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Coordination Polymers with Inorganic Main Chains

S.V.Vinogradova and O.V.Vinogradova

A specific set of properties distinguishes coordination polymers with inorganic main chains. The review deals with modern ideas about the structures of these polymers, the possible ways of synthesising them, and a survey of the available data on the properties of metal-containing polymers such as polyphosphinates, polyarsinates, etc.
The bibliography includes 125 references

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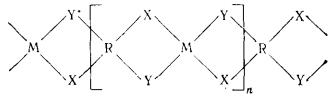
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I. INTRODUCTION

Extensive experimental data have now accumulated on the synthesis and properties of polymeric organic derivatives of the elements and inorganic polymers. Polymers of this kind include in particular polyorganosiloxanes which have found numerous practical applications and also polyorganosiloxanes containing other elements, which possess a set of valuable properties [1]. Coordination polymers can also have main chains consisting of inorganic elements only. The available information about the synthesis and properties of coordination polymers has been described in a number of review publications [2-11].

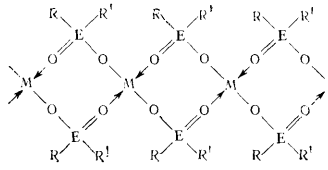
Coordination polymers can be divided into two types on the basis of the structure of the main chain.

1. Polymers with chains consisting of organic derivatives of the elements:



where M is a metal atom with a valence ≥ 2, X = −O−, −S−, =N−, etc., and Y = >CO, −N<, −N=O, >C=S, etc.

2. Polymers with inorganic chains:



where M is a metal atom, E the atom of an acid-forming element, for example phosphorus, arsenic, or sulphur, and R and R′ are organic groups.

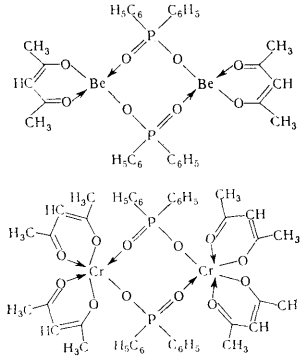
Coordination polymers of the second type, i.e. polymers with inorganic chains, appear to be the most promising. Some of them are fairly thermostable, are capable of flowing under load, and are soluble in the usual organic solvents.

The present review is devoted to coordination polymers with inorganic main chains. Polymers of this type, namely metal polyphosphinates, polyphosphinothioates, and polyarsinates, constitute an unusual group of coordination polymers with the ligands in bridge positions between the metal atoms. The chemistry of bridge coordination polymers has developed mainly during the last decade, although metal derivatives of phosphinic acids were known as early as 1896. [12]

One of the first experimental studies indicating the polymeric nature of the compounds of phosphinic acid with certain metals concerned the viscosity of the product synthesised by Healy and Kennedy [13] by the reaction of di-n-butylphosphinic acid with uranyl acetate, published in 1959. In 1962 Coates and Golightly [14] synthesised cobalt polyphosphinates. The reports of Block and coworkers on the polymeric nature of a number of metal phosphinates were published in the same year [15-18].

II. THE STRUCTURE OF COORDINATION POLYMERS WITH INORGANIC MAIN CHAINS

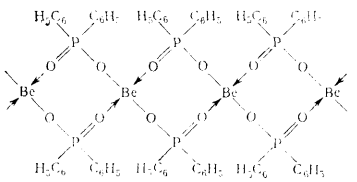
The hypothesis of the bridging properties of phosphinate anions, each of which is linked to two metal atoms, was already put forward in the first reports dealing with the synthesis of polyphosphinates. The bridge type of bond in beryllium and chromium polyphosphinate dimers was demonstrated by Block and coworkers [15,16,18] on the basis of an ebullioscopic determination of their molecular weights, infrared spectroscopic data, and microanalysis.



These dimers were obtained by the interaction of diphenylphosphinic acid with an excess of beryllium acetylacetonate *in vacuo* at 100°C and with an excess of chromium acetylacetonate at 240°C. [15,18] Subsequently the structure of the

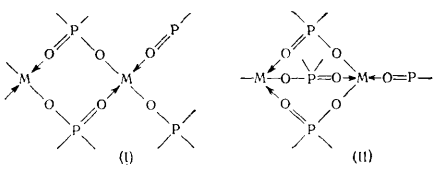
chromium phosphinate dimer was confirmed by an X-ray diffraction study of its single crystals[19]. In these cyclic derivatives the metal atoms are incorporated in the chelate ring with acetylacetone and simultaneously in an eight membered coordination ring with the phosphinate groups[20].

In those cases where diphenylphosphinic acid was introduced into the reaction with beryllium acetylacetonate in a twofold molar excess, the acetylacetonate groups were completely split off and the product was a polycyclic polymer with phosphinate bridges, having the following structure according to the authors[19]:



Block proposed a similar structure also for the polyphosphinates of other metals: cobalt and zinc[16,21-27] and chromium[15,28-34].

Later the Italian investigators Ripamonti, Giancotti, Giordano, and others[35-42] established by X-ray diffraction that certain polyphosphinates of the type MX_2 (M is a bivalent metal and X the phosphinate anion) have a structure different from structure (I) proposed by Block. Their X-ray diffraction study of zinc polydi-n-alkylphosphinates and poly-n-butylphenylphosphinate showed that the chain structure in these crystalline polymers corresponds to structure (II), which includes alternating single and triple bridges:



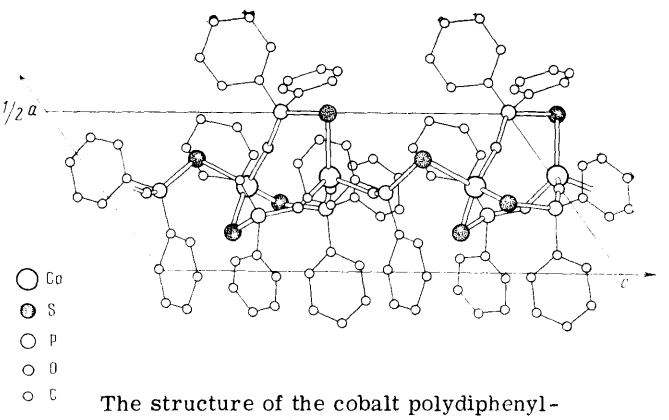
(I) (II)

According to the authors, this structure provides the best explanation of the elastic properties of the amorphous metal polyphosphinates at low temperatures, estimated from the brittleness temperatures[22], since polymeric chains with a type (II) structure should be fairly elastic owing to the possibility of rotation about the P–O and O–M single bridge bonds[35,38,39]. X-Ray diffraction data for cobalt polydi-n-alkylphosphinates[35,38,39] and mixed zinc-containing polymers based on di-n-butyl- and diphenyl-phosphinic acids with the general formula $\{Zn[(C_4H_9)_2PO_2]_{2-2x}[(C_6H_5)_2PO_2]_{2x}\}_n$[39,40] also support structure (II).

Giordano et al.[40] concluded on the basis of an X-ray diffraction study of zinc poly-n-butylphenylphosphinate that the phenyl and n-butyl side groups of the phosphorus atoms in the polymer chain are distributed in a non-ordered fashion.

