA–Ni(II)	39.0	6.2	5.4	15.1
	C <sub>76</sub> H <sub>127</sub> N <sub>9</sub> O <sub>38</sub> · Ni <sub>6</sub> · 12H <sub>2</sub> O	38.9	5.6	4.8	14.0
5	PTMA–Cu(II)	38.6	6.1	5.3	16.1
	C <sub>76</sub> H <sub>127</sub> N <sub>9</sub> O <sub>38</sub> · Cu <sub>6</sub> · 12H <sub>2</sub> O	39.0	6.2	4.7	15.2
6	PTMA–Zn(II)	38.4	6.1	5.3	16.5
	C <sub>76</sub> H <sub>127</sub> N <sub>9</sub> O <sub>38</sub> · Zn <sub>6</sub> · 12H <sub>2</sub> O	36.8	3.9	6.4	15.0
7	PTMA–Cd(II)	34.3	5.4	4.7	25.3
	C <sub>76</sub> H <sub>127</sub> N <sub>9</sub> O <sub>38</sub> · Cd <sub>6</sub> · 12H <sub>2</sub> O	35.0	4.9	3.9	23.4
8	PTMA–Hg(II)	28.0	4.5	4.0	37.7
	C <sub>76</sub> H <sub>127</sub> N <sub>9</sub> O <sub>38</sub> · Hg <sub>6</sub> · 12H <sub>2</sub> O	28.6	3.6	4.8	34.0
9	PTMA–Mg(II)	42.8	6.8	5.9	6.8
	C <sub>76</sub> H <sub>127</sub> N <sub>9</sub> O <sub>38</sub> · Mg <sub>6</sub> · 12H <sub>2</sub> O	42.0	5.9	6.2	7.0
10	PTMA–Ca(II)	41.0	6.5	5.6	10.8
	C <sub>76</sub> H <sub>127</sub> N <sub>9</sub> O <sub>38</sub> · Ca <sub>6</sub> · 12H <sub>2</sub> O	45.0	6.0	5.9	10.6
11	PTMA–Pb(II)	28.8	4.5	3.9	38.5
	C <sub>76</sub> H <sub>127</sub> N <sub>9</sub> O <sub>38</sub> · Pb <sub>6</sub> · 12H <sub>2</sub> O	29.0	3.2	4.6	36.2
12	PTMA–Ce(IV)	32.3	5.1	4.5	29.8
	C <sub>76</sub> H <sub>127</sub> N <sub>9</sub> O <sub>38</sub> · Ce <sub>6</sub> · 12H <sub>2</sub> O	33.1	4.7	4.2	25.7

<sup>a</sup> For each compound, the upper values represent theoretical analysis and the lower values show the results obtained experimentally.

In this region, two bands due to asymmetric and symmetric NH frequencies are generally observed near 3500 and 3400 cm<sup>-1</sup>, respectively.<sup>35</sup> The broad band observed for the PTMA in this region suggests the merger of *asym*(NH) and *sym*(NH) and the OH of the terminal hydroxyl groups of the polyester, as glycol has been taken in excess during the PTMA synthesis. Further, the lowering of the frequencies and the broadening of the band in this region suggests intramolecular hydrogen bonding,<sup>3b</sup> which is possible between carbonyl oxygen and amine hydrogens as shown in Figure 1.

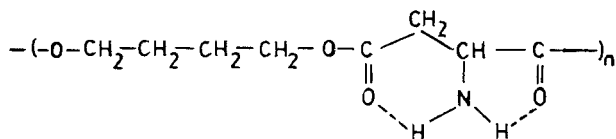
Two strong bands appear at 2940 and 2880 cm<sup>-1</sup> due to the CH asymmetric and symmetric stretching modes of the —CH<sub>2</sub>— group.<sup>34</sup> In the C=O region, a split band with peaks at 1725 and

