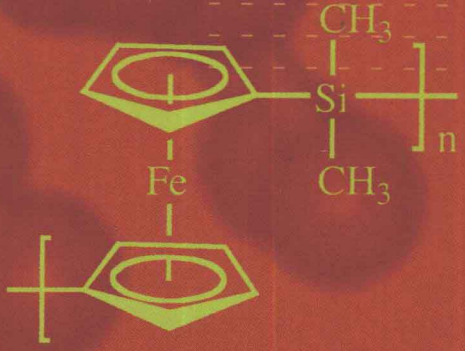
Vadapalli Chandrasekhar

Inorganic and Organometallic Polymers



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Inorganic and Organometallic Polymers

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Preface

This book has its origins in courses taught by the author to various undergraduate and graduate students at the Indian Institute of Technology, Kanpur, India. The diversity of inorganic chemistry and its impact on polymer chemistry has been profound. This subject matter has grown considerably in the last decade and the need to present it in a coherent manner to young minds is a pedagogic challenge. The aim of this book is to present to the students an introduction to the developments in Inorganic and Organometallic polymers.

This book is divided into eight chapters. Chapter 1 provides a general overview on the challenges of Inorganic polymer synthesis. This is followed by a survey of organic polymers and also includes some basic features of polymers. Chapters 3-8 deal with prominent families of inorganic and organometallic polymers. Although the target group of this book is the undergraduate and graduate students of chemistry, chemical engineering and materials science it is also hoped that chemists and related scientists in industry would find this book useful.

I am extremely thankful to my wife Sudha who not only encouraged me throughout but also drew all the Figures and Schemes of this book. I also thank my children Adithya and Aarathi for their constant concern on the progress of this book. I express my acknowledgment to the editorial team of Springer-Verlag for their cooperation.

July 2004 Vadapalli Chandrasekhar, Kanpur

Contents

1 Inorganic Polymers: Problems and Prospects 1
1.1 Introduction 1
1.2 Procedures for Synthesizing Organic Polymers 2
1.3 Inorganic Polymers: A Review of Synthetic Strategies 5
1.3.1 Unsaturated Inorganic Compounds 6
1.3.2 Inorganic Polymers from Acyclic Monomers 7
1.3.3 Ring-Opening Polymerization of Cyclic Inorganic Compounds 16
1.3.4 Polymers Containing Inorganic Rings or Motifs as Pendant Groups 21
1.4 Summary of Polymerization Procedures for Inorganic Polymers . 22
References 25

2 Organic Polymers – A Brief Survey 27
2.1 Introduction 27
2.2 Natural Polymers 28
2.3 Synthetic Polymers 29
2.4 Free-radical Polymerization 30
2.4.1 Initiators 31
2.4.2 Mechanism of Polymerization 33
2.4.3 Branching 34
2.4.4 Chain Transfer 35
2.4.5 Summary of the Main Features of Free-radical Polymerization 36
2.5 Polymerization by Ionic Initiators 36
2.5.1 Anionic Polymerization 37
2.5.2 Cationic Polymerization 40
2.6 Ziegler-Natta Catalysis 43
2.6.1 Mechanism of Polymerization of Olefins Using the Ziegler-Natta Catalysts 45
2.6.2 Supported Ziegler-Natta Catalysts 50
2.6.3 Recent Developments in Ziegler-Natta Catalysis 50
2.6.4 Summary of the Ziegler-Natta Catalysis 55

此为试读,需要完整PDF请访问: www.ertongbook.com

2.7 Olefin Metathesis Polymerization 56
2.8 Atom Transfer Radical Polymerization 58
2.9 Ring-opening Polymerization 60
2.10 Group-Transfer Polymerization 62
2.11 Condensation Polymers 63
2.11.1 Polyesters 64
2.11.2 Polycarbonates 67
2.11.3 Polyamides 67
2.11.4 Polyimides 69
2.11.5 Polysulfones 71
2.11.6 Thermoset Resins 71
2.12 Some Basic Features About Polymers 75
2.12.1 Molecular Weights of Polymers 75
2.12.2 Glass Transition Temperature of Polymers 76
2.12.3 Elastomers, Fibers and Plastics 77
References 80

