

# **INORGANIC POLYMER CHEMISTRY**

**F. G. R. GIMBLETT**

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LONDON  
BUTTERWORTHS

1963

Suggested U.D.C. number: 546-92

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Butterworth and Co. (Publishers) Limited

1963

*Printed in England by the Pitman Press, Bath*

## PREFACE

DURING the past ten years, notably the last five, a considerable interest in the subject of inorganic polymer chemistry has developed. This interest may be attributed to the renaissance of Inorganic Chemistry as a subject rather than a collection of facts and to the search for new high-temperature-resistant materials. The volume of papers on this subject has accordingly increased enormously during this period and this is reflected in the number of references at the end of each chapter in this book.

Although several reviews and two books have been written on various aspects of inorganic polymers, no account of the subject as a whole has yet been published. This book is an attempt to fulfil this purpose and to set out some basic principles common to various inorganic polymers. For this reason it is not an encyclopaedic reference work and no attempt has been made to catalogue all known inorganic polymers along with their preparation and properties. The criterion employed for discussing a particular polymer has been its ability to illustrate a particular principle or the possibility of its behaviour suggesting undiscovered principles. This approach to the subject has been a difficult one, for although many workers have investigated the preparation of polymers there have been far fewer physicochemical studies of these materials. If future constructive progress is to be made in this subject less attention must be paid to pure preparative work and more to structural, molecular-weight and kinetic studies of these polymers.

It may be fairly stated that this book is designed for the final Honours student or research worker, particularly the latter, in the hope that the very many gaps in knowledge of this subject will stimulate his interest and work in this field.

I would like to thank many of my colleagues at Brunel College for their stimulating discussions on various aspects of this extensive subject and in particular, Dr. C. F. Bell for his help in correcting the proofs of this book. I must also record my gratitude to my wife for her considerable help in editing and rewriting the manuscript and also for her patience, endurance and encouragement without which this book would never have been completed.

Finally, I should like to record my gratitude to the authors and publishers of numerous books and journals for their kind permission to reproduce figures and tables as indicated in the text.

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March, 1963

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## THE OCCURRENCE, CLASSIFICATION AND BONDING OF INORGANIC POLYMERS

### 1.1. INTRODUCTION

In his classical work during the years 1920–30, STAUDINGER<sup>1-8</sup> demonstrated that many materials in organic chemistry possessed chain formulae. Thus natural and synthetic peptides, rubber and materials such as polystyrene and paraformaldehyde all exist as macromolecular structures, *i.e.* they contain large numbers of simple molecular units (monomers) covalently linked together to form extremely long, and in many cases infinite, chains. Since the investigations of Staudinger, it has been well established that many organic materials can be polymerized to form long-chain compounds and a careful study has been made of the principles of such polymerization processes, the structures, and properties of the polymers formed. It has been shown that many organic polymers do not possess infinite *linear* chains but that under certain conditions branched polymers and crosslinked three-dimensional networks may be obtained. These branched and crosslinked structures possess different physical properties from infinite linear polymers and investigations of these differences have led to significant advances in the field of organic high-polymer chemistry. The accumulation of knowledge regarding organic polymers is so great that it may be fairly stated that the understanding and technological application of such polymers has been one of the major achievements of the last twenty years.

The formation of organic polymers may be attributed to the ability of the tetrahedral carbon atom to undergo unlimited covalent combination with other carbon atoms, leading to linear polymers (where each atom is linked to two other atoms), branched polymers (where some carbon atoms are linked to three other atoms), and three-dimensional polymers (where some carbon atoms are linked to four other atoms). Such polymers, where the covalently linked atoms of the chains are of the same element, *i.e.* carbon, may be termed 'homo-chain' polymers. It is also possible to obtain 'hetero-chain' polymers where elements other than carbon, *e.g.* nitrogen, oxygen and sulphur, are covalently linked at various regular intervals in otherwise predominantly carbon chains. In organic polymer chemistry homo-chain polymers occur much more frequently than hetero-chain polymers.

