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Molecular Chemistry and Nanosciences

1.1 INTRODUCTION

Nanosciences study *nano-objects*, *i.e.* nanometric-size objects ($1\text{ nm} = 1 \times 10^{-9}\text{ m}$) and their transformation into *nanomaterials*.^{*†} Unquestionably, they represent a most promising field of material sciences for the next few years. The main challenge will be the control of physical and chemical properties by methods operating at atomic or molecular level.

However, in the mind of many scientists, physics is the major factor in nanosciences, chemistry playing but a minor role. This opinion is largely the consequence of the historical development of nanosciences, as explained in the next section.

The purpose of this book is to amend this view by pointing out the potential of chemistry in this area. We shall present in Section 1.2 the two principal approaches in nanosciences (the ‘top-down’ approach which relies mostly on physics and the ‘bottom-up’ approach which is essentially a matter of chemistry), and relate in Section 1.3 how chemistry has evolved from an exploratory to a creative science. Chemistry can now tackle successfully a great variety of problems, from the creation of new

^{*}Thus nanosciences are defined by the size of the objects, rather than by the nature of the phenomenon studied as in optics, electricity, etc. It follows that they are by definition multidisciplinary.

[†]Nanomaterials differ from ‘ordinary’ materials in that their properties can be traced back to those of their nano-object component: in other words, these properties are already incorporated at the nanoscale.

materials to the synthesis of auto-organized systems which can almost mimic living matter. With the synthetic methods already perfected and/or to be discovered in the near future, chemistry can convert nano-objects into a vast number of operational materials, exemplified by carbon and ceramic fibers, the forerunners of nanomaterials (Section 1.4).

Nanosciences are multidisciplinary, with physics and chemistry as natural partners. Chemistry can create new molecules, particles, nano-objects, etc., which can lead to innovative designs for new materials, *e.g.* materials in which several physical or chemical properties interact. If their preparation is the chemist's responsibility, the study and utilization of these materials' original properties come under the remit of the physicist. Other disciplines may be involved as well. For instance, mechanics will be implicated because no materials exist without mechanical properties. Mechanical attributes can also be fine-tuned at the nanometric scale. Biology is less directly involved because most biological entities exceed a micrometer in size; however, it will benefit from the development of nano-objects capable of working in a biological environment. The most illustrative example is that of biosensors capable of detecting and measuring certain substances *in situ* (*e.g.* in blood). Furthermore, modeling biological properties may suggest new designs for nanomaterials. Thus the membrane phospholipids have served as a model for the development of vesicle-forming surfactant compounds.

Modern science is demanding, requiring expert knowledge from each contributing discipline. Only close cooperation between experienced and competent specialists, who are able to communicate with each other, understand each other and conceive a joint project, can lead to new and significant achievements.

1.2 SCOPE AND ORIGIN OF NANOSCIENCES: THE 'TOP-DOWN' AND 'BOTTOM-UP' APPROACHES

Although chemists handle objects of nanometric sizes daily, physicists must be credited with formalizing the concept of nanosciences. This is due to two reasons.

The first one is purely scientific. It comes from the quasi-certitude that exploration of the 'nanoworld',¹ that is to say matter at the nanometer scale, will lead to the discovery of new, unexpected physical properties. Indeed, it is known that physical properties are dependent on the observation scale: studies at the micrometric scale will not reveal the same

properties as studies at the nanometric scale. Investigation of the behavior of isolated units (metal atoms, particles, molecules) becomes possible with the invention of the atomic force microscope and the scanning tunneling microscope. Some results obtained are spectacular and open up exciting vistas to scientists. For example, physicists have been able to study the transition of a single electron from the fundamental to the excited state in semiconductors as well as in suitably chosen organic molecules. IBM scientists have written their company's acronym on an appropriate surface by displacing atoms one by one. To recap, physics has the instruments for exploring the nanoworld and the capacity to study and exploit the (optical, electrical, magnetic, etc. . .) properties of nano-objects.

The second reason, more technological, has economic motivations. The mass diffusion of electronic products and their involvement in almost everyday activity have generated a mounting need for smaller and yet more powerful microprocessors. This demand is quantified by the famous Moore law which predicts that the performance of electronic components increase by one order of magnitude every two years. Microprocessors are, therefore, miniaturized and tend towards 'nanoprocessors'. This approach has been termed 'top-down' and corresponds to the first manifestation of the nanoscience concept. From an economic point of view, the top-down methodology is unquestionably the most important approach at present and has created a lively international competition.