3 Cyclo- and Polyphosphazenes 82
3.1 Introduction 82
3.2 Cyclophosphazenes 83
3.2.1 Preparation of Chlorocyclophosphazenes 86
3.2.2 Preparation of Fluorocyclophosphazenes and other Halogeno- and Pseudohalogenocyclophosphazenes 89
3.2.3 Chlorine Replacement Reactions of Chlorocyclophosphazenes 90
3.2.4 Other Methods of Preparing P-C Containing Compounds ... 94
3.2.5 Reactions of Chlorocyclophosphazenes with Difunctional Reagents 95
3.2.6 Isomerism in Cyclophosphazenes 99
3.2.7 Mechanism of the Nucleophilic Substitution Reaction 100
3.2.8 Cyclophosphazenes as Ligands for Transition Metal Complexes 104
3.2.9 Structural Characterization of Cyclophosphazenes 106
3.2.10 Nature of Bonding in Cyclophosphazenes 108
3.3 Polyphosphazenes 112
3.3.1 Historical 112
3.3.2 Poly(dichlorophosphazene) 113
3.3.3 Condensation Polymerization of $Cl_3P{=}N\text{-}P(O)Cl_2$ 116
3.3.4 Polymerization of $Cl_3P{=}NSiMe_3$ 118
3.3.5 ROP of Substituted Cyclophosphazenes 123
3.3.6 Poly(organophosphazene)s Prepared by Macromolecular Substitution of $[NPCl_2]_n$ 126

3.3.7 Preparation of Polyphosphazenes Containing P-C Bonds by Thermal Treatment of Phosphoranimines 131
3.3.8 Modification of Poly(organophosphazene)s 136
3.3.9 Modification of Poly(alkyl/arylphosphazene)s 140
3.3.10 Structure and Properties of Polyphosphazenes 142
3.3.11 Potential Applications of Polyphosphazenes 150
References 153

4 Cyclophosphazene-Containing Polymers 155
4.1 Introduction 155
4.2 Polymers Containing Cyclophosphazenes as Pendant Groups 156
4.2.1 Synthesis of Cyclophosphazene Monomers Containing Vinyl Groups 158
4.2.2 Polymerization of Cyclophosphazene Monomers 165
4.2.3 Other Ways of Making Polymers Containing Cyclophosphazene Pendant Groups 172
4.2.4 Applications of Polymers Containing Cyclophosphazene Pendant Groups 173
4.3 Cyclolinear and Cyclomatrix Polymers 178
References 181

5 Other Inorganic Polymers that Contain Phosphorus, Boron and Sulfur 183
5.1 Poly(heterophosphazene)s 183
5.2 Poly(carbophosphazene)s 184
5.3 Poly(thiophosphazene)s 189
5.4 Poly(thionylphosphazene)s 193
5.4.1 Polymerization of $[\{NPCl_2\}_2\{NS(O)Cl\}]$ and $[\{NPCl_2\}_2\{NS(O)F\}]$ 194
5.5 Other P-N-S Polymers 199
5.6 Metallacyclophosphazenes 200
5.7 Other Phosphorus-Containing Polymers 203
5.7.1 Polyphosphinoboranes 203
5.7.2 Polymers Containing P=C bonds 204
5.8 Poly(alkyl/aryloxothiazenes) 205
5.9 Borazine-based Polymers 206
References 207

6 Polysiloxanes 209
6.1 Introduction 209
6.2 Historical Aspects of Poly(dimethysiloxane) 215
6.3 Ring-Opening Polymerization of Cyclosiloxanes 219

6.3.1 Cyclosiloxanes 220
6.3.2 Ring-opening Polymerization of Cyclosiloxanes by Ionic Initiators 224
6.3.3 Preparation of Copolymers by Ring-Opening Polymerization 230
6.3.4 Summary of the Ring-Opening Polymerization of Cyclosiloxanes 231
6.4 Condensation Polymerization 232
6.5 Crosslinking of Polysiloxanes 234
6.5.1 Other Ways of Achieving Crosslinking 234
6.6 Hybrid Polymers 239
6.7 Properties of Polysiloxanes 241
6.7.1 Glass-Transition Temperatures and Conformational Flexibility 241
6.8 Applications of Polysiloxanes 244
References 246