1715 cm<sup>-1</sup> is observed. The splitting of this band suggests the different environment around C=O groups of the polyester chain as shown in Figure 1. The slight lowering of the C=O frequency from the normal predicted wavenumber may be the result of hydrogen bonding as shown in Figure 1. The other characteristic absorptions arising from the C=O group<sup>36</sup> appear at 1220 and 1170 cm<sup>-1</sup>. A weak band in the region 1640 cm<sup>-1</sup> appears for the  $\delta_{\text{NH}}$  vibration of the amino group.<sup>35</sup> The bands at 1420 and 1470 cm<sup>-1</sup> are assigned to the CH deformation of CH and CH<sub>2</sub> groups adjacent to the carbonyl group, respectively.<sup>37</sup> Bands due to CN (ref. 35c) and NH wagging modes<sup>38</sup> appear at 1050 and 860–830 cm<sup>-1</sup>. A weak and broad band at 740 cm<sup>-1</sup> is assigned to —(CH<sub>2</sub>)<sub>4</sub>— of the polyester chain.<sup>35d</sup> The spectra of the PTMA–metal

**Table II Important IR Spectral Assignments of PTMA and Its Metal Complexes**

(a)						
Assignments	PTMA	PTMA Complexes				
		Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
NH ( <i>asym</i> and <i>sym</i> ) and OH	3500– 3200 (br)	3600– 3180 (br)	3640– 3100 (br)	3540– 3200 (br)	3600– 3200 (br)	3540– 3200 (br)
CH ( <i>asym</i> )	2940 (s)	2960 (m)	2960 (m)	2960 (w)	2960 (m)	2940 (w)
CH ( <i>sym</i> )	2860 (s)	2860 (m)	2880 (m)	2880 (w)	2860 (m)	2860 (s)
C=O	1725 (s)	1705 (s)	1710 (s)	1710 (s)	1710 (s)	1690 (s)
$\delta$ NH $\delta$ HOH	1640 (m)	1630– 1590 (br)	1620– 1600 (br)	1630– 1590 (br)	1630– 1600 (br)	1610– 1590 (br)
$\delta$ CH <sub>2</sub>	1470 (s)	1460 (m)	1470 (m)	1460 (m)	1465 (s)	1460 (m)
$\delta$ CH <sub>2</sub> O	1420 (s)	1410 (w)	1420 (m)	1410 (s)	1400 (m)	1410 (m)
C–O	1260 (s) 1200 (s)	1260 (s) 1200 (m)	1260 (s) 1190 (m)	1250 (s) 1200 (m)	1280 (s) 1160 (s)	1260 (s) 1200 (m)
C–N	1050 (s)	1100 (s)	1100 (m)	1120 (m)	1100 (w)	1100 (m)
NH <sub>2</sub>	880 (m)	880 (m)	880 (w)	860 (w)	830 (w)	840 (m)
H <sub>2</sub> O	660 (m)	680 (s)	660 (s)	650 (m)	660 (m)	680 (m)
M–O	—	620 (s)	620 (s)	680 (m)	630 (m)	610 (s)
M–N	—	540 (s)	530 (m)	540 (m)	560 (s)	545 (m)
(b)						
Assignments	PTMA Complexes					
	Cd(II)	Hg(II)	Mg(II)	Ca(II)	Pb(II)	Ce(IV)
NH ( <i>asym</i> and <i>sym</i> ) and OH	3600– 3280 (br)	3580– 3200 (br)	3580– 3200 (br)	3600– 3200 (br)	3600– 3200 (br)	3600– 3100 (br)
CH ( <i>asym</i> )	2960 (m)	2960 (m)	2940 (m)	2940 (m)	2940 (w)	2940 (m)
CH ( <i>sym</i> )	2860 (m)	2860 (m)	2860 (m)	2860 (w)	2860 (w)	2860 (m)
C=O	1695 (s)	1700 (s)	1710 (s)	1695 (s)	1700 (s)	1700 (s)
$\delta$ NH $\delta$ HOH	1630– 1620 (br)	1620– 1570 (br)	1630– 1590 (br)	1630– 1600 (br)	1655– 1620 (br)	1620– 1590 (br)
$\delta$ CH <sub>2</sub>	1460 (m)	1470 (s)	1470 (s)	1460 (m)	1460 (m)	1460 (br)
$\delta$ CH <sub>2</sub> CO	1410 (w)	1410 (w)	1420 (s)	1425 (m)	1400 (s)	1400 (m)
C–O	1260 (m) 1200 (s)	1260 (s) 1200 (m)	1280 (s) 1195 (s)	1260 (s) 1200 (m)	1250 (s) 1200 (s)	1250 (m) 1195 (s)
C–N	1100 (w)	1100 (m)	1090 (w)	1100 (w)	1070 (m)	1100 (w)
NH <sub>2</sub>	860 (m)	830 (w)	890 (w)	880 (br)	870 (s)	860 (br)
H <sub>2</sub> O	660 (s)	670 (s)	670 (m)	—	690 (s)	650 (s)
M–O	610 (s)	805 (m)	595 (w)	590 (m)	590 (m)	595 (m)
M–N	555 (s)	510 (s)	535 (m)	510 (m)	530 (s)	520 (s)