There is also a symmetrical approach called 'bottom-up' in which the nanomaterial is chemically assembled from elementary chemical components, just like a wall is constructed from bricks and mortar. While the top-down approach is essentially a miniaturization technology from which chemistry is absent, the bottom-up approach, based on synthesis, fits perfectly with chemical methodology. The building blocks – molecules, molecular complexes, atoms or aggregates, all entities whose sizes vary from tenths of a nanometer to tens of nanometers – are familiar to chemists. The assembling methods (the mason's mortar) use inclusion and polymerizations of organic or inorganic entities. As shall be explained in the next chapter, chemistry possesses all the necessary requirements for developing nanosciences by the bottom-up approach.

One of the most illuminating examples concerns the *selective elimination* of lead from drinking water.²⁻⁴ After passage through a filtering cartridge, the Pb^{2+} concentration is $<5 \mu\text{g l}^{-1}$. The concentration of other ions (Na^+ , Ca^{2+} , Mg^{2+} , etc.) is unchanged. This achievement, unbelievable just 10 years ago, is now possible because coordination chemists can prepare compounds capable of chelating selectively different metal ions. These compounds are incorporated into solids by polymerizations. In this

case, a Pb^{2+} -selective chelating molecule was bonded to silica, resulting in a material, which can be shaped into cartridges. This example is proof that chemistry can synthesize operational and selective nanomaterials.

However, physics is not absent from the bottom-up approach. Some nano-objects, for example fullerenes and carbon nanotubes, can only be obtained by physical methods. There exist also physical assembling methods: vapor phase deposition, molecular beam, etc. All these approaches can lead to new materials.

1.3 CHEMICAL MUTATION: FROM AN EXPLORATORY TO A CREATIVE SCIENCE

During the last fifty years, science has progressively metamorphosed.[‡] Let us illustrate these changes with some examples, with particular emphasis on synthesis, which is the foundation of chemical creativity.

A revolution in structural determination launched this chemical mutation. In the late 1950s, recording spectrographs gradually allowed chemists to complete chemical analyses with physical methods (IR, UV, NMR, EPR, MS, X-ray diffraction, etc.) An exhaustive list would take too long and be too difficult to provide, with the number of these identification methods being very large and increasing by the day. Note, however, that chemical quantitative analysis remains *a necessary safeguard* in material sciences (we shall return to this point in Chapter 6).

These analytical tools have permitted a better comprehension of reactivity. Mastering the concepts governing the formation of chemical entities, the organization of solids and molecular structure has enabled chemists to synthesize incredibly complex molecules. Thus, Professor Y. Kishi's group has prepared palytoxin, a natural product isolated from soft coral. This compound^{5,6} possesses 62 chiral carbons and has 2^{62} ($\sim 4 \times 10^{18}$) stereoisomers (Figure 1.1). On account of the precision of existing synthetic methods, it has been possible to produce the natural isomer.

[‡]At the end of the nineteenth century, classical physics was a coherent corpus of doctrines, able to rationalize practically all known phenomena, thanks to mechanics, thermodynamics and electromagnetism. As for chemistry, which was largely empirical during the nineteenth century, it had sufficiently progressed by the middle of the twentieth century to be considered as 'having come of age'. Indeed, fundamental concepts like covalent bond or aromaticity, initially introduced empirically, can be explained by quantum mechanics. Students no longer need to learn by rote hundreds of reactions; they have only to understand a dozen mechanisms (additions, eliminations, substitutions, rearrangements, etc.) Also, the number of complex multistage syntheses already realized show that organic chemists could synthesize practically any existing molecule.