7 Polysilanes and Other Silicon-Containing Polymers 249
7.1 Introduction 249
7.2 Historical 251
7.3 Synthesis of Polysilanes 254
7.3.1 Synthesis of Polysilanes by Wurtz-type Coupling Reactions 255
7.3.2 Polymerization by Anionic Initiators 260
7.3.3 Polysilanes Obtained by Catalytic Dehydrogenation 265
7.3.4 Summary of the Synthetic Procedures for Polysilanes 268
7.4 Modification of Polysilanes 269
7.5 Physical Properties of Polysilanes 272
7.5.1 NMR of Polysilanes 273
7.5.2 Electronic Spectra of Polysilanes 276
7.6 Optically Active Polysilanes 278
7.7 Applications of Polysilanes 280
7.8 Polysilynes 281
7.9 Polycarbosilanes and Polysiloles 284
7.9.1 Polycarbosilanes 284
7.9.2 Polysiloles 288
References 292

8 Organometallic Polymers 296
8.1 Introduction 296
8.2 Polygermanes and Polystannanes 297
8.2.1 Synthesis of Polygermanes 298

8.2.2 Synthesis of Polystannanes 300
8.2.3 Electronic Properties of Polygermanes and Polystannanes .. 302
8.3 Ferrocene-Containing Polymers 303
8.3.1 Synthetic Strategies 304
8.3.2 Strained Ferrocenophanes 310
8.3.3 Poly(ferrocenylsilane)s 312
8.3.4 Other Ferrocenyl Polymers Prepared from Strained Ferrocenophanes 318
8.3.5 Other Related Polymers 320
8.3.6 Properties and Applications of Poly(ferrocenylsilane)s and Related Polymers 321
8.4 Polyyne Rigid-rod Organometallic Polymers 324
8.4.1 Properties and Applications of Rigid-Rod Polyynes 332
References 333

Index 337

1 Inorganic Polymers: Problems and Prospects

1.1 Introduction

One of the indicators of the progress of human civilization is the type of materials that are accessible to society. Just as the Metal (Bronze and Iron) Age marked the beginning of a new chapter of human civilization at the end of the Stone Age, the advent of organic polymers in the last century has heralded a new era. Conventional materials such as iron, steel, wood, glass or ceramics are today being either supplemented or replaced by polymeric materials. From commonplace and routine (elastomers, fibers, thermoplastics) to special and high technology applications (electronic, electrical, optical, biological) polymers are being increasingly utilized. This dramatic impact of polymers has become possible because of two important factors. Firstly, the intrinsic versatility of carbon to form bonds to itself and to other hetero atoms such as oxygen, nitrogen or sulfur has enabled the extension of the principles of organic chemistry to polymer synthesis. This methodology has allowed the assembly of a large variety of polymers that possess varying properties which can fulfill wide and diverse needs. Secondly, the accessibility of inexpensive petroleum feed stocks from the beginning of the last century has allowed a large-scale availability of the building blocks of polymer synthesis and this in turn has helped the mass production of polymeric materials. From exotic laboratory materials polymers have become bulk commodities [1-3].

In spite of such wide-ranging applications and ubiquitous presence carbon-based polymeric materials probably do not have the capability to fulfill *all* the demands and needs of new applications [2]. For example, many organic polymers are not suitable for applications at extreme temperatures. Typically, at very low temperatures they become very brittle while at high temperatures they are oxidatively degraded. Also, most organic polymers are a fire hazard because of their excellent flammability properties. Most often it is required to blend fire-retardant additives to organic polymers to make them less hazardous with respect to inflammability. Another impor-

tant limitation is that the petroleum feed stocks are not going to last for ever. Clearly this stock is going to run out fairly quickly given the rate of its consumption. Even if one considers that coal reserves are much larger and hence may provide the necessary basis for the continuation of the organic polymers there is going to be a need for supplementing these conventional systems with polymers that contain inorganic elements. It is to be noted that silicon is the second most widely present element in the earth's crust (27.2 % by weight), while carbon ranks seventeenth in the order of abundance (180 ppm). If one takes into account the presence of carbon in oceans and atmosphere also, its abundance goes up to the fourteenth position [4]. Thus, it makes chemical sense to look for alternative polymeric systems based on non-carbon backbones. Lastly, another compelling reason to look for newer polymeric systems containing inorganic elements is the line of thinking that if organic polymers themselves are so diverse in terms of their structure and property, it should be possible to find entirely new types of polymeric systems with completely different properties in some combination of inorganic elements. These are a few reasons that have motivated research scientists across the world to find ways of assembling new types of polymers that are based on inorganic elements [5-9]. It must be stated at the outset that most of these efforts have resulted in polymers which not only contain inorganic elements but also have organic groups either as side groups or in the main-chain itself. While there are some examples of *pure inorganic polymers* they still remain *rare*. In order to appreciate the problems of inorganic polymer synthesis it is worthwhile to briefly examine the synthesis of organic polymers. A more detailed survey of organic polymer synthesis is presented in Chap. 2.