The ability to undergo unlimited covalent combination with other atoms is not restricted to carbon, however, and many other elements of the Periodic Table are capable of similar behaviour. It should be noted that in inorganic polymer chemistry the vast majority of polymers have hetero-chain structures, and that inorganic homo-chain polymers are formed by elements closely situated to carbon in the Periodic Table, as illustrated in *Figure 1.1*.

The structures of both homo- and hetero-chain inorganic polymers are dependent upon the valency of the elements forming the chains. Whereas

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organic polymers based on carbon chains consist of 4-valent interconnected atoms, inorganic polymers can, in theory, consist of chains of similar atoms of valency within the limits 2-4 or combinations of atoms of different valency. In homo-chain materials, the structure of the polymers will depend only upon the valency of the element forming these polymers. Thus elemental sulphur and sulphur chain compounds have been shown to contain only linear polymer chains, and the same is true of the analogous selenium materials.

Period	Group															
	I	II	III	IV	V	VI	VII	VIII			O					
1	(H)						H				He					
2	Li	Be	B	C	N	O	F				Ne					
3	Na	Mg	Al	Si	P	S	Cl				Ar					
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni						
	Cu	Zn	Ga	Ge	As	Se	Br				Kr					
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd						
	Ag	Cd	In	Sn	Sb	Te	I				Xe					
6	Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt						
	Au	Hg	Tl	Pb	Bi	Po	At				Rn					
7	Fr	Ra	Ac**	(Th)	(Pa)	(U)										

\* Lanthanide elements

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tu	Yb	Lu
----	----	----	----	----	----	----	----	----	----	----	----	----	----

\*\* Actinide elements

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md
----	----	---	----	----	----	----	----	----	----	----	----

Figure 1.1. Periodic distribution of the elements which form homo-chain polymers

Phosphorus and the other elements in Group Vb, being trivalent, should be capable of forming three-dimensional loosely linked networks. In fact, sheet polymers are formed with strong directional bonding in the plane of these sheets and relatively weak forces operating between individual sheets. Boron, in Group IIIb, which is also trivalent, forms the loosely linked three-dimensional network mentioned above, and the various crystalline varieties of this element have complicated cage-like structures. Carbon, with a valency of 4, forms both strongly bound three-dimensional networks (diamond) and sheet-like structures (graphite), but similar elements in Group IVb, silicon and germanium, form only three-dimensional networks.

It may appear that hetero-chain polymers, being based on a large number of possible combinations of elements, should be capable of showing a

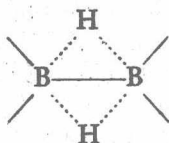


## INTRODUCTION

variety of structural types, depending on the valencies of the elements concerned. It is found, in practice, that most hetero-chain polymers contain a repeat unit of two different atoms and that one of these atoms is usually the divalent oxygen atom or the trivalent nitrogen atom. The majority of hetero-chain polymers are polyoxyacid anions in which the monomer unit consists of two chain atoms, one of which is the divalent oxygen atom while the other may be divalent (S), trivalent (P, As, B) or tetravalent (Si, Ge, Sn). Thus the structures formed by these polyoxyacid anions are dependent upon the valency of the second atom in the monomer unit. The polysulphates are capable of forming linear chain anions only, while the polyphosphates, arsenates and borates form linear or branched chains, or three-dimensional networks, but to date no evidence has been obtained for sheet-like structures of these anions. The oxyacid anions containing a Group IVb element in their monomer unit are capable of forming linear or branched chains, sheet or three-dimensional networks, a situation which is demonstrated by the structures of the silicates in the solid state (see Chapter 6).

A number of hetero-chain polymers exists in which one of the atoms in the monomer unit is the trivalent nitrogen atom, or the related phosphorus or arsenic atoms, while the other atom can have a valency in the range 2-4. In most polymers containing nitrogen, the nitrogen atom behaves in an essentially divalent manner and utilizes its third valency by forming linkages of a double-bond character with the second monomer atom. This is the case in phosphonitrilic chain polymers where the third valency of nitrogen is involved in  $p_\pi-d_\pi$  bonding with the phosphorus atom. An exception are the boron-nitrogen polymers, where the third valency of the nitrogen atom is involved in linkages with hydrogen, halogen or carbon atoms. This does not involve the formation of side-chains for these atoms merely block the third valency of nitrogen. The larger phosphorus and arsenic atoms should, however, be capable of forming side-chains but this possibility has not yet been investigated.