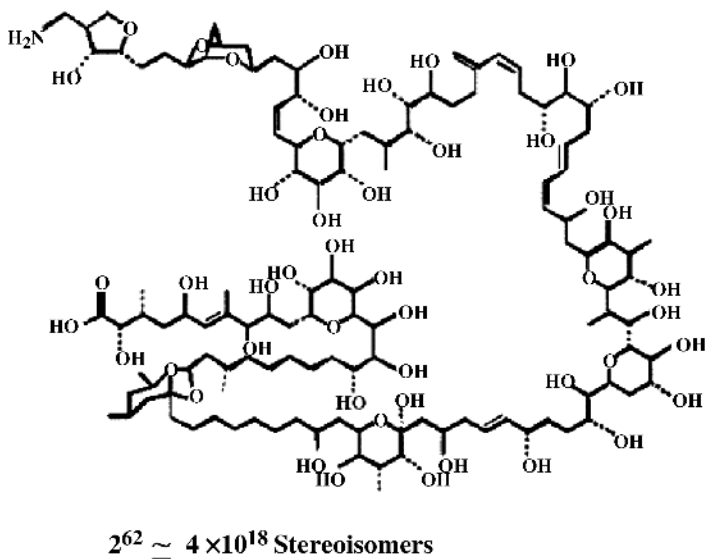


Figure 1.1 Palytoxin. Reproduced by permission of *L'actualité chimique*

Other exotic molecules have also been made. One instance is cubane⁷ (Figure 1.2) whose carbon atoms have valence angles of 90° instead of $109^\circ 28'$. Figure 1.2 also shows a tetrahedral polymetallic cluster which can be resolved into its two optical isomers⁸ and a ladder polymer in which carbon atoms have been replaced by silicon atoms.⁹ Very different elements can now be bonded together and the size of polymetallic clusters controlled.^{10,11} An outstanding achievement of inorganic chemistry is the synthesis of superconductor ceramics (YBaCuO).^{12,13}

These – far from exhaustive – examples demonstrate that *chemists can now synthesize any imaginable structure*. Chemistry has left for good the exploratory domain to become a science of creation.

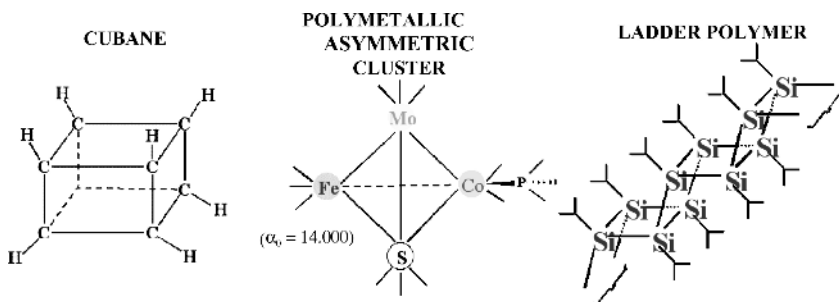


Figure 1.2 Some unusual compounds which have been synthesized. Reproduced by permission of *L'actualité chimique*

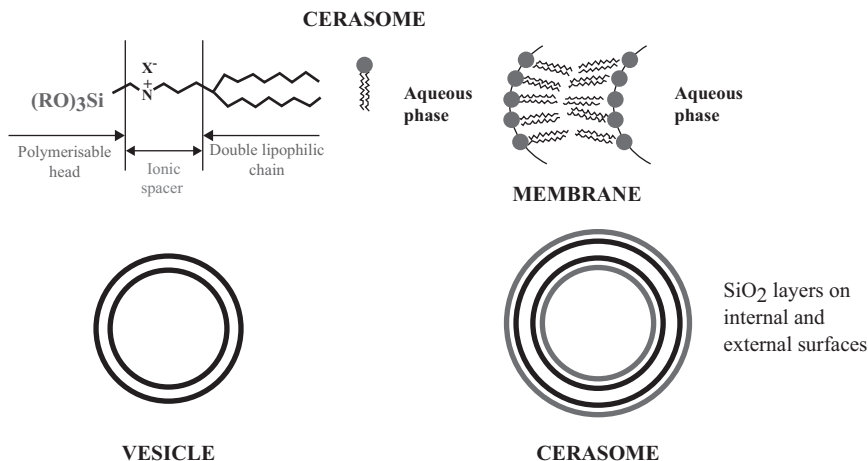


Figure 1.3 Preparation of vesicles with their internal and external surfaces protected by a film of SiO₂

Let us mention also the recently published example of the cerasomes.¹⁴ These vesicles have been obtained using specific chemical methods mimicking the formation of biological membranes. The membrane of these vesicles is coated externally and internally with a molecular layer of silica, giving rise to well-defined systems, which, however, can undergo controlled exchanges (Figure 1.3).