s, strong; m, medium; w, weak; br, broad; *asym*, asymmetric; *sym*, symmetric.



**Figure 1** Intramolecular hydrogen bonding in PTMA.

complexes show a hump or a very broad band in the region  $3600\text{--}3200\text{ cm}^{-1}$ . The greater broadness of this band than that of the ligand PTMA is attributed to the merger of NH (metal-coordinated),<sup>39</sup> the OH of the polyester terminal, and metal-coordinated water molecules. The presence of the coordinated water in complexes is further confirmed by the bands in the region  $1600\text{--}1570\text{ cm}^{-1}$  for HOH deformation and  $670\text{--}650\text{ cm}^{-1}$  for the rocking mode of the coordinated water.<sup>40,41</sup> The band due to the C=O of the ligand is shifted to a lower-frequency region in the spectra of the complexes and merges with the other bands in the region; this observation positively indicates the involvement of the C=O group in the complexation. The  $\delta\text{NH}$  at  $1640\text{ cm}^{-1}$  in the PTMA spectrum shifts to a lower frequency and appears as a broad band, which accounts for the participation of the amino group in the coordination. The participation of nitrogen and oxygen in the coordination in all the complexes is further supported by the appearance of M—O and M—N modes in the regions  $690\text{--}620$  and  $560\text{--}410\text{ cm}^{-1}$ , respectively.

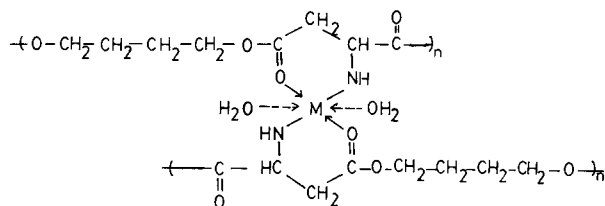
### Magnetic Susceptibility Measurement

The magnetic moment values of the polyester-metal are summarized in Table III for different polyester-metal complexes. The magnetic-moment data support the octahedral geometry of the metal complexes.

The magnetic moment of the PTMA-Co(II) complexes in the present case is found to be  $4.2\ \mu_{\text{B}}$ . This value is consistent with the high-spin

**Table III** Magnetic Moment Values of PTMA-Metal Complexes

Sample No.	Compounds	$\mu_{\text{eff}}$ ( $\mu_{\text{B}}$ )	Geometry Proposed
1	PTMA-Co(II)	4.2	Octahedral
2	PTMA-Ni(II)	2.96	Octahedral
3	PTMA-Cu(II)	2.2	Octahedral
4	PTMA-Mn(II)	6.2	Octahedral



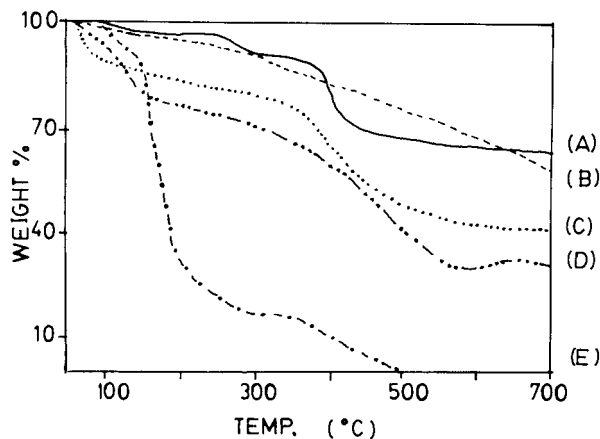
**Figure 2** Structure of PTMA-metal complex.