1.2 Procedures for Synthesizing Organic Polymers

Most organic polymers can be synthesized by using any of the following three general synthetic methods: (1) Polymerization of unsaturated organic monomers. (2) Condensation of (usually) two difunctional monomers with each other. (3) Ring-opening polymerization of cyclic organic rings to linear chain polymers [1-3].

Vinyl monomers such as $CH_2{=}CH_2$ (and others such as $CF_2{=}CF_2$), mono substituted ethylenes $CH_2{=}CH(R)$ (such as propylene, styrene, vinyl chloride, acrylonitrile, methyl methacrylate, etc.), some disubstituted olefins $CH_2{=}CRR'$ (such as isobutylene), dienes (such as 1,3-butadiene, isoprene) and also monomers such as acetylene can be polymerized by various polymerization methods to afford linear chain polymers. In all of these po-

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lymerization reactions two new C-C single bonds are created in place of one C=C double bond. This process is thermodynamically favorable. Representative examples of polymers that have been synthesized by this method are shown in Fig. 1.1.

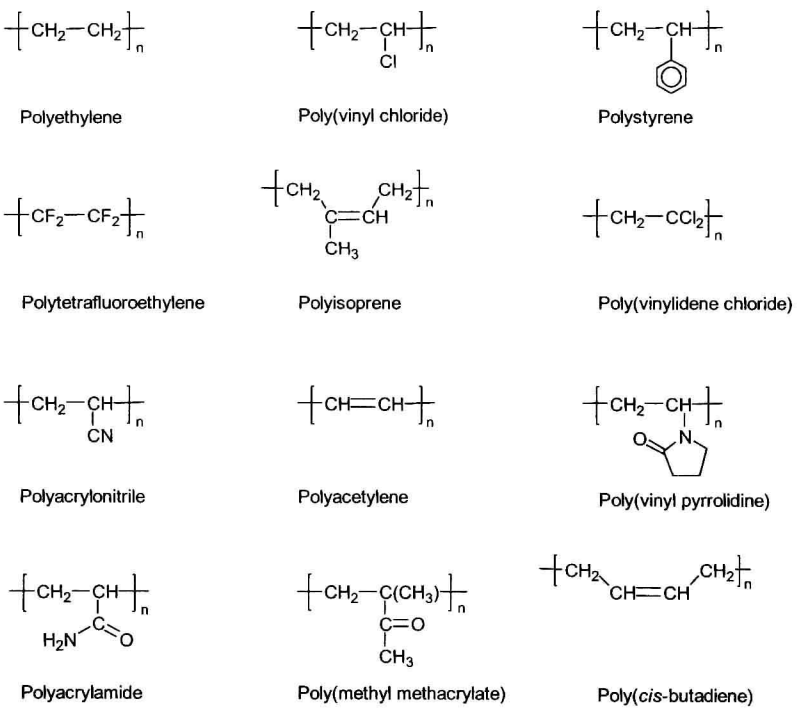
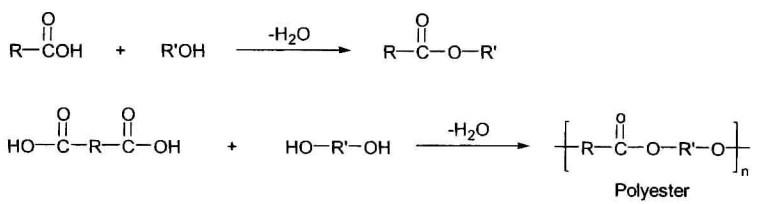


Fig. 1.1. Representative examples of organic polymers prepared from unsaturated organic monomers

The second method of obtaining organic polymers involves the exploitation of functional group chemistry of organic molecules. Thus, for example the reaction of a carboxylic acid with an alcohol affords an *ester*. Instead of condensing two mono functional derivatives in reacting two difunctional compounds (dicarboxylic acids and diols) one obtains a *polyester* (see Eq. 1.1).