This example shows that chemistry can synthesize not only *new structures* but also structures with *novel properties*, for physical properties can now be correlated with chemical structures. Since the 1970s, material sciences, particularly the chemistry of inorganic solids, have extensively studied the physical properties of chemical products. Later on, macromolecular and molecular chemistries successfully prepared, from organic or organometallic building blocks, materials having special physical properties. Organic conductors were a historical watershed: for the first time, molecular systems prepared by methods of organic synthesis showed conducting or even superconducting properties, which until then were specific of metals.^{15,16} Things fell into place when scientists realized that delocalized π electrons in unsaturated organic molecules are comparable with the electrons responsible for metal conduction and can therefore induce the same properties. Subsequently, several other types of polymers with various physical properties have been discovered.¹⁷ Figure 1.4 presents some conducting polymers, a piezoelectric polymer and some polysilanes endowed with (semiconduction, photo-oxidation, thermochromism) properties related to the Si–Si σ bond.¹⁸ Study of these properties has led to a most interesting theoretical development.

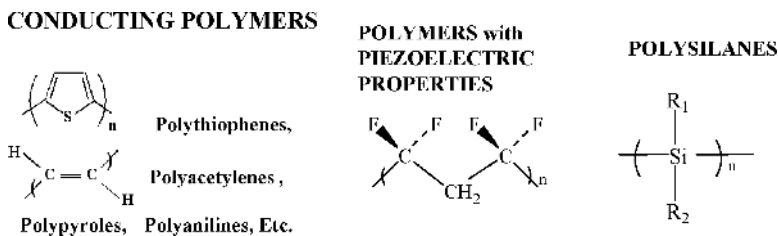


Figure 1.4 Examples of polymers with remarkable physical properties. Reproduced by permission of *L'actualité chimique*

The outstanding optical properties of lanthanides are another significant example. They are responsible for color TV, for signal transmission by optic fibers as well as for remarkable photoluminescent properties. Let us also draw attention to the nonlinear optical (NLO) properties of new organic molecules (Figure 1.5). Nonlinear optics is the branch of optics, which describes the behavior of light in nonlinear media, in which the polarization responds nonlinearly to the electric field of the light. This nonlinearity is only observed at very high light intensities, such as those provided by pulsed lasers.

In the last few years, chemistry has succeeded in creating new entities having expected or unexpected properties. Here are two examples.

The first example is a new technology for generating metallic nanoparticles in mild conditions. This discovery by Bruno Chaudret¹⁹ advantageously replaces the preparation of nanoparticles by reduction of metallic salts. It is based on the very mild decomposition of coordination complexes in which the metal is feebly chelated (π complexes). The growth of the nanoparticle is controlled by weakly coordinating additives, which limit the growth while protecting the metallic entities (Figure 1.6).

The second example comes from dendrimer chemistry (dendrimers being molecules replicating in space from a center, like a cauliflower). The different branches are identical and the size of such molecules can be quite large (Figure 1.7). Phosphorus compounds are very convenient

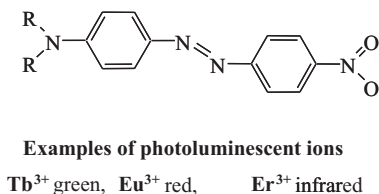


Figure 1.5 Molecule with NLO properties used for frequency doubling. Reproduced by permission of *L'actualité chimique*