Inorganic hetero-polymers in which one of the chain atoms is the normally univalent hydrogen atom also exist. Examples of such polymers are the boron and aluminium hydrides, which both possess electron-deficient structures, so that the bonding in the monomer units is not of the usual covalent type. In the boron hydrides, the empty boron orbitals are avoided by suggesting the formation of three-centre B—H—B bonds, hence the monomer unit has the structure



The abnormality of this bonding does not violate any of the principles which have been discussed above.

Finally, the structures of the polynuclear cationic polymers and related coordination polymers should be mentioned. As will be discussed in Chapter 3, these are formed by linking metal atoms with suitable ligands. The structures of the polymers formed depend upon the distribution in space of the

coordination sites of the metal atom. A two-coordinate metal atom will be capable of forming only linear polymers, provided that the sites are situated at an angle of  $180^\circ$  apart. If the angle is less than  $180^\circ$ , then the possibility arises of forming cyclic coordination polymers of relatively low degrees of polymerization. Tetrahedrally and octahedrally coordinated metal atoms will be capable of forming linear polymers, provided that the excess coordination sites are occupied by blocking ligands: in the absence of such ligands, complex three-dimensional polymers will be formed.

Inorganic polymers, therefore, like their organic counterparts, possess structures which are determined solely by the valency of one element whose atoms occur in their monomeric units. Unlike organic macromolecules whose three-dimensional structures are usually completely random and conform to no set pattern, many inorganic macromolecules exist as stable crystals which possess a high degree of regularity in three dimensions. This difference between random network organic polymers and crystalline inorganic polymers led FLORY<sup>9</sup> to suggest that the latter materials are not appropriately described as polymers. This conclusion is not sound when recent investigations of inorganic crystalline polymers are taken into account. Thus, as will be described in Chapter 6, when crystalline silicates are melted there is ample evidence to suggest that polysilicate anions are present in the melt. The same is true of silica, a completely three-dimensional polymer, whose structure is preserved in the molten state. As has been pointed out by ANDERSON<sup>10</sup>, very little is known of the conditions necessary for the formation of ordered three-dimensional polymer structures, and research into this problem could explain one of the more obvious differences between inorganic and organic polymers.

There exists one other major difference between inorganic and organic polymers, namely the tendency for many materials to form small cyclic structures, either in place of linear inorganic polymers or prior to the formation of large structures. Organic materials such as vinyl compounds seldom form cyclohexane derivatives during polymerization to long-chain materials, either as intermediates or side products. Under some circumstances, the polymerization of ethylene oxide can lead to the formation of dioxan and formaldehyde can be polymerized via trioxan, but there is no difficulty in polymerizing these materials under conditions which avoid the formation of six-membered rings. The polymerizations of sulphur, selenium and phosphonitrilic chloride all proceed either from a cyclic monomer or via the formation of such a material. The same is true for siloxanes, boron-nitrogen polymers and polyphosphates, and GEE<sup>11</sup> has attempted to explain this behaviour on thermodynamic grounds. In many cases, however, definite conclusions are difficult to make, owing to the fragmentary nature of the information available on many inorganic polymers. The thermodynamic approach has achieved some success in the cases of sulphur, selenium and phosphonitrilic chloride polymers, however, and this will be discussed in detail in Chapter 7.