The influence of the nature of the side groups at the phosphorus atom on the conformation of the polyphosphinate macromolecules has been investigated[37] for mixed beryllium polyphosphinates incorporating di-n-butyl- and diphenyl-phosphinate anions as bridging ligands. It was shown that the skeletal structure of beryllium polydiphenylphosphinate and of mixed polymers with a high content of diphenylphosphinate groups differs from the structure of beryllium polymers in which di-n-butylphosphinate groups predominate. It was found that, depending on the nature of the organic groups, the macromolecule can have a helical or extended conformation, the former being probably characteristic of diphenylphosphinate polymers and the latter of di-n-alkylphosphinate polymers. It is believed that, when a critical content of the more bulky diphenylphosphinate group is reached in the mixed polymer, the extended chain conformation becomes energetically less favourable owing to the appearance of a steric factor, which leads to the generation of a helical structure of the mixed polymers.

X-Ray diffraction was also used by Bruckner et al.[43] to investigate the structure of cobalt polydiphenylphosphinomonothioate (see Figure). The Figure shows that the structure of the monoclinic crystals of this polymer contains two types of cobalt atoms, those of one type being linked to one sulphur atom and three oxygen atoms and those of the other type to three sulphur atoms and one oxygen atom, i.e. the structure is analogous to structure (II) of metal polyphosphinates.



The structure of the cobalt polydiphenylphosphinomonothioate chain.

Thus the distribution of phosphinate groups in the bridge positions between the metal atoms in the polymer chain may be regarded as established for metal polyphosphinates and related polymers. As mentioned above, the structure of the polymer chain of metal-containing polymers based on phosphinic acids can be described in terms of two main structures: (I) and (II), differing in the distribution of the phosphinate groups between the metal atoms. However, one should note that data favouring structure (II) have been obtained only for bivalent metal polyphosphinates with a coordination number of four. Furthermore, they are based on a study of the structure of single crystals grown under special conditions.

The polyphosphinate single crystals were obtained on slow evaporation of the solvent from the polymer solution in water[44] or in a benzene–alcohol mixture[39,40]. Block[45] noted that structure (II) is in principle impossible for certain polyphosphinates, for example for the *trans*-form of chromium polydiphosphinate having the general formula $|Cr(H_2O)(OH)(OPRR'O)_2|_n$.

It follows from the foregoing that it is as yet impossible to reach an unambiguous conclusion about the distribution of the phosphinate bridge groups in the polymers. It is probably also impossible to rule out the possibility of a structure of the polyphosphinates in which the polymer chain includes units of two types corresponding to structures (I) and (II).

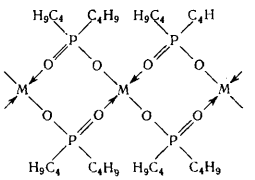
In the treatment below we shall employ the structural formulae of the coordination polymers with inorganic main chains which were proposed by the authors of the studies quoted.

III. SYNTHESIS OF METAL POLYPHOSPHINATES BY THE POLYCOORDINATION REACTION

Metal polyphosphinates have been reviewed by Block[45] and in separate chapters in a number of monographs[46-50]. They can be obtained by the reaction of diorganophosphinic acids with metal salts, by the oxidative decarbonylation of metal carbonyls, by the pyrolysis of complex metal salts with phosphinic acids, and by other methods.

Metal polyphosphinates are usually obtained by the polycoordination of diorganophosphinic acids and various metal-containing compounds: chlorides, acetates, nitrates, acetylacetonates, carbonyls, and organometallic derivatives. The Table shows that the metal polyphosphinates described in the literature differ appreciably in their polymerisation coefficients.

The polycoordination of phosphinic acids with metal salts can be achieved in solution[18,22,23,41,56-58,61,64,65-69,75], in the melt[16,18,51,65,75], and at an interface[16,35,41,44,54]. Thus zinc, cobalt, and manganese polydibutylphosphinates were obtained from the corresponding metal salts and di-n-butylphosphinic acid or its sodium salt by polycoordination in solution and at an interface[41,69]:



where M = Zn, Co, or Mn.

The interaction of phosphinic acids with metal salts is a polycondensation process. The formation of metal-containing coordination polymers by the polycoordination method has a number of characteristic features due to the nature of the M–O bonds arising in this process: ionic–covalent and coordinate.

The polycoordination reactions of phosphinic acids with metal salts proceed readily even at the usual temperatures. However, the ease of formation of coordination compounds

Metal polyphosphinates and their properties.

No.	Repeat unit	Degree of polymerisation	Polymer solvent	[η], dl g⁻¹	M.p., °C	Temperature of the onset of weight loss, °C		References
						in air	in an inert atmosphere	
1	2	3	4	5	6	7	8	9
1	Be [OP(CH$_3$)$_2$O]$_2$				465	522[a]	540[a]	13, 18, 51, 52
2	Be [OP(C$_4$H$_9$)$_2$O]$_2$	138; 37	Benzene, $CHCl_3$, CCl_4	0.42[b] (benzene)	452	—	410[a]	
							515[a]	37, 51, 53
3	Be [OP(C$_6$H$_{11}$)$_2$O]$_2$	62; 215	Hydrocarbons, CCl_4			457[a]	445[a]	51, 53
4	Be [OP(C$_7$H$_{15}$)$_2$O]$_2$	32; 140	Hydrocarbons				420[a]	51, 53
5	Be [OP(CH$_3$)(C$_6$H$_5$)O]$_2$	94; 15	Benzene		infusible	500[a]	525[a]	51, 53
6	Be [OP(C$_6$H$_5$)$_2$O]$_2$		—		infusible	545[a]	530, 610[a]	16,18,37,51,52,54
7	Be [OP(C$_6$F$_5$)$_2$O]$_2$		—		infusible		470[a]	51
8	Be [OP(CF$_3$)(C$_6$H$_5$)O]$_2$	30; 157	Toluene					53, 55
9	Be [OP(CH$_3$)$_4$O]$_2$		—				515[a]	51
10	Zn [OP(CH$_3$)$_2$O]$_2$		Water		340		440	23, 39, 54
11	Zn [OP(C$_4$H$_9$)$_2$O]$_2$	>25; 56	Benzene, $CHCl_3$, CCl_4	0.3–0.7[b] 5.45[b] (benzene), $CHCl_3$)	177, 250	185, 200	250	21, 22, 24, 35, 38, 39, 44, 56, 57
12	Zn [OP(C$_6$H$_{13}$)$_2$O]$_2$		Non-polar solvents		152			38
13	Zn [OP(C$_7$H$_{15}$)$_2$O]$_2$	200	Benzene, toluene, $CHCl_3$	18.5[b] (benzene), $CHCl_3$)	140	170		57
14	Zn [OP(C$_8$H$_{17}$)$_2$O]$_2$		Benzene, toluene, $CHCl_3$, CCl_4	5.22[b] (benzene),	150–160	170		57, 58
15	Zn [OP(C$_9$H$_{19}$)$_2$O]$_2$		Benzene, toluene, $CHCl_3$, CCl_4	0.25[b] (benzene)	150–160	170		57
16	Zn [OP(C$_{10}$H$_{21}$)$_2$O]$_2$		Non-polar solvents		151			38
17	Zn [OP(C$_{12}$H$_{25}$)$_2$O]$_2$		Benzene, toluene $CHCl_3$, CCl_4	0.15[b] (benzene)		170		57
18	Zn [OP(C$_4$H$_9$)$_2$O] [OP(C$_6$H$_{13}$)$_2$O]		Benzene, toluene, $CHCl_3$, CCl_4	0.4[b] (benzene)	150			38
19	Zn [OP(C$_4$H$_9$)$_2$O] [OP(C$_7$H$_{15}$)$_2$O]		Benzene, toluene, $CHCl_3$, ether		155–165	180		59
20	Zn [OP(C$_4$H$_9$)$_2$O] [OP(C$_8$H$_{17}$)$_2$O]	>20	Chloroform	0.4–0.5 (benzene, $CHCl_3$)	120, 150			22, 54
21	Zn [OP(C$_4$H$_9$)$_2$O] [OP(C$_{10}$H$_{21}$)$_2$O]		Benzene, $CHCl_3$, CCl_4					38
22	Zn [OP(cyclo-C$_6$H$_{11}$)$_2$O]$_2$		—		360–380	170		59
23	Zn [OP(CH$_3$) (C$_6$H$_5$)O]$_2$	>30	Benzene, $CHCl_3$, H_2O	0.02 ($CHCl_3$)	200		415, 425	16, 23, 39, 54, 60
24	Zn [OP(CH$_3$)$_2$O] [OP(C$_6$H$_5$)$_2$O]	7	Benzene, $CHCl_3$		120		430	23, 24, 39, 54
25	Zn [OP(CH$_3$)(C$_6$H$_5$)O] [OP(C$_6$H$_5$)$_2$O]	>25	Benzene $CHCl_3$	0.02 ($CHCl_3$)	150		430	24
26	Zn [OP(C$_4$H$_9$)$_2$O] [OP(C$_6$H$_5$)$_2$O]		Benzene, $CHCl_3$, ethanol	0.53[b] (benzene)		200		56
27	Zn [OP(C$_4$H$_9$)$_2$O][OP(CH$_3$–C$_6$H$_3$–O–C$_6$H$_3$–CH$_3$)O]		Ethanol, benzene, $CHCl_3$	0.81[b] (benzene)			195	56
28	Zn[OP(C$_4$H$_9$)]O][OP(CH=CHC$_6$H$_4$)O]		$CHCl_3$	0.13[b] ($CHCl_3$)				56
29	Zn [OP(CH=CHC$_6$H$_4$)$_2$O]		Sovol		340–360	285, 170	335	56, 61, 59
30	Zn[OP(CH$_3$–C$_6$H$_3$–O–C$_6$H$_3$–CH$_3$)O]$_2$		—	—	450	465		56
31	Zn [OP(C$_6$H$_5$)$_2$O]$_2$			—	—	425	450, 495, 460	16, 23, 39, 54, 56, 59, 62
32	Co [OP(CH$_3$)$_2$O]$_2$		Water		342–343		445	14, 24
33	Co [OP(C$_2$H$_5$)$_2$O]$_2$	9	Benzene			285[a], 310[a]		59
34	Co [OP(C$_4$H$_9$)$_2$O]$_2$	20	Benzene, CCl_4, water			295, 330[a]		35, 44, 63, 64