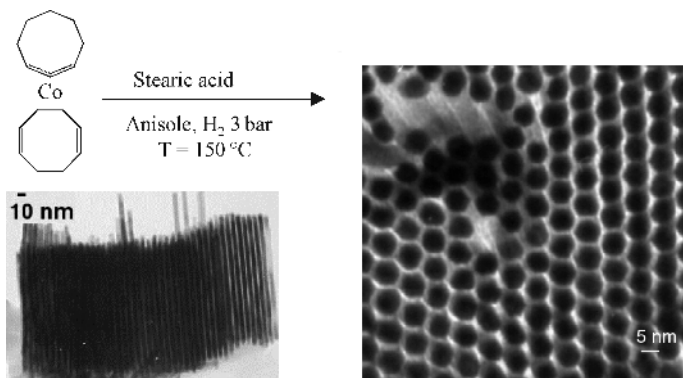


Figure 1.6 Nanorod superlattice of Co nanoparticles obtained by controlled decomposition of a Co π complex. Reproduced with permission from *Angewandte Chemie International Edition*, Unprecedented crystalline super-lattices of monodisperse cobalt nanorods by Dumestre, Frederic; Chaudret, Bruno; Amiens, Catherine; Respaud, Marc; Fejes, Peter; Renaud, Philippe; Zurcher, Peter, 42, 5213–5216. Copyright (2003) Wiley-VCH

as they permit regular growth of the dendrimers and can be analyzed by ^{31}P NMR.²⁰ From a close collaboration with biologists and physicians, Jean-Pierre Majoral and his group have been able to establish that phosphorus dendrimers show unexpected therapeutic properties.²¹

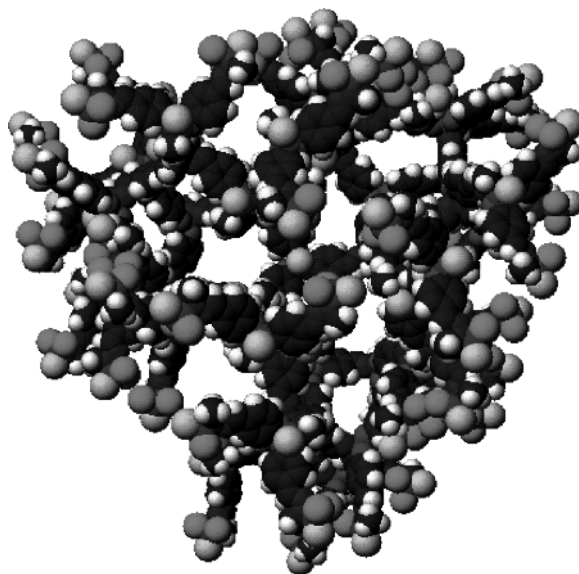


Figure 1.7 Molecular model of a phosphorus dendrimer presenting 48 P(S)Cl₂ groups on its surface (See Plate 1 for color representation)

They remarkably increase immune defenses against cancerous cells by developing ‘Natural Killers’ (NK), which are the equivalent of white blood cells, capable of phagocytosing the malignant cells. This totally unpredictable discovery illustrates how many surprises the creative power of chemistry can have in store. In the present case, the biological mechanisms, which induce the growth of NK, are completely unknown.

1.4 CARBON AND CERAMIC FIBERS: THE NANOMATERIAL ‘ANCESTORS’

Carbon and ceramic fibers meet the definition of nanomaterials. These compounds with remarkable mechanical properties have been prepared from a *single molecular precursor*, assembled and shaped in the course of a series of chemically controlled steps. Carbon fibers were prepared in the 1960s, with ceramic fibers being prepared in 1975. These materials cannot be obtained by classical thermal methods. In both cases, innovative approaches have opened up new horizons of research. However, only carbon fibers, of low production costs and wide applications, have been a commercial and industrial success. Ceramic fibers have outstanding properties. Unfortunately, their cost has not encouraged industrial production.

1.4.1 Carbon Fibers

We shall now sketch out the preparation of the polyacrylonitrile (PAN) carbon fiber. The story begins in the early 1960s with the discovery of unexpected properties of the solids obtained by pyrolysis of PAN. Figure 1.8 shows schematically the reactions occurring during the successive pyrolyses carried out at temperatures ranging from 200 to 1300 °C under inert atmosphere (He) and various orientation constraints. In the first stage, this polymer is transformed into heterocyclic polycondensates. In the second stage, the hydrogen and nitrogen are eliminated. The solid becomes a nanometric ribbon of polyaromatic units. Under the imposed constraints, these ribbons twist together, becoming entangled into larger fibers, in the manner of jute fibers, which wind up and give a string, then a rope.