## 1.2. CLASSIFICATION OF INORGANIC POLYMERS

The first attempt to classify inorganic polymers was made by MEYER<sup>12</sup> in 1942, who based his classification upon the structures exhibited by various

## CLASSIFICATION OF INORGANIC POLYMERS

polymers in the solid state. At this time the number of known inorganic polymers was relatively small and in the light of modern knowledge such a classification would be completely unacceptable. Meyer proposed that inorganic polymers could be subdivided into three types depending on whether they exhibited linear, sheet or three-dimensional structures in the solid state. It would be impossible to include in this scheme the small cyclic polymers commonly encountered in inorganic polymer chemistry, branched-chain molecules which exist in the polyphosphate and phosphonitrilic systems and also many of the discrete ions found in solutions of

																		H			He																
																		3	4	5	6	7	8	9	10												
																		Li	Be	B	C	N	O	F	Ne												
																		11	12	13	14	15	16	17	18												
																		Na	Mg	Al	Si	P	S	Cl	Ar												
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																				
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																				
																		37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54		
																		Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86						
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn						
																		87	88	89	90	91	92	93	94	95	96	97	98	99	100	101					
																		Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md					

Figure 1.2. Elements capable of forming hetero-chain polymers and their relative positions in the Periodic Table

borates, germanates and isopolyacids. Further, from the discussion above, it follows that the structures assumed by inorganic polymers depend on the valency of their chain atoms and hence a more logical classification would be based on the types of atoms present in the monomer unit.

A classification on this basis has been attempted by KORSHAK and MOZGOVA<sup>13</sup>, who subdivided inorganic polymers into those containing homo- and hetero-chains. The elements which form homo-chain polymers have already been depicted in Figure 1.1 and those forming hetero-chain polymers are shown in Figure 1.2 which is based on the Bohr representation of the Periodic Table. It should be noted that all the elements which form homo-chain polymers also form hetero-chain polymers. From Figure 1.2, it is apparent that those elements which have no tendency to form inorganic polymers are those of unsuitable valency, i.e. of valency one or zero. The ability of elements to form homo- and hetero-chain polymers has been discussed by Korshak and Mozgova in terms of the bond energies involved

in these polymers. Typical values for the bond energies in homo- and hetero-chain polymers are shown in *Table 1.1 (a)* and *(b)*.

In *Table 1.1 (a)* the bond energies of N—N and O—O bonds are recorded for comparative purposes. Neither of these elements is capable of homo-chain polymer formation and it is suggested<sup>13</sup> that the reason for this is the low energy of the bonds formed. Korshak and Mozgova have assumed that homo-chain polymers are formed only by those elements whose interatomic bond energies are greater than a value of 37.0 kcal/mole. The bond energies of all inorganic homo-chain polymers are less than the value of 80.0 kcal/mole

*Table 1.1. Bond energies of some homo- and hetero-chain polymers*

*(a) Homo-chain polymers<sup>14, 15</sup>*

<i>Bond</i>	<i>Energy kcal/mole</i>	<i>Bond</i>	<i>Energy kcal/mole</i>
C—C	80.0	Sb—Sb	42.0
S—S	63.0	Ge—Ge	39.2
P—P	53.0	As—As	39.0
Se—Se	50.0	N—N	37.0
Te—Te	49.0	O—O	34.0
Si—Si	45.0		

*(b) Hetero-chain polymers<sup>14, 16</sup>*

<i>Bond</i>	<i>Energy kcal/mole</i>	<i>Bond</i>	<i>Energy kcal/mole</i>
B—O	119.3	C—N	66.0
B—N	104.3	As—O	64.5
Si—O	89.3	Al—C	61.6
B—C	89.0	C—S	61.5
P <sup>III</sup> —O	81.7	Si—S	60.9
C—O	79.0	C—Si	57.6

observed for carbon chain polymers. The polymers therefore have a lower stability than their organic counterparts. Inorganic hetero-chain polymers, however, exhibit high bond energies, in many cases greater than that of the C—C bond, and in most cases greater than that of homo-chain inorganic polymers. This fact explains the greater tendency for hetero-chain formation in inorganic chemistry and also the high thermal stability of the polymers formed.