(1.1)

This methodology is quite general and can be utilized to prepare several types of polymers such as polyamides, polyimides, polyurethanes, polyethers etc. The polymer properties depend on the type of functional groups that link the polymer building blocks. Further modulation is achievable by varying the nature of the difunctional monomer within each class of polymers. It is not always necessary to condense two difunctional monomers. Some polymers such as polyethers are prepared by the oxidative coupling of the corresponding phenols. A few examples of polymers that can be prepared by the condensation reactions are shown in Fig. 1.2.

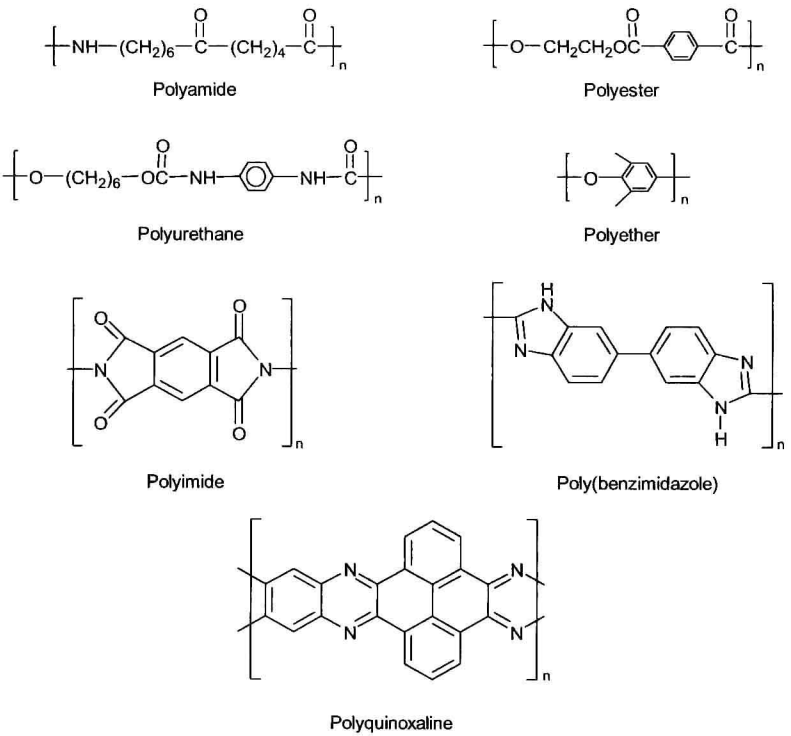


Fig. 1.2. Polymers prepared from the condensation reactions of organic monomers

The third method of polymer preparation involves a ring-opening polymerization (ROP) of cyclic monomers to polymeric chains. Thus, monomers such as ethylene oxide, propylene oxide or even tetrahydrofuran can be used as monomers for ROP. Cyclic amides (lactams) and cyclic esters (lactones) can also be polymerized. It is important to note that all cyclic organic compounds cannot be converted into linear chains. For example, well-known organic molecules such as benzene, cyclohexane, dioxane, tetrahydropyran etc., cannot be polymerized to the corresponding

polymers. Some examples of organic polymers that can be obtained by ROP are shown in Fig. 1.3.

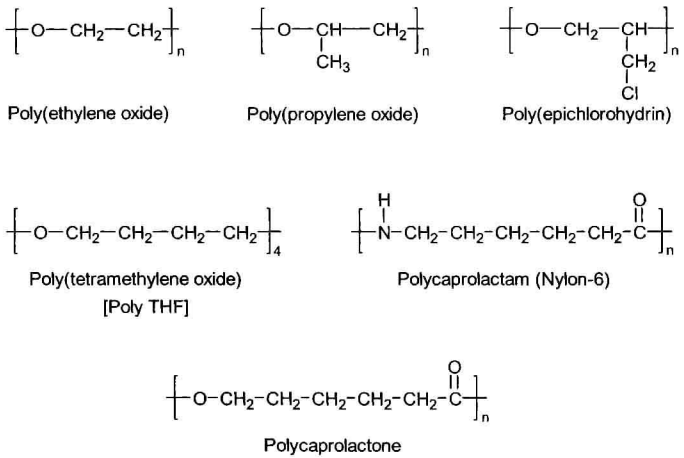


Fig. 1.3. Polymers prepared by the ring-opening polymerization of cyclic organic monomers