Table (cont'd)

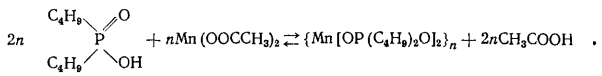
No.	Repeat unit	Degree of polymerisation	Polymer solvent	[η], dl g^{-1}	M.p., °C	Temperature of the onset of weight loss, °C		References
						in air	in an inert atmosphere	
1	2	3	4	5	6	7	8	9
35	Co [OP(CH$_3$) (C$_6$H$_5$)O]$_2$	>30	Benzene, $CHCl_3$, water	0.02—0.05	275			
		13		($CHCl_3$)	226—227		445	14, 24
36	Co [OP(C$_6$H$_5$)O]$_2$		Benzene, water		infusible		485	14, 24, 54, 65
37	Co [OP(CH$_3$)$_2$O] [OP(C$_6$H$_5$)$_2$O]	14	$CHCl_3$		275			14, 24
38	Co [OP(CH$_3$)(C$_6$H$_5$)O] [OP(C$_6$H$_5$)$_2$O]	8	$CHCl_3$		140			24
39	Co[OP(CH$_3$C$_6$H$_3$—O—C$_6$H$_3$—CH$_3$)O]$_2$					360, 450[a]		65
40	Mo [OP(C$_6$H$_5$)$_2$O]$_2$		THF, $CHCl_3$, DMF		230—235	200		66, 67, 68
41	W [OP(C$_6$H$_5$)$_2$O]$_2$				300	340	390	66, 67, 68
42	UO_2[OP(C$_2$H$_5$)$_2$O]$_2$	14	Benzene			260, 380[a]		63
43	UO_2[OP(C$_4$H$_9$)$_2$O]$_2$	11	Benzene			300, 420[a]		63
44	UO_2[OP(C$_6$H$_5$)$_2$O]$_2$	9	Benzene			395, 460		58, 63
45	Mn [OP(C$_4$H$_9$)$_2$O]$_2$		Benzene, toluene	0.87[b] (benzene)	220	230		57, 69
46	Mn [OP(C$_7$H$_{15}$)$_2$O]$_2$		Benzene, toluene	0.80[b] (benzene)	200	225		57
47	Mn [OP(C$_8$H$_{17}$)$_2$O]$_2$	25	Benzene, toluene	0.60[b] (benzene)	215	200		57, 58
48	Mn [OP(C$_9$H$_{19}$)$_2$O]$_2$		Benzene, toluene,$CHCl_3$	0.45[b] (benzene)	190	170		57
49	Mn [OP(C$_{12}$H$_{25}$)$_2$O]$_2$		Benzene, toluene, $CHCl_3$	0.13[b] (benzene)	89—93	170		57
50	Mn [OP(*trans*-C$_6$H$_{11}$)$_2$O]$_2$		Insoluble		—	230		59
51	Mn [OP(C$_6$H$_5$)$_2$O]$_2$		Insoluble		440	450	470	66, 67, 68
52	Mn [OP(C$_4$H$_9$)$_2$O]$_3$		Insoluble		—	180		69
53	Al(OC$_3$H$_7$)$_2$[OP(CH$_3$)$_2$O]	3	Aromatic hydrocarbons, alcohols, ethers					70
54	Al [OP(CH$_3$)$_2$O]$_3$		—	—	infusible		495[a]	71
55	Al [OP(CH$_2$CH$_2$CF$_3$)$_2$O]$_3$		—	—	355		120, 370[a]	71
56	Al [OP(C$_5$H$_{11}$)$_2$O]$_3$	—	—		390—415			71
57	Al [OP(C$_6$H$_{13}$)$_2$O]$_3$	—	—	—	380—410			71
58	Al [OP(C$_8$H$_{17}$)$_2$O]$_3$	—	THF		385—415			71
59	Al [OP(C$_5$H$_{11}$)$_2$O][OP(C$_7$H$_{15}$)$_2$O]$_2$	—	THF		335 (400)			71
60	Al[OP(C$_6$H$_{13}$)$_2$O]$_{1.5}$[OP(C$_8$H$_{17}$)$_2$O]$_{1.5}$		THF		300—310		170, 425[a]	71
61	Al [OP(C$_7$H$_{15}$)$_2$O] [OP(C$_4$H$_9$)·(C$_6$H$_5$CH$_2$)O]$_2$	270—670	THF, toluene, heptane	10—30 (THF)	285—300		170, 400[a]	71
62	Al [OP(C$_8$H$_{17}$)$_2$O] [OP(C$_4$H$_9$)·(C$_6$H$_5$CH$_2$)O]$_2$	23—1050	THF, toluene, heptane	15—37 (THF)	300—320		170, 380[a]	71
63	Al [OP(C$_8$H$_{17}$)$_2$O]$_{1.5}$[OP(C$_{18}$H$_{37}$)$_2$O]$_{1.5}$	12—29	THF	8—31 (THF)	330—370	170, 315[a]		71
64	Al[OP(C$_4$H$_9$)(C$_7$H$_7$)O]$_2$[OP(C$_7$H$_{15}$)$_2$O]	700	THF	35 (THF)	295		400	72
65	Al [OP(C$_4$H$_9$)(C$_7$H$_7$)O]$_2$[OP(C$_8$H$_{17}$)$_2$O]	560	THF	37 (THF)	315		400	72
66	Al [OP(C$_6$H$_5$)$_2$O]$_3$		—	—	infusible	480[a]		73
67	Al(F) [OP(CH$_3$)$_2$O]$_2$		—	—	385—430		500	74, 75
68	Al(F) [OP(C$_5$H$_{11}$)$_2$O]$_2$		—		250—260		350	74
69	Al(F) [OP(C$_6$H$_{13}$)$_2$O]$_2$	140	THF		185—230		350	74
70	Al(F) [OP(C$_8$H$_{17}$)$_2$O]$_2$		THF		200—220		350	74
71	Al(F)[OP(C$_6$H$_{13}$)$_2$O][OP(C$_8$H$_{17}$)$_2$O]		THF		110—130		350	74
72	Al(F)[OP(C$_7$H$_{15}$)$_2$O][OP(C$_{12}$H$_{25}$)$_2$O]		THF		70—85		350	74
73	Al(F)[OP(C$_6$H$_5$)$_2$O]$_2$				420—450		500	74
74	Al(Cl)[OP(C$_8$H$_{13}$)$_2$O]$_2$	6	THF					74
75	Fe(AcAc)[OP(C$_6$H$_5$)$_2$O]$_2$	15	$CHCl_3$, ethanol, benzene				340	75
76	Fe(CO)[OP(C$_6$H$_5$)$_2$O]$_3$					90		66, 67
77	Fe(CO)$_2$[OP(C$_7$H$_5$)$_2$O]$_2$		Benzene				300	76
78	Fe [OP(C$_6$H$_5$)$_2$O]$_3$						300	67
79	Zr [OP(C$_6$H$_5$)$_2$O]$_3$		Organic solvents			455[a]		73, 77
80	Cr(H$_2$O)(OH) [OP(CH$_3$)$_2$O]$_2$	>60	$CHCl_3$, water	0.13 ($CHCl_3$)		350		30, 32
81	Cr(H$_2$O)(OH) [OP(C$_8$H$_{17}$)$_2$O]$_2$		$CHCl_3$	0.30—0.67 ($CHCl_3$)				21, 78, 79