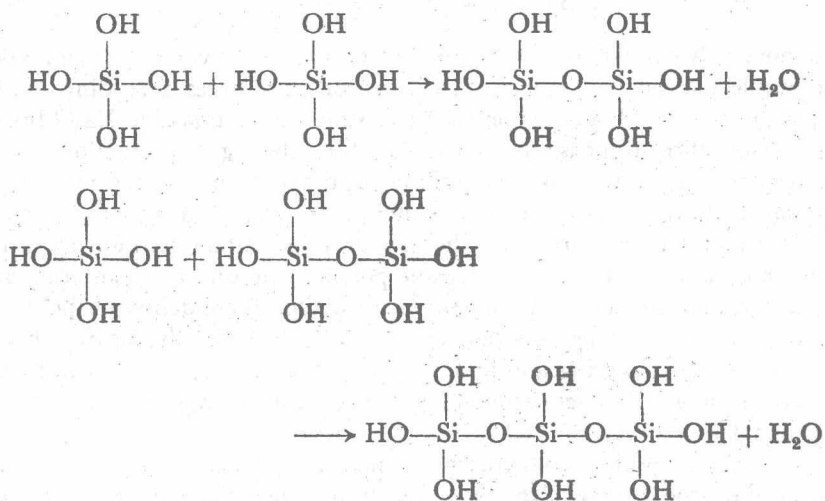
The bonding in inorganic polymers and its relation to their chemical and thermal stability has been discussed by BURG<sup>17</sup>. He has suggested that the thermal stability of the materials (SiH<sub>2</sub>)<sub>n</sub> and (GeH<sub>2</sub>)<sub>n</sub>, which are inorganic analogues of polyethylene, may be improved by replacing the hydrogen atoms with organic groups. Thus (SiH<sub>2</sub>)<sub>n</sub> and (GeH<sub>2</sub>)<sub>n</sub> yield volatile silanes and germanes on heating, which suggests that the lability of the hydrogen leads to rupture of the chains in these materials. Replacing the hydrogens with methyl groups would inhibit this breakdown and also prevent attack by electrophilic and nucleophilic agents on the Si or Ge atoms. This is due

to a combination of steric effects and interaction between the C—H bonding electrons and the 3*d* orbital electrons of the silicon or germanium atoms.

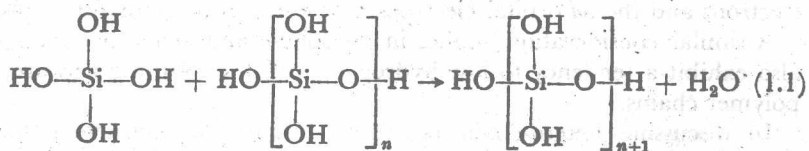
A similar consideration applies in phosphine and arsine polymers which also exhibit a tendency to lose hydrogen, with the resulting rupture of the polymer chains.

In discussing hetero-chain polymers, BURG<sup>17</sup> has considered the isoelectronic series  $(R_2AlF)_n$ ,  $(R_2SiO)_n$ ,  $(R_2PN)_n$  and  $(R_2SC)_n$ . The first member of this series would exhibit largely ionic bonding. However, the tendency of aluminium to six-coordinate with fluorine, oxygen or nitrogen would make these polymers very liable to attack by bases such as water. In the silicones the  $Si_{3d}$  sphere is occupied by  $\pi$ -bonding with the oxygen atoms and the steric interaction of the bulky R groups will prevent attack by all but the strongest bases. It has already been pointed out that in the phosphonitrilic polymers  $p_\pi-d_\pi$  bonding occurs between the nitrogen and phosphorus chain atoms. Such bonding is capable of preventing attack at the phosphorus atom by weak bases, but strong bases can replace the halide groups in the phosphonitrilic halide series. In substituted phosphonitrilics, however, additional C—P  $\pi$  bonding will occur which will reduce the tendency to attack by bases at the phosphorus atom. Finally, in the  $(R_2SC)_n$  polymers, the strong  $\pi$  character of the S—C—S bonding should lead to the formation of linear polymers. These, however, will be very readily attacked by moisture due to the extremely basic action of the carbon atom, and this attack may be promoted by the easy transfer of R groups from the sulphur to the carbon atom.