These fibers can be spun into great lengths by industrial methods. In composites, they can play the role of the metallic structure in reinforced

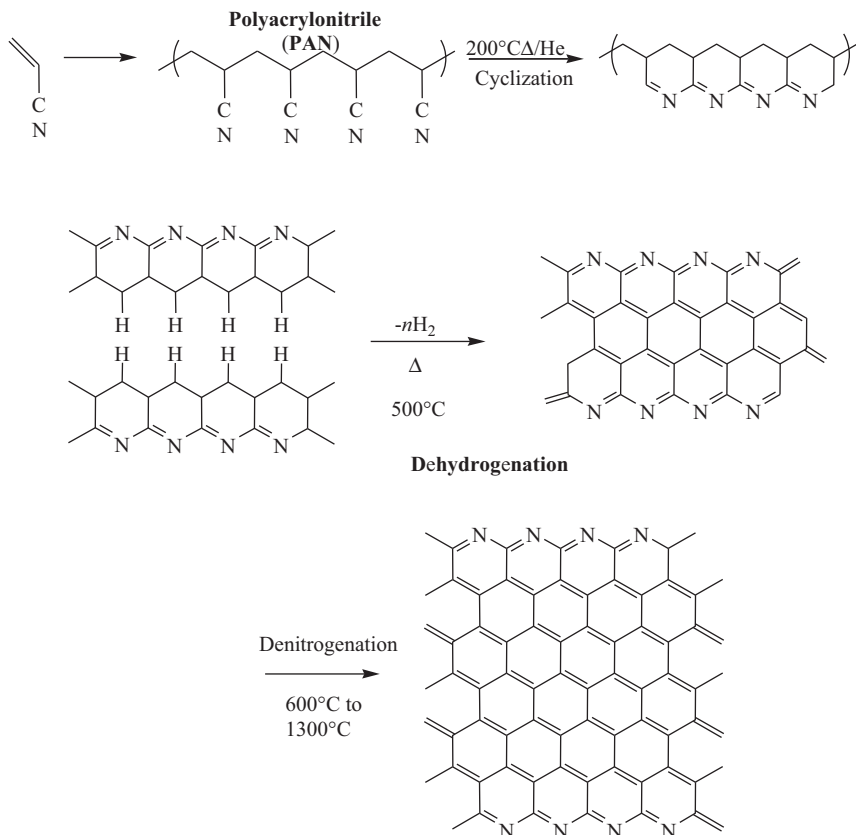


Figure 1.8 Schematic representation of the preparation of carbon fibers from polyacrylonitrile (PAN) by successive polycondensations of carbon atoms

concrete. Their inclusion in a polymer matrix results in materials, which are remarkably resistant to stretching and deformations.

At present, there exist a great number of carbon fibers. Those with weak mechanical properties are used for filtration, thermal isolation, gas adsorption and heat dissipation in braking systems. Those having good mechanical properties are utilized in composites intended for more exacting applications (e.g. in aeronautics). Composites of carbon fibers in appropriate matrices offer, for the same weight, the best resistance to the mechanical constraints experienced by a flying aeroplane. Many carbon fibers, other than PAN fibers, have been prepared from other polymers (polyesters, polyamides, etc.). Each has different characteristics and different uses.

The making of carbon fibers represents an important innovation, not only technologically, but also conceptually: organic textile polymers have been transformed by a simple thermal treatment into materials capable of competing with metals for some applications. In addition, they are easily shaped and are much lighter.

It is perhaps slightly inaccurate to present these fibers as being conceived from the molecular scale, since PAN has been known for a long time. It is clear, however, that the discovery of PAN fibers would not have occurred, had chemists not studied the development of the polymer polycondensation and realized the possibility of obtaining materials with properties radically different from those of the initial polymer. Carbon fibers have served as models for the ceramic fibers to be discussed in the next section.

1.4.2 SiC, Si₃N₄ Ceramic Fibers

If carbon fibers can be considered as remote ancestors of nanomaterials, their 'homo erectus' so to speak, then the SiC and Si₃N₄ fibers are truly the 'first' nanomaterials, their Cro-Magnon ancestors.

The discovery of carbon fibers was the fruit of observation and their industrial success the outcome of perspicacity. Their story represents a beautiful example of serendipity. However, the invention of ceramic fibers was definitely not fortuitous. The conquest of space has created a need for materials with exceptional mechanical properties, capable of resisting temperatures above 1000 °C. Carbon materials, very sensitive to oxidation, cannot meet these requirements, but ceramic materials like SiC and Si₃N₄ can resist high temperatures, even in oxidative media.