82	Cr(H$_2$O)(OH) [OP(CH$_3$)(C$_6$H$_5$)O]$_2$	>25	$CHCl_3$	0.1—0.78 ($CHCl_3$)	infusible		365	30, 32, 54, 78—82
83	Cr(H$_2$O)(OH [OP(C$_6$H$_5$)$_2$O]$_2$	345	Benzene, $CHCl_3$,THF	0.04—1.0 ($CHCl_3$)		355	375	28, 30, 32, 34, 78, 79, 82, 83
84	Cr(OH) [OP(C$_8$H$_{17}$)$_2$O]$_2$		Ethanol					78
85	Cr(OH) [OP(CH$_3$)(C$_6$H$_5$)O]$_2$		Ethanol					78
86	Cr(OH) [OP(C$_6$H$_5$)$_2$O]$_2$		$CHCl_3$	0.12—1.0 ($CHCl_3$)				78
87	Cr(OH)[OP(C$_6$H$_5$)$_2$OH][OP(C$_6$H$_5$)$_2$O]$_2$	26						84
88	Cr(CO) [OP(C$_6$H$_5$)$_2$O]$_3$	10	Ethanol, benzene		340	200		67, 76
89	Cr [OP(CH$_3$)$_2$O] [OP(CH$_3$)(C$_6$H$_5$)O]$_2$		—	—		200	490 155	33, 82, 85, 86
90	Cr [OP(CH$_3$)(C$_6$H$_5$)O]$_2$[OP(C$_8$H$_{17}$)$_2$O]						~400	87
91	Cr [OP(C$_6$H$_5$)$_2$O]$_3$		—	—		320		86
92	Cr(AcAc) [OP(C$_6$H$_5$)$_2$O]$_2$	19	Benzene, $CHCl_3$			300[a]	336	15, 88—91
93	Cr(AcAc) [OP(C$_6$H$_5$)$_2$O] [OP(CH$_3$·C$_6$H$_3$OC$_6$H$_3$CH$_3$)O]	16	Benzene, $CHCl_3$			150, 320[a]		88
94	TiO [OP(CH$_3$)$_2$O]$_2$	34	Organic solvents		230—250		450	92, 93
95	TiO [OP(CH$_3$)(C$_6$H$_5$)O]$_2$	18	Benzene, $CHCl_3$	0.06—0.14 ($CHCl_3$)	280		435	93
96	TiO [OP(C$_6$H$_5$)$_2$O]$_2$	>20	Benzene, $CHCl_3$	0.06—0.14 ($CHCl_3$)	300		450	93—96
97	TiCl$_2$[OP(C$_8$H$_5$)O]$_2$	>20	Benzene, $CHCl_3$	0.03 ($CHCl_3$)	300		370	93
98	Ti(OC$_4$H$_9$)$_2$[OP(CH$_3$)$_2$O]$_2$	5						93, 97, 98
99	Ti [OP(C$_6$H$_5$)$_2$O]$_4$		$CHCl_3$, ethanol, DMF, chlorobenzene		135	350[a]	200	73, 99

[a] The temperature corresponding to the decrease of the weight of the polymer by 10%.
[b] Intrinsic viscosity. [All the figures in this column appear to be intrinsic viscosities (Ed. of Translation)].

does not always ensure the formation of polymers with high molecular weights, since chain growth is frequently arrested at the stage involving the formation of low-molecular-weight or oligomeric compounds.

In order to find the optimum conditions for the synthesis of various metal polyphosphinates and other coordination polymers with inorganic main chains, Korshak and coworkers [69] investigated the characteristics of this process. They chose for investigation the polycoordination of di-n-butylphosphinic acid with manganese acetate under different conditions. The resulting coordination polymer—manganese polydi-n-butylphosphinate—is comparatively readily soluble in hydrocarbon solvents, which permits the determination of the viscosity of its solutions.

A study was made of the influence on the yield and intrinsic viscosity of the resulting manganese polydi-n-butylphosphinate of factors such as the nature of the reaction medium, the temperature and duration of the reaction, reactant concentration, and reactant ratio. It was found that the acetic acid liberated in the reaction degrades the manganese polydi-n-butylphosphinate formed under the conditions of the synthesis of the coordination polymer; consequently the polycoordination of phosphinic acid with manganese acetate must be regarded as a reversible polycondensation process:



Polymers with the highest molecular weights were obtained in a high-boiling solvent (Dinil) at about 140°C *in vacuo* (30 mmHg) in a stream of an inert gas.

Korshak and coworkers [57,69] showed that the interaction of di-n-butylphosphinic and other phosphinic acids with metal acetates takes place even when a powdered mixture of the two components is ground at room temperature. The amount of acetic acid liberated under these conditions during 10–15 min grinding of the starting materials in a thin layer is 70–80% of theoretical. Owing to the large surface area of the powdered mixture, acetic acid is very rapidly removed from reaction sphere as a result of its volatility. Subsequent treatment of the reaction mass with ethanol leads to the formation of a polymer with a high molecular weight.