octahedral geometry. The higher  $\mu_{\text{eff}}$  value of the Co(II) complexes is attributed to the orbital contribution. Octahedral Ni(II) complexes are expected to show paramagnetism due to two unpaired  $d$ -electrons. The magnetic moment value of Ni(II) octahedral complexes generally lies between  $2.9$  and  $3.4\ \mu_{\text{B}}$  depending upon the magnitude of orbital contribution.<sup>42</sup> The experimental magnetic moment value for the PTMA-Ni(II) complex is found to be  $2.96\ \mu_{\text{B}}$ , which is in agreement with the octahedral geometry. In the present study, the magnetic moment value for the PTMA-Cu(II) complex is found to be  $2.2\ \mu_{\text{B}}$ , which is in consonance with the octahedral geometry.<sup>42</sup> The Mn(II) ion, having a  $d^5$  configuration, generally forms high-spin complexes because of the additional stability of the half-filled  $d$ -shell. The magnetic moment value is in the expected range of octahedral geometry.<sup>43</sup> Keeping in mind the stoichiometry of the complexes obtained from the analytical results, the metal-oxygen and metal-nitrogen bonding concluded from the IR studies, and the octahedral geometry suggested by magnetic measurements, the structure proposed for the PTMA-metal complexes is as shown in Figure 2.

### Thermal Analysis of PTMA and Its Complexes

The TG data of the PTMA and its complexes is depicted in Figure 3. The ligand PTMA shows a 2.73% weight loss up to  $100^\circ\text{C}$ , which may be due to the loss of absorbed water. The observed percentage weight loss in the range  $100\text{--}143^\circ\text{C}$  is 8%, which corresponds to the percentage weight of the  $-\text{O}-\text{CO}-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{COOH}$  unit.

The mechanism of the decomposition of the polyester has been suggested on the basis of the decomposition of simple esters.<sup>44</sup> In the first step, a carboxyl compound and a vinyl ester is formed as a result of *cis*-elimination in the presence of  $\beta$ -H atoms preceded by the formation of a six-membered chelate ring through H bonding. In the case of PTMA also, a thermal degradation of the



**Figure 3** TGA of PTMA and its complexes: (A) PTMA–Pb(II); (B) PTMA–Ni(II); (C) PTMA–Mn(II); (D) PTMA–Co(II); (E) PTMA.

terminal fragments can occur through the formation of the six-membered chelate ring (Fig. 4). Above 143°C, a rapid weight loss is observed in the ligand PTMA and 75% of weight is lost up to 220°C and it is decomposed completely into volatile products up to 500°C.

The perusal of Figure 3 clearly indicates that the metal complexes of the polyester ligand PTMA exhibit superior thermal stabilities to those of the ligand. For Co(II) and Mn(II) complexes, the initial weight loss up to 120–140°C corresponds to the theoretical amount for two water molecules. Therefore, it is suggested that coordinated water molecules are lost up to this temperature range. In the case of Ni(II) and Pb(II) complexes, the weight corresponding to two water molecules is gradually lost up to 300°C. It is suggested that for Ni(II) and Pb(II) all the coordinated water molecules present in the polymeric complexes are not lost suddenly in a sharp temperature range but gradually over a wider temperature range. Below 140°C, the order of the stability of the complexes with respect to metal ions is Mn(II) < Co(II) < Ni(II) < Pb(II). This stability order tallies with the familiar order of the stability of hydration for the first transition series.<sup>45</sup> The highest stability of the Pb(II) complex may be due to the large radius and the high ionization potential of Pb(II).<sup>45</sup> A steeper decrease in the weight of the complexes is observed only above 360°C, which may be due to the onset of the decomposition of the main chain of PTMA. Complexes attain a constancy in weight, except for Ni(II), at about 650–700°C. The residual weight