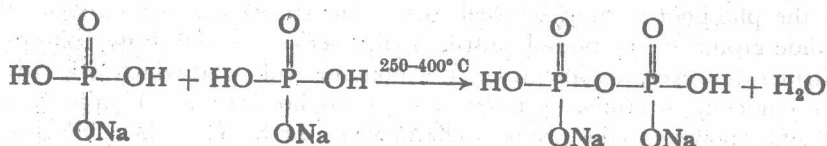
A third method of classification has been proposed by SOWERBY and AUDRIETH<sup>18</sup> and has been extended by SHAW<sup>19</sup>. It has been suggested that inorganic polymers should be classified according to their method of preparation into (i) condensation, (ii) addition and (iii) coordination polymers. This classification, which is used extensively in this book, points out the similarities between the methods of preparation of inorganic and organic polymers. Thus the preparation of polysilicic acid, which may be represented by the equations



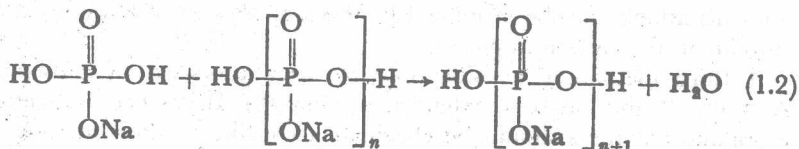
or in general



is an example of condensation polymerization as encountered in organic polymer chemistry, since the formation of the polymer involves the elimination of a simple molecule ( $\text{H}_2\text{O}$ ). Similar reactions are involved in the preparation of other polyoxyacid anions in solution (see Chapter 4) and these materials must also be classified as inorganic condensation polymers, as are the polynuclear cationic polymers (Chapter 3) and the polyphosphates. The latter are prepared through the high-temperature dehydration of acid hydrogen phosphates, *viz.*



or in general



and will be discussed in Chapter 2, together with other high-temperature methods for producing inorganic polymers. Some of these high-temperature processes, *e.g.* the formation of silicates by sintering methods, which may be represented by the equation



are not really condensation reactions, for they do not involve the elimination of simple molecules. In fact, the formation of silicates according to this equation is a depolymerization reaction, since the metal oxide  $\text{Na}_2\text{O}$  breaks down the three-dimensional silica structure during the reaction. It is convenient, however, to discuss sintering and also hydrothermal methods of preparing inorganic polymers in Chapter 2, for two reasons: (i) the methods involve high temperatures as in the dehydration method used for preparing polyphosphates, and (ii) the inorganic polymers produced by sintering and hydrothermal methods may be obtained via typical condensation polymerization reactions under different circumstances. Thus silicates which can be prepared by sintering and hydrothermal methods are also formed by the reactions depicted in equation (1.1). The same is true for borates and germanates.

In inorganic addition polymers, the molecular formula of the structural unit is the same as that of the monomer from which the polymer is derived,



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in contrast to condensation polymers where the formula of the structural unit lacks certain atoms which were present in the monomer. In comparison with condensation polymers, few addition polymers have been identified in inorganic polymer chemistry. Organic addition polymerizations have been shown to proceed by free-radical or ionic mechanisms and the same is true for inorganic addition polymers. Sulphur and selenium undoubtedly polymerize through a free-radical process and it has been suggested that phosphonitrilic chloride polymerizes through an anionic mechanism<sup>20</sup>.

Inorganic coordination polymers are formed by the linking of metal atoms with suitable organic or inorganic ligands. SHAW<sup>19</sup> has suggested that a third class is unnecessary for these polymers and prefers to include them with addition polymers. This conclusion is based on the argument that addition polymers are formed either through a decrease in the number of  $\pi$ -bonds in the system and a corresponding increase in the number of  $\sigma$ -bonds or, when polymerization proceeds from a ring monomer, through the breaking and formation of  $\sigma$ -bonds. Coordination polymers are formed during processes which involve an increase in the number of  $\sigma$ -bonds in the system, and on this basis are similar to inorganic addition polymers.

In this book, however, it is proposed to include inorganic coordination polymers with condensation polymers and in particular with polynuclear cationic species. This conclusion is based on structural considerations, for all coordination polymers possess metal atoms connected by bridging groups and, furthermore, considerations which apply during the formation of cationic species in solution apply with equal validity to coordination polymers.