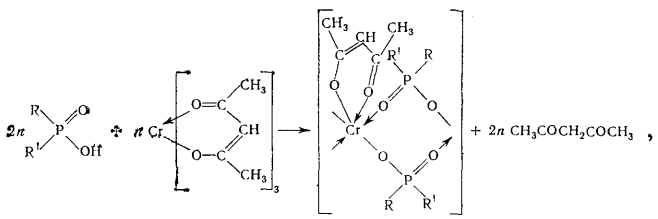
When the reaction is carried out in two stages, in the solid phase and in ethanol, the polymer with the maximum molecular weight is formed from di-n-butylphosphinic acid and manganese acetate taken in various proportions when stoichiometric amounts of the components interact [69], as in the single-stage polycoordination in solution. Thus, as in many other instances of polycondensation, in the formation of a coordination polymer with bridge ligands the rule of the non-equivalence of functional groups operates [101].

Korshak, Vinogradova, and coworkers [57,69,102] synthesised manganese and zinc polyphosphinates based on diphenyl-, dicyclohexyl-, distyryl-, di-n-butyl-, di-n-heptyl-, di-n-octyl-, di-n-nonyl-, and other phosphinic acids by the polycoordination of the acids with metal acetates and acetylacetonates. The molecular weights of manganese polydi-n-octylphosphinate with an intrinsic viscosity $[\eta] = 0.60$ dl g^{-1} (benzene, 50°C, $c = 1$ g dl^{-1}) and zinc polydi-n-butylphosphinate with $[\eta] = 5.45$ dl g^{-1} (benzene, 25°C, $c = 1$ g dl^{-1}), determined ebullioscopically in benzene, proved to be 8000 and 18 000 respectively. The molecular weight of zinc polydi-n-heptylphosphinate with $[\eta] = 18.50$ dl g^{-1} (benzene, 25°C, $c = 1$ g dl^{-1}), determined by the light scattering method in toluene, amounted to 74 000.

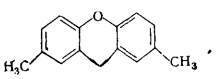
The interaction of phenylmethylphosphinic acid with zinc acetate in ethanol, leading to the formation of zinc polyphenylmethylphosphinate $\{Zn[OP(C_6H_5)(CH_3)O]_2\}_n$ with a molecular weight of 5600 has been described [16,54].

Slota et al. [51] synthesised a number of polymers of beryllium diorganophosphinates by the reaction of stoichiometric amounts of beryllium acetylacetonate with dimethyl-, 1,4-tetramethylene-, phenylmethyl, diphenyl-, and other phosphinic acids. The reaction was carried out in the melt, initially in an inert gas stream at 130°C and then *in vacuo* at 200°C. The resulting beryllium-containing polymers based on phenylmethyl-, di-n-butyl-, and di-n-pentyl-phosphinic acids had molecular weights of 30 000, 50 000, and 26 000 respectively.

Block and coworkers [30–34,78,86] and other investigators [79,87,88,90,103,104] made a detailed study of the synthesis of chromium-containing polyphosphinates. The polymer with tervalent octahedral chromium atoms is formed when a mixture of the monomeric chelate (chromium acetylacetonate) and substituted phosphinic acids is heated in the range 170–250°C in the melt or in a high-boiling solvent in an inert gas atmosphere via the mechanism



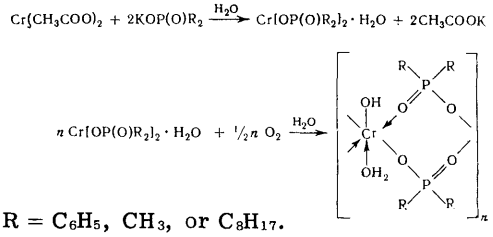
where R = C_6H_5 and R′ = C_6H_5, CH_3, or



The molecular weight of the benzene-soluble fraction of this polymer was about 10 000. [88–91]

The acetylacetonate group present in chromium polydiphenyl phosphinate as an additional chelating ligand can be replaced by another bidentate ligand, for example picolinic acid, as a result of exchange reactions occurring at elevated temperatures [89,91].

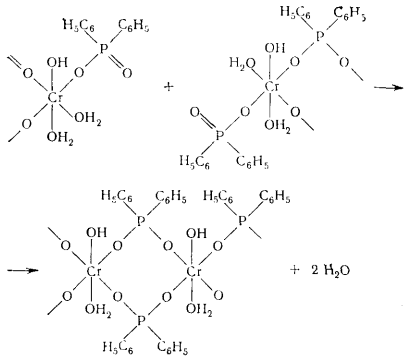
The examination of the structures of chromium polyphosphinates in terms of molecular models [105] showed that, when the dimensions of the additional ligand at the metal atom are greater than those of the acetylacetonate ligand, an appreciable steric hindrance arises in the chain and prevents the formation of high-molecular-weight polymers. For this reason, further studies were directed to the synthesis of chromium polydiphenylphosphinates with small additional ligands at the metal atom, such as water molecules and hydroxy-groups [30,32,78–83], instead of organic bidentate ligands. In particular, Block and coworkers [30,32,34] developed a method for the preparation of a polymer by the oxidation of the chromium(II) phosphinate complex in accordance with the mechanism



where R = C_6H_5, CH_3, or C_8H_{17}.

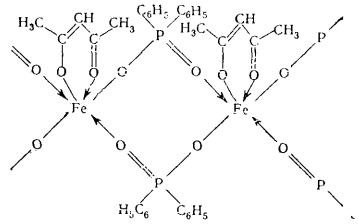
The oxidation of the insoluble intermediate chromium-(II) complex $Cr[OP(C_2H_5)_2O]_2.nH_2O$ was achieved by mixing in air its suspension in a water–tetrahydrofuran (THF) mixture for 12 h. The resulting oligomer with five or six repeating chain units {$[\eta] = 0.03-0.04$ dl g^{-1} in chloroform} is readily soluble in benzene, chloroform, THF, and dioxan. On heating solutions of such oligomers in chloroform at 55°C for about 100 h, polymer chains with polymerisation coefficients up to 345 and intrinsic viscosities in chloroform $[\eta] = 0.7-1.0$ dl g^{-1} are formed.

The high-molecular-weight polymer is probably formed as a result of the interaction of the terminal groups of the oligomers with elimination of the water coordinated to the metal, via the mechanism



When other oxidants are used, ligands such as the nitro- and nitroso-groups can be introduced into the polymer chain instead of the hydroxide ion [80]. Additional treatment of the polymer $[Cr(H_2O)(OH)(OPR_2O)_2]_n$ with one mole of phosphinic acid per unit leads to the formation of chromium polytriphosphinates, i.e. in these polymers the additional ligands at the metal atom are the phosphinate anions which function as bridges in the main chain [33,82,85]. After the introduction of the third phosphinate group per chromium atom in the chain, the polymer ceases to be fusible and soluble.

The interaction of iron(III) acetylacetonate with diphenylphosphinic acid in solution, in the melt, or at an interface at 80–108°C led to the formation of iron(III) polydiphenylphosphinate [75]:

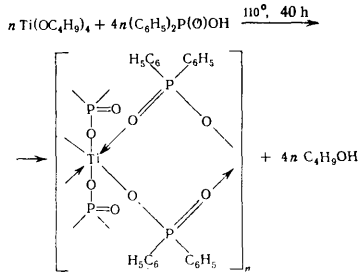


The resulting polymer was divided into four fractions, the first of which consisted of the dimer, the second and third of linear polymers with molecular weights of 4000 and 8800 respectively, and the fourth was insoluble.