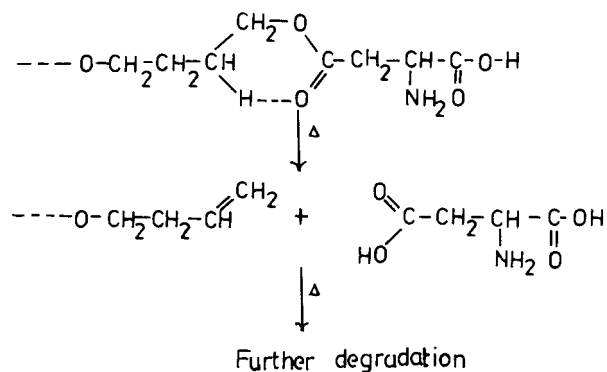
in all the complexes is more than the metal content.

It is apparent from Figure 3 that the Pb(II) and Ni(II) complexes are comparatively more thermally resistant than are the Mn(II) and Co(II) complexes. The rate of weight loss in the case of the Ni(II) complex is almost uniform throughout, suggesting greater regularity in its polymeric structure than in that of the other polymeric complexes. The order of stability on the basis of the residual weight at 700°C appears to be Co(II) < Mn(II) < Ni(II) < Pb(II). This order does not match the Irving–Williams<sup>45</sup> order of stability for the complexes of divalent metal ions. The deviation from the Irving–Williams order probably reflects that the correlations between the chemical structure and stability cannot be drawn for the coordination polymers by comparison with the data for analogous complexes, as the polymer chain environment may affect the course of degradation.<sup>29</sup>

The enhancement in the thermal stability of polyester–metal complexes in comparison to the ligands may be due to the following facts:

1. Increase in the molecular weight due to the linking of different polyester chains on account of the coordination.
2. Formation of a three-dimensional or network structure due to complexation.
3. Formation of the six-membered ring in the backbone of the polyester chain which increases the stiffness of the polyester chain.

Bottei and Frangman<sup>46</sup> suggested that the six-membered ring is more stable than is the five-membered ring. On the basis of the increased stability of the polyester–metal complexes, we propose the formation of a six-membered ring (Fig.



**Figure 4** Degradation mechanism.

2) instead of the five-membered ring in polyester-metal complexes.

### Application Aspect

Although the coordination polymers synthesized from PTMA may or may not find applications immediately but the theoretical and empirical knowledge accumulated in the course of the investigations of homogeneous and heterogeneous catalysts and the chemistry of high molecular complex and organometallic compounds may be helpful in designing catalytic systems of the desired activating ability in the future.

The development of immobilized catalytic systems has led to progress in many fields of metal complex catalysis. These systems are characterized by physical or chemical bonding of one of the components or a catalytic complex to a solid support carrier which may be inorganic (oxidic) or organic (polymeric) in nature. Such catalysts combine the high activity of homogeneous catalysts with the technological advantage over those of inorganic ones.<sup>47</sup>

With the exception of a small group of catalytic RNA molecules, all enzymes catalyzing the reactions of cell metabolism are proteins, which, in turn, are composed of amino acid units. Several enzymes require cofactors as additional chemical components which may be either one or more complex organic or metalloorganic molecules called a coenzyme. The metal complexes of polymers based on amino acids would be of special interest as they may operate at higher temperatures also, whereas the biological systems work well at ambient temperatures only.

Pitha<sup>48</sup> reviewed the physiological activities of synthetic analogs of polynucleotides. Synthetic polymers are not biodegradable; hence, it is expected that the effects of these polymers on cells or animals would be strong and long-lasting. However, the effectiveness of polymers is low because of the very low ability of polymers to penetrate into the interior of cells and the cells may capture foreign polymers in membrane-coated vesicles. In general, synthetic polymers do not possess strong pharmacological or physiological activities, but the design and synthesis of physiologically active polymers may be described as a field of the future.

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