## REFERENCES

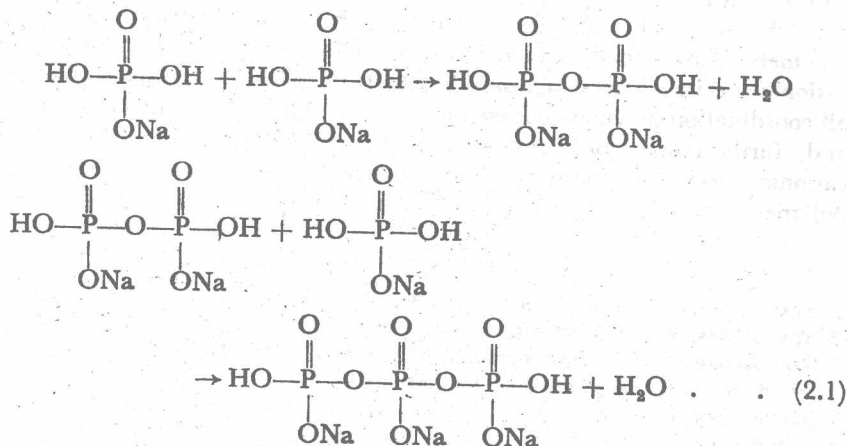
- <sup>1</sup> STAUDINGER, H. *Ber. dtsh. chem. Ges.* **53** (1920) 1073
- <sup>2</sup> STAUDINGER, H. and FRITSCHI, J. *Helv. chim. acta* **5** (1922) 785
- <sup>3</sup> STAUDINGER, H. *Ber. dtsh. chem. Ges.* **57** (1924) 1203; *Kautschuk* (1927) 63
- <sup>4</sup> STAUDINGER, H. *Ber. dtsh. chem. Ges.* **59** (1926) 3019
- <sup>5</sup> STAUDINGER, H., FREY, K., and STARCK, W. *Ber. dtsh. chem. Ges.* **60** (1927) 1782
- <sup>6</sup> STAUDINGER, H. and LÜTHY, M. *Helv. chim. acta* **8** (1925) 41
- <sup>7</sup> STAUDINGER, H. *Helv. chim. acta* **8** (1925) 67
- <sup>8</sup> STAUDINGER, H., JOHNER, H., SIGNER, R., MIE, G. and HENGSTENBERG, J. *Z. phys. Chem.* **126** (1927) 434
- <sup>9</sup> FLORY, P. J. *Principles of Polymer Chemistry* Cornell University Press, New York 1953
- <sup>10</sup> ANDERSON, J. S. *Chem. Soc. Special Publication No. 15*, p. 5, London 1961
- <sup>11</sup> GEE, G. *Chem. Soc. Special Publication No. 15*, p. 67, London 1961
- <sup>12</sup> cf. MEYER, K. H. *Natural and Synthetic High Polymers* 2nd edn., Interscience, New York 1950
- <sup>13</sup> KORSHAK, V. V. and MOZGOVA, K. K. *Uspekhi Khim.* **28** (1959) 783
- <sup>14</sup> HARTMAN, H. *Theorie der Chemischen Bindung* Springer, Berlin 1954
- <sup>15</sup> PITZER, K. S. *Quantum Chemistry* Prentice-Hall, New York, 1953
- <sup>16</sup> PRITCHARD, H. O. and SKINNER, H. A. *Chem Rev.* **55** (1955) 748
- <sup>17</sup> BURG, A. B. *Chem. Soc. Special Publication No. 15* p. 17, London 1961
- <sup>18</sup> SOWERBY, D. B. and AUDRIETH, L. F. *J. chem. Educ.* **37** (1960) 2, 86, 134
- <sup>19</sup> SHAW, R. A. *Thermal Degradation of Polymers* S.C.I. Monograph No. 13, p. 24, London 1961
- <sup>20</sup> GIMBLETT, F. G. R. *J. Polymer Sci.* **60** (1962) S29

## HIGH-TEMPERATURE CONDENSATION PROCESSES

### 2.1. INTRODUCTION

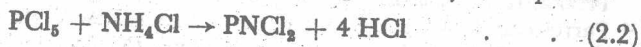
It is possible to distinguish between two types of reaction which at high temperature lead to the formation of inorganic condensation polymers. These are (a) condensation reactions and (b) solid-state reactions.