Flagg and Schmidt [71,72,74,75,106–108] synthesised coordination polymers with Al–O–P linkages in the main inorganic chain. Aluminium-containing coordination polymers with the general formula $[Al(OPRR'O)_3]_n$ are usually obtained from triethylaluminium or the ether adduct of tetrahydroaluminate and the corresponding phosphinic acids via the mechanism

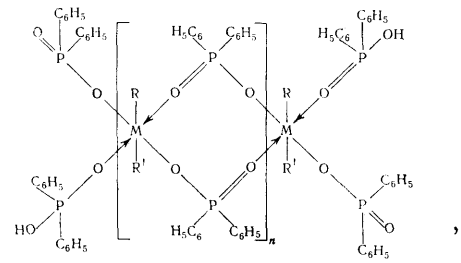
$$3nR_2P(O)OH + nR'_3Al \xrightarrow{THF,\ -70^\circ} \{Al[OPR_2O]_3\}_n + 3nR'H$$

Sutton and Wood [73] described the synthesis of a titanium-containing polymer by the interaction of tetrabutoxytitanate with diphenylphosphinic acid in toluene:



IV. SYNTHESIS BY THE OXIDATIVE DECARBONYLATION OF METAL CARBONYLS

Podall and Japalucci [76,84] proposed the oxidative decarbonylation of metal carbonyls for the synthesis of metal polyphosphinates. As a result of the oxidation-reduction reactions occurring under the influence of ultraviolet irradiation, they obtained polymers with the following tentative structure from chromium hexacarbonyl, iron pentacarbonyl, and diphenylphosphinic acid:



where R = R′ = CO for M = Fe and R = CO and R′ = $-O-\underset{\displaystyle H_5C_6\quad C_6H_5}{\overset{\displaystyle\quad}{P}}-O-$ for M = Cr.

Iron polydiphenylphosphinate proved to be insoluble, but fractions soluble in benzene and chloroform were isolated from chromium polydiphenylphosphinate. The minimum molecular weight of these fractions corresponded to the dimer and the maximum molecular weight was 7130.

Iron-containing metal polyphosphinates were obtained from iron nonacarbonyl in a much higher yield than from the pentacarbonyl, the reaction occurring in the absence of ultraviolet irradiation [68]. The corresponding metal-containing polymers were also obtained from manganese, tungsten, and molybdenum carbonyls [66–69].

The study by Korshak, Vinogradova, and coworkers [69] on the oxidative decarbonylation of manganese decacarbonyl with di-n-butylphosphinic acid under different conditions showed that manganese polydi-n-butylphosphinate with the maximum intrinsic viscosity {$[\eta] = 1.13$ dl g^{-1}, benzene, 70°C, $c = 1$ g dl^{-1}} was obtained when the process was carried out in benzene under ultraviolet irradiation. The reaction proceeds via the mechanism

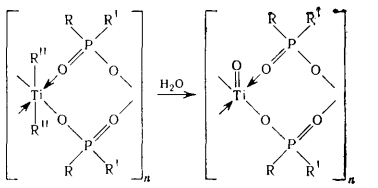
$$4n\,(C_4H_9)_2\overset{\displaystyle O}{\underset{\displaystyle OH}{P}} + nMn_2(CO)_{10} \xrightarrow{h\nu} \{[(C_4H_9)_2PO_2]_2Mn\}_n + 10\,nCO + 2nH_2$$

Other Methods for the Synthesis of Polyphosphinates

Dahl and Block [93] described the preparation of a coordination polymer of titanium (with $n = 18$) by the pyrolysis of the complex of titanium tetrachloride with diethyl diphenylphosphinate:

$$n\,TiCl_4 \cdot [OP(C_6H_5)_2OC_2H_5]_2 \xrightarrow{\Delta} \{TiCl_2[OP(C_6H_5)_2O]\}_n + 2nC_2H_5Cl\ .$$

It was shown that titanium polyphosphinates with a higher molecular weight can be obtained by the hydrolysis of dichloro- or dialkoxy- titanium polyphosphinates via the mechanism



where R and R′ = C_6H_5 and R″ = Cl or OC_4H_9.

Synthesis of Mixed Metal Polyphosphinates

The synthesis of mixed metal polyphosphinates by the interaction of two different phosphinic acids with metal-containing compounds under conditions analogous to those in the synthesis of homopolymers has been described [22-24, 38,39,54,56,59,71].

Thus mixed polyphosphinates with molecular weights up to 10 000 were synthesised by the joint polycoordination of two phosphinic acids with zinc, cobalt, and beryllium chlorides, acetates, and acetylacetonates [23,24,37-39,54].

Flagg and Schmidt [71] synthesised a large group of mixed high-molecular-weight aluminium polyphosphinates by the reaction of aluminium hydride or ethoxide with phosphinic acids of different structure in THF solution at −70°C. Thus the aluminium-containing polyphosphinates

$$\{[(C_4H_9)(C_6H_5CH_2)PO_2]_2Al[O_2P(C_8H_{17})_2]\}_n$$

and $\{[(C_4H_9)(C_6H_5CH_2)PO_2]_2Al(O_2P(C_7H_{15})]_2\}_n$

are soluble polymers with anomalously high intrinsic viscosities (up to 37 dl g^{-1}, 25°C, THF) and molecular weights of $(20-78) \times 10^4$.

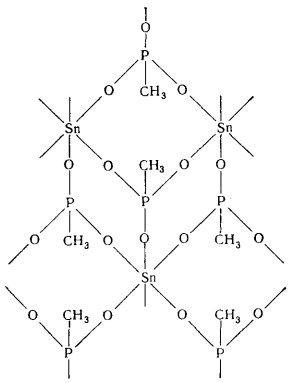
Korshak et al. [88] synthesised chromium-containing mixed polyphosphinates based on diphenyl- and 2,2′-(4,4′-dimethyl-1,1′-oxydiphenyl)-phosphinic acid by polycoordination in the melt at 175−200°C. In contrast to homopolymers, the mixed chromium polyphosphinates based on the above acid are fully soluble in chloroform and have molecular weights up to 10 000.

V. SYNTHESIS OF OTHER COORDINATION POLYMERS WITH INORGANIC MAIN CHAINS

Comparatively few studies dealing with coordination polymers containing bridge ligands other than phosphinate anions have been published. The synthesis of coordination bridge polymers based on phosphinomonothioic and phosphinodithioic acids containing cobalt, manganese, uranyl, and chromium in the inorganic main chain has been described [43,63,104,109-112]. For example, the interaction of diethyl- and diphenyl-phosphinothioic and diethyl- and diphenyl-phosphinodithioic acids with cobalt and uranyl acetates in benzene or ethanol yielded polyphosphinomonothioates and polyphosphinodithioates with molecular weights of 3000−6000. [63]

Callicaris et al. [112] showed that, in contrast to zinc polydiethylphosphinate, zinc diethylphosphinodithioate has a dimeric structure, which led the authors to the conclusion that phosphinodithioic acids are much less capable of forming polymers with metal ions than their phosphinomonothioic and phosphinic analogues.

Owens et al. [113] described a tin-containing polymer based on methylphosphonic acid, which was obtained by the pyrolysis of a tin tetrachloride complex of di-isopropyl methylphosphonate at 140−190°C and had the following structure:



Korshak and coworkers [68,114] achieved the oxidative decarbonylation of the metal carbonyls $M_2(CO)_{10}$, $Fe(CO)_5$, $Fe_2(CO)_9$, $W(CO)_6$, and $Cr(CO)_6$ by toluene-*p*-sulphonic acid. Toluene-*p*-sulphonic acid was also used as the ligand in polycoordination with manganese acetate. The molecular weight of the polymer from manganese acetate and toluene-*p*-sulphonic acid, determined by the light scattering method, proved to be 16 200 and that of the polymer from iron pentacarbonyl and toluene-*p*-sulphonic acid was 7900.