1.3 Inorganic Polymers: A Review of Synthetic Strategies

In light of the previous discussion on the synthesis of organic polymers we can now look at the strategies that would be needed for assembling inorganic polymers. It must be borne in mind that many inorganic compounds such as inorganic oxides (for example, SiO_2, B_2O_3, Al_2O_3 etc.,) or inorganic nitrides (for example, Si_3N_4, BN etc.,) are technically polymeric substances which are built from simple structural blocks [4]. However, substances of this type are not considered in this discussion. Only inorganic polymeric substances that are analogous in terms of their solution behavior to organic polymers are considered. Thus, most organic polymers are soluble in some kind of organic solvents (some such as Kevlar are soluble in mineral acids) and more importantly they retain their macromolecular structure in solution. Further, many organic polymers retain their properties upon melting. These properties are possible because of the essentially covalent linkages that are present in these organic polymer chains. Inorganic polymer synthesis needs to address the issue of formation of covalent bonds between similar or dissimilar inorganic elements so that polymeric structures are realized. As will be shown in subsequent sections such element-element linkages can be accomplished in many ways.

1.3.1 Unsaturated Inorganic Compounds

We will first look at the possibility of utilizing inorganic compounds that contain double or triple bonds between them, as monomers for organic synthesis. In order to keep the discussion simple we can limit ourselves by looking at such compounds belonging to the elements of Groups 14 and 15. Thus, the silicon analogue of ethylene is $H_2Si{=}SiH_2$. Even before we consider this compound it is worthwhile to note that many silicon analogues of alkanes viz., Si_nH_{2n+2} have been prepared by the German chemist Alfred Stock [4]. He noted that these silanes were extremely reactive and burnt spontaneously in air. In fact, Stock had to develop hitherto unknown vacuum-line techniques for handling such pyrophoric compounds. From this reactivity behavior it is anticipated that the corresponding silicon analogues of ethylene in particular and other olefins in general would be extremely reactive. For a long time compounds of silicon that contain double bonds between them could not be prepared and either cyclic- or oligomeric compounds, (or in some instances even some polymeric products) were the result of such investigations [10]. Similarly, it was not possible to isolate compounds of other main-group elements which contain double bonds between them. Several such failures have led to the *promulgation* of a *double-bond role*. This stated that heavier main-group compounds containing double bonds cannot be prepared. The rationale for this rule emanates from two possible reasons. Heavier main-group elements are larger in size and hence their inter-atomic distances are also longer (in comparison to carbon). Consequently, the additional *p*-orbital overlap between heavier main-group elements to generate a double bond would be quite weak. The double-bond rule held its own for a long time until its demise in 1981. In this year the double bond rule was firmly thrown out and a series of main group compounds containing double bonds were isolated and characterized [10-11]. The synthetic technique that contributed to this success was the utilization of sterically hindered groups for kinetically stabilizing these reactive compounds. The idea was to use large-sized substituents to *sterically protect* the double bonds once they were formed. Using this methodology stable compounds containing Si=C, Si=Si, P=C, P=P, P=As, Sb=Sb and even Bi=Bi double bonds were synthesized and characterized [12] (Fig. 1.4). It can be seen that the size of the sterically hindered group increases with the increase in the size of the main-group element. Although, the problem of preparing multiple-bonded compounds containing heavy main-group elements was thus solved, the very method of stabilizing these compounds defeats the possibility of using them as monomers for polymer synthesis. For example, it was found that the *in situ* generated disilene

iPr$_2$Si=SiiPr$_2$ undergoes spontaneous oligomerization to the cyclic tetramer [iPr$_2$Si]$_4$ (see Eq. 1.2) [13].