Condensation reactions are those in which a simple molecule is eliminated during reaction at high temperatures between like or unlike molecules. The dehydration of sodium dihydrogen phosphate is an example of the reaction between like molecules.



In this case the simple molecule eliminated is the water molecule and theoretically this reaction could continue indefinitely until an infinitely long-chained sodium polyphosphate is formed. In practice, however, as will be discussed below, it is possible to regulate the length of the chain by chemical and/or physical means.

The preparation of phosphonitrilic chlorides with low degrees of polymerization is an example of a condensation reaction between unlike molecules. Hydrogen chloride is eliminated in this reaction, which occurs between phosphorus pentachloride and ammonium chloride in the solid state<sup>1</sup> at 145° C. The overall reaction may be expressed by the equation



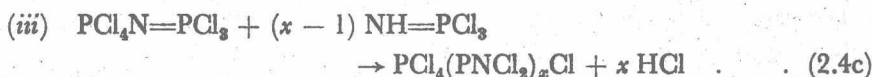
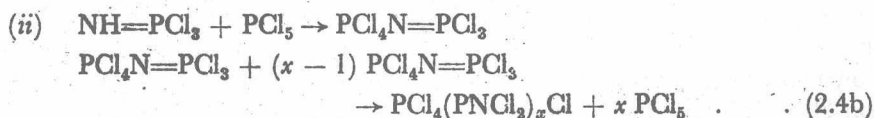
the degree of polymerization of the phosphonitrilic chloride being omitted. It is believed<sup>2</sup> that the reaction is more complicated than as represented in equation (2.2). The first step in the reaction is considered to be





## INTRODUCTION

This material is unstable and breaks down by successive elimination of the elements of HCl until the molecule  $\text{NH}=\text{PCl}_3$  is obtained. The condensation now proceeds by three paths



In reaction (2.4a) the final product is the polymer  $(\text{PNCl}_2)_x$  and in reactions (2.4b) and (2.4c) the final product is the entity  $\text{PCl}_4(\text{PNCl}_2)_x\text{Cl}$ . Both of these materials can be isolated under suitable conditions.

Examples of solid-state processes are numerous and include the reactions of alkali and alkaline earth metal oxides with  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3$  at high temperature. Thus the formation of calcium metasilicate,  $\text{CaSiO}_3$ , may be visualized as



Calcium metasilicate is also formed when  $\text{CaCO}_3$  and silica are reacted together in 1:1 molar ratio at 700–1200° C. In this case,  $\text{CO}_2$  is generated as a byproduct of the reaction, not as an elimination product but due to the initial decomposition of the carbonate to the oxide



which then takes part in the aggregation reaction as in equation (2.5).

Finally, although not included under the heading of solid-state reactions, there is the formation of inorganic polymers by crystallization from the melt. This method is an extension of the former method into the liquid state, for the chemical principles involved are the same as for the corresponding solid-state reactions. The inorganic polymers formed in the liquid state are crystallized from the melt by holding the latter at a suitable temperature for a suitable length of time—a process known as tempering.

## 2.2. VARIATION OF THE STRUCTURE OF INORGANIC POLYMERS BY CHEMICAL METHODS

Before discussing the mechanisms and chemistry of the various methods available for preparing inorganic polymers by high-temperature processes, it is first necessary to discuss the means available for modifying the structures of the polymers formed. It has already been mentioned in Section 2.1 that in the dehydration of sodium dihydrogen phosphate, an infinite-chain polymer would be formed if no chemical and/or physical means were used to prevent this. In general, chemical methods are the most convenient for modifying the structures of inorganic condensation polymers.

The structures of phosphates, silicates, borates and aluminates formed in high-temperature reactions are profoundly influenced by the ratio of metal oxide to non-metal oxide used in the preparation. Thus in the preparation