Korshak and coworkers [67,68,115] obtained metal polyarsinates by the reaction of diphenylarsinic acid with iron, chromium, manganese, and tungsten carbonyls and also with manganese and zinc acetates. The tungsten polyarsinate contained residual carbonyl groups and the degree of its polymerisation was 3-4. [115]

Metal polyarsinates, some of which proved soluble in water, were synthesised by the polycoordination of di-n-alkylarsinic acids with zinc acetate and chromium nitrate in solution [86,116].

VI. PROPERTIES OF COORDINATION POLYMERS WITH INORGANIC MAIN CHAINS

Metal polyphosphinates are usually powdered substances. Some of them have a characteristic colour (for example cobalt polyphosphinates are pale-blue and chromium polyphosphinates are green). The Table shows that certain metal phosphinates exhibit a high thermal stability. For example beryllium polydimethyl- and polydibutylphosphinates have melting points of 465° and 452°C respectively [51]. Polyphosphinates based on acids with aromatic substituents at the phosphorus atom are as a rule infusible, but cobalt polymethylphenylphosphinate and also certain mixed polyphosphinates whose chain contains the anions of both aromatic and aliphatic phosphinic acids are capable of passing to a fluid state [23,24,51].

X-Ray diffraction studies on metal phosphinates showed that they usually have a crystalline structure [11,22,24-33,35-44,58].

Crystalline polyphosphinates can be converted into an amorphous form by rapid cooling of the polymer melts. A characteristic feature of bivalent metal (zinc and cobalt) polydialkylphosphinates in the amorphous form is their high frost resistance. For example, amorphous zinc polydi-n-butylphosphinate with a molecular weight of about 10 000, obtained by rapid cooling of the polymer melt (150°C), had a brittleness temperature of −40°C.[22] Mixed bivalent metal polyphosphinates have even lower brittleness temperatures. Thus zinc polyphosphinate based on di-n-butyl- and di-n-octyl-phosphinic acids remained elastic down to −100°C.[22,54]

Amorphous metal homopolyphosphinates crystallise slowly at room temperature, but certain mixed coordination polymers in the amorphous form do not show a tendency towards crystallisation at the usual temperatures[22].

Giancotti, Giordano, and coworkers[38] explained the high elasticity of mixed polymers by the disordered distribution of their alkyl side groups at the phosphorus atom on the basis of X-ray diffraction and differential thermographic studies.

Giancotti et al.[42] observed solid-phase transitions between two crystalline forms of zinc polyphosphinates between −13° and 77°C. They showed that above the transition temperature, i.e. in the β-form, the carbon chains of the aliphatic substituents at the phosphorus atom are flexible and capable of twisting; they are more ordered in the α-form.

Bivalent metal polyphosphinates with aliphatic substituents at the phosphorus atom are completely or partly soluble in organic solvents[22,24,38,51,57,69]. Homopolyphosphinates with aromatic substituents are largely insoluble[23,51,65].

Korshak, Krukovskii, and coworkers showed[56] that the solubility of mixed zinc polyphosphinates based on di-n-butylphosphinic acid, which also contain the residues of diphenyl-, distyryl-, and 2,2′-(4,4′-dimethyl-1,1′-oxydiphenyl)-phosphinic acids, increases with increase of the content of dibutylphosphinate groups in the polymer.

Mixed bivalent metal polyphosphinates based on phosphinic acids containing only aliphatic alkyl substituents at the phosphorus atom showed the highest solubility[22,38].

The available literature data on the behaviour of metal polyphosphinates in solution are difficult to compare, since they refer to polyphosphinates containing in the chain metal atoms of different valence. Furthermore, different experimental techniques were used in the investigations.

Thus the viscosity of solutions of chromium polydiphosphinate $\{Cr(H_2O)(OH)[OP(C_6H_5)_2O]_2\}_n$ in chloroform was found to increase with time; after keeping the polymer in chloroform at 55°C for several days, the intrinsic viscosity increased from 0.03−0.04 to 1.0 dl g^{-1}.[32,34]

Slota et al. observed a decrease of the molecular weights of beryllium-containing polyphosphinates with time in different solvents[53,55].

Examination of the relations quoted in a number of studies between the intrinsic viscosities of metal polyphosphinate solutions and polymer concentration shows that they are not linear. The intrinsic viscosities of solutions of many polymers increase sharply with increase of the concentration[22,23,44,56], which has been attributed[56] to the instability of metal polyphosphinates in solution.

The explanation of such concentration variation of the intrinsic viscosities of metal polyphosphinates by the aggregation of the molecules of the coordination polymer as a result of hydrogen bonding[55] is apparently invalid in the light of the results of Kuchen and Hertel[110], who showed that the concentration variation (in benzene) of the molecular weight of cobalt polydiethylphosphinothioate is the same at 37°, 45°, and 60°C. This suggests that the bond strengths in the association complexes are much higher than those of hydrogen bonds.

Korshak et al. showed[57] that 0.5−1% solutions of metal polyphosphinates in benzene and toluene are stable over a period of time. However, measurements of the intrinsic viscosities of manganese and zinc polyphosphinate solutions in benzene and toluene at different concentrations revealed a sharp decrease of the intrinsic viscosity with dilution of the solution. The anomalously low intrinsic viscosities of dilute manganese and zinc polyphosphinate solutions indicate the degradation of the macromolecules in solutions at low concentrations.

Indeed measurements of the molecular weight of manganese polydi-n-octylphosphinate in benzene by the ebullioscopic method and of zinc polydi-n-heptylphosphinate in the same solvent by sedimentation in an ultracentrifuge showed that the molecular weights of these polymers decrease sharply in both cases with decrease of the concentration of the solutions.

It has been shown for metal polydialkylphosphinates that the degradation of bivalent metal polyphosphinates in organic solvents is reversible and takes place almost instantaneously when the solution is diluted even at room temperature.

Delman et al.[117] demonstrated the high polydispersity of chromium polyphosphinates determined by the gel-chromatographic method.

In certain studies attempts were made to prepare films from coordination polymers[22,51,54,64,80,82,87]. However, non-plasticised films prepared from melts or solutions of homopolyphosphinates are brittle[82]. Their elasticity can be improved by the introduction of 20−60% of a plasticiser relative to the weight of the polymer. Thus a film containing 30% of the "Aroclor 1254" plasticiser and having a tensile strength of 133 kgf cm^{-2} was obtained from a polymer based on bivalent chromium acetate and diphenylphosphinic acid (molecular weight about 10 000).[30]

American investigators[82,86,87] described the preparation of moulded articles, transparent films, and fibres from a chromium-containing polytriphosphinate obtained by the cross-linking of linear polymers of the type $\{Cr(H_2O)(OH)[OPRR'O]_2\}_n$ with low-molecular-weight cross-linking agents, which consisted of acid having the general formula R′R″P(O)OH.