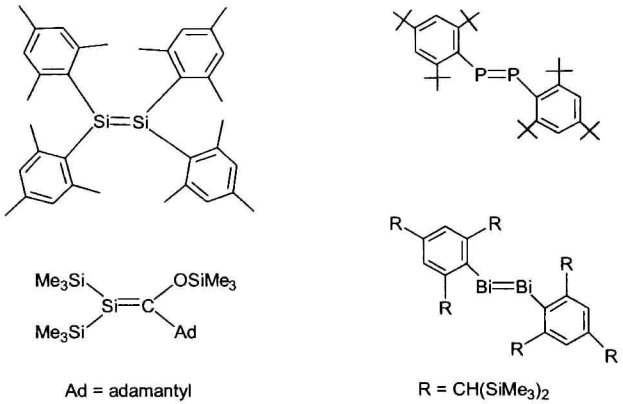
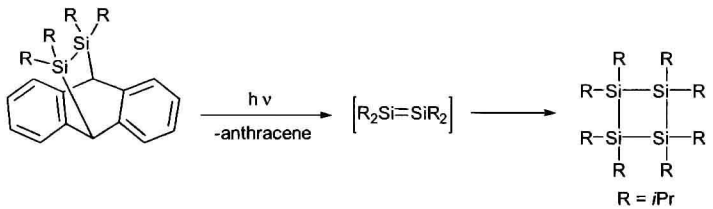


Fig. 1.4. Compounds of main-group elements that contain double bonds between them



(1.2)

Unsaturated organic compounds such as olefins also are reactive; however, their reactivity can be suitably directed to afford various kinds of products including polymers. Manipulating the reactivity of the newly discovered *unsaturated* inorganic compounds, to afford polymeric products still remains a synthetic challenge. Recently it was observed that MesP=CPh$_2$ could be polymerized by either radical or ionic initiators to afford moderate molecular weight polymers, [MesPCPh$_2$]$_n$ (Mes = 2,4,6-Me$_3$-C$_6$H$_2$-) [14].

1.3.2 Inorganic Polymers from Acyclic Monomers

Various types of polymerization reactions involving appropriate *inorganic acyclic monomers* have been quite effectively utilized for the preparation of polymers containing inorganic elements or inorganic groups. Some of

these examples are illustrated in this section. These polymerization strategies are of two types.

1. A reaction where a *small molecule* is eliminated from a *single monomer* to generate the polymer.
2. A reaction between *two appropriate difunctional monomers* to eliminate a small molecule and afford a polymeric material.

1.3.2.1 Polymer Synthesis from a Single Monomer

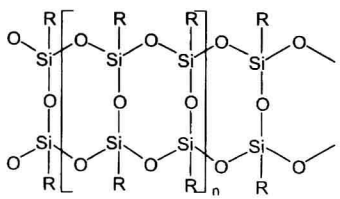
Various types of reactions have been used for the synthesis of polymers starting from a *single monomer*. Thus, for example, *dehydration* of diorganosilane diols affords the corresponding polymeric organosiloxanes. The most widely known inorganic polymer viz., poly(dimethylsiloxane), $[Me_2SiO]_n$, can be prepared in this manner (other routes for the synthesis of this polymer are also known) [15-17]. Although the reaction involved in the synthesis of poly(dimethylsiloxane) is the hydrolysis of dimethyldichlorosilane, the immediate product of the reaction is $Me_2Si(OH)_2$ which is the actual monomer that undergoes self condensation by the elimination of water. This process of dehydration leads to the formation of $[Me_2SiO]_n$ (see Eq. 1.3).

$$Me_2SiCl_2 + 2H_2O \xrightarrow{-2HCl} Me_2Si(OH)_2 \qquad (1.3)$$

$$nMe_2Si(OH)_2 \xrightarrow{-nH_2O} [Me_2SiO]_n$$

The dehydration reaction has also been used to prepare ladder-type polymers. Thus, the hydrolysis of $PhSiCl_3$ affords $PhSi(OH)_3$ which undergoes a self condensation reaction to generate a ladder-like polymer which is known as polysilsesquioxane (see Eq. 1.4) [15, 16].

$$4n\ RSi(OH)_3 \xrightarrow{-6H_2O} \qquad (1.4)$$



Polysilsesquioxane

Metal-assisted *dehalogenation* reaction, analogous to the well-known Wurtz reaction has been very effectively employed for the preparation of polysilanes which contain catenated organosilicon units. Thus, the reaction of a variety of diorganodichlorosilanes with finely divided sodium in a

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