Mixed polymer films are very elastic. A thin film, which did not change its size up to 100°C and remained flexible on cooling down to −100°C, was obtained from a mixed zinc polymer based on di-n-butyl- and di-n-octylphosphinic acids (molecular weight 10 000) by pressing at about 150°C.[22,54]

The thermal stabilities of coordination polymers with inorganic main chains were estimated from thermogravimetric data. It was found that they depend both on the nature of the metal entering into the coordination centre and on the structure of the ligand forming the bridge group. Thus various metal polydiphenylphosphinates can be arranged in the following series in terms of the temperatures corresponding to 10% increase of their weight in an inert atmosphere (at a heating rate of 5 deg min^{-1}):

$$Mn(580°) < (Zn(520°) > W(510°) > Fe(453°) > Mo(425°) > Cr(390°)^{67,102}.$$

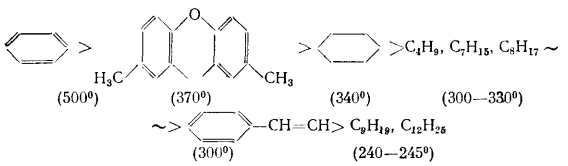
When the given ligand is replaced by a diphenylarsinic acid residue, the thermal stability of the corresponding coordination polymers falls and the relative stability series of the metals changes:

$$Cr\,(390^0) > Fe\,(380^0) > Mo\,(360^0) > W\,(320^0) > Mn\,(240^0)$$ [67].

Polymers based on toluene-*p*-sulphonic acid exhibit the highest thermal stability. Thus manganese polysulphonate does not begin to decompose in an inert atmosphere until 520°C and its weight decrease by 10% at 600°C. [67,114]

According to thermogravimetric data (heating rate 4.5 deg min^{-1}), the weight of coordination polymers based on phosphinic acids with aliphatic substituents at the phosphorus atom begins to decrease in air at a temperature as low as 160–230°C. [57,69,102]

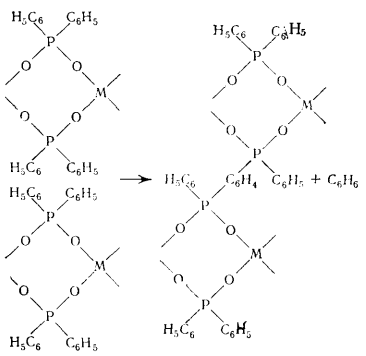
It has been established that manganese polyphosphinates form the following sequence of substituents at the phosphorus atom as a function of the temperature (indicated in brackets) corresponding to the 10% decrease in the weight of the polymer in air at a heating rate of 4.5 deg min^{-1}:



Among the bivalent metal polyphosphinates described, cobalt polydiphenylphosphinate proved to have the highest thermal stability: its weight begins to decrease in an inert atmosphere at 485°C. [24]

Investigations have shown [23,24,51,63] that the alkyl or aryl groups at the phosphorus atom are the first to be split off in the thermal degradation of bivalent metal polyphosphinates.

Only benzene has been detected in the volatile decomposition products of zinc polydiphenylphosphinate at 500°C; it is probably liberated via the mechanism [24]



Golgotui and Rosca [63] noted that the most stable bonds in metal polyphosphinates are the O–M and O–P linkages in the inorganic main chain of the macromolecules, which persist in the solid decomposition products characterised as $M(PO_3)_2$ or $MO.P_2O_5$. According to Saraceno and Block [32], chromium polyphosphinates with the structure $\{Cr(H_2O)(OH)[OP(C_6H_5)_2O]_2\}_n$ begin to lose weight at about 375°C in dry nitrogen, at 355°C in air, and at 335°C in moist oxygen. The authors attribute the initial decrease of the weight of the polymers at 370–420°C to the elimination of the residual acetate groups from the polymer and not to its true decomposition.

Comparison of the temperatures corresponding to the onset of weight loss by chromium polydiphosphinate (296 to 300°C), obtained from chromium acetylacetonate and diphenylphosphinic acid, and chromium acetylacetonate itself (approximately 250°C) [118] led Block et al. [15] to the conclusion that the side ligand at the chromium atom (acetylacetone) is the first to be split off on heat treatment.

The study of beryllium [51], chromium [32], zinc [23], and manganese [102] polyphosphinates subjected to a prolonged heat treatment under isothermal conditions revealed a fairly high thermal stability. Thus, on heating in air at 440°C for 20 h, zinc polydiphenylphosphinate lost only about 2.8% of its weight [23].

The literature data available at present therefore permit the conclusion that the thermal decomposition of metal polyphosphinates does not involve the inorganic main chain in the initial stage and proceeds as a result of the elimination of the organic substituents at the phosphorus atom or the additional ligands linked to the metal atom.

When the oxygen atom is replaced by sulphur in the phosphinate group, the thermal stability of the polymers diminishes. This can be traced on the basis of the results of the thermogravimetric analysis of cobalt-containing coordination polymers based on diethylphosphinic, diethylphosphinothioic, and diethylphosphinodithioic acids [63]. These polymers can be arranged in the following series in terms of the temperatures corresponding to the onset of their weight loss in air:

$$\{Co[(C_2H_5)_2PO_2]_2\}_n > \{Co[(C_2H_5)_2POS]_2\}_n > \{Co[(C_2H_5)_2PS_2]_2\}_n$$
(285°) (195°) (185°)

The chemical stability of metal polyphosphinates has been very little studied. It has been shown that pyridine has a degrading effect on zinc polydi-n-butylphosphinate [56] The dissolution of cobalt polydiphenylphosphinate in pyridine is accompanied by the formation of adducts in which the phosphinate : pyridine ratio is 1 : 1. [18]

Slota et al. [53] studied the degrading influence of water on beryllium-containing polyphosphinates and suggested that the bonds formed by the residues of the phosphonic acid, present as an admixture in the initial phosphinic acid, are unstable with respect to hydrolysis.

Under the influence of concentrated inorganic acids and bases, bivalent metal polyphosphinates decompose with the liberation of the corresponding phosphinic acids even at room temperature. Acetic acid degrades polymers to a much smaller extent. Manganese polyphosphinates with aliphatic substituents and zinc polyphosphinate resist the action of water [102].

Rose and Block [23] noted the stability of zinc polyphosphinates with respect to radiation.

The resistance of metal polyphosphinates to the action of water together with their high thermal stability and heat resistance constitutes an important factor, which provides a basis for the development of various materials from them. However, there is so far very little information about the practical applications of bridge coordination polymers. It is contained mainly in the patent literature. In particular, it has been noted that polyphosphinates can be used as protective coatings [119]. Titanium and chromium polyphosphinates as components of coatings impart antistatic properties to organic plastics [120]. The study of the influence of metal polyphosphinates on the polymerisation of aminoalkyl acrylates showed that metal polyphosphinates are responsible for the formation of gel-like structures in the monomer at low concentrations (of the order of several per cent). It has been shown that the

introduction of small amounts of polyphosphinates into the initial monomeric composition gives rise to a structural viscosity, which is reflected in the supermolecular structure and improves the physicomechanical properties of the coatings based on the polymers [59,121].

Certain chromium triphosphinate polymers can be used as thickening agents for silicones which enables them to be used at elevated pressures [120,122].

According to an American patent [123], chromium polyphosphinate additives are used as photostabilisers and thermostabilisers for poly(vinyl chloride) and its copolymers. Chromium polymethylphenylphosphinate is a satisfactory stabiliser of the viscosity of greases and hydraulic liquids based on phosphate esters (for example, tricresyl phosphate) [124]. Heat resistant (up to 300°C) metal polyphosphinates manufactured in the USA are recommended as coatings, composition for the formation of hermetic seals, and adhesives [125].

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Derivatives of the
Elements, USSR
Academy of Sciences,
Moscow