Ceramic materials were the first nanomaterials to be prepared. Their final properties had been planned at the molecular scale and their synthesis was carried out step by step from a single molecule. The synthesis was designed to prepare a SiC (or Si₃N₄) ceramic fiber.

Long before the formulation of the nanoscience concept, Verbeek²² (1974, Germany) and Yajima^{23,24} (1975, Japan) independently worked out a method for preparing SiC (Yajima) and Si₃N₄ (Verbeek) ceramic fibers with excellent thermomechanical properties.

We shall deal here with the SiC case, which is much better known than the Si₃N₄ case, since Yajima, having an academic position, has abundantly published, whereas Verbeek, who works in industry, has filed patents. Silicon carbide, a covalent material, is a material highly resilient to mechanical constraints (abrasion, traction or torsion). Its chemical and

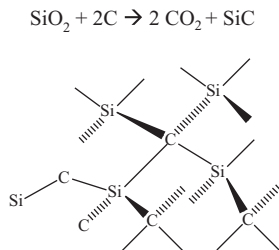


Figure 1.9 SiO_2 carboreduction

mechanical stabilities at high temperatures ($\sim 1500^\circ\text{C}$) are truly remarkable.

Powdered and solid SiC have been known for a long time. The simplest way to prepare them is by total carboreduction of SiO_2 (Figure 1.9). However solid SiC, being too resistant, cannot be drawn into fiber, molded or coated. Compacting SiC or Si_3N_4 powders is also hopeless. Both Verbeek and Yajima have independently invented a completely new method for preparing ceramics. The guiding principle is the following: the ceramics must pass through an intermediate state *viscous enough to permit the material to be drawn into fibers*. Clearly this stage should precede the final stage of ceramization. These authors have then elaborated a general scheme similar to the different steps of the sol-gel process. The difference is that the sol-gel process proceeds at room temperature whereas the final ceramization, according to Yajima and Verbeek, requires a high temperature (Figure 1.10).

The Yajima process (Figure 1.11) is based on the polymerization of dimethyldichlorosilane, $(\text{CH}_3)_2\text{SiCl}_2$, a compound produced in great quantities by the silicon industry.

Polymerization of $(\text{CH}_3)_2\text{SiCl}_2$ in the presence of sodium metal gives a polysilane with Si-Si bonds. Heated at 350°C , its linear skeleton undergoes the so-called Kumada rearrangement²⁵ (Figure 1.12).

This rearrangement produces polycarbosilane chains containing the Si-C-Si bonds of the ceramics. The functional Si-H bonds, which are

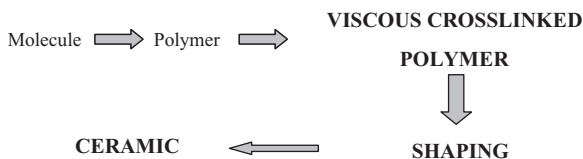


Figure 1.10 Schematic representation of SiC shaping

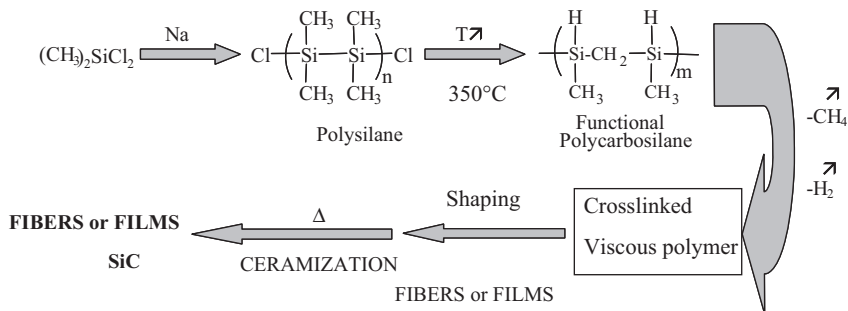


Figure 1.11 Schematic representation of the chemical transformations necessary for SiC shaping. Reproduced with permission from *Journal of Organometallic Chemistry, Organosilicon Chemistry and Nanoscience* by Robert Corriu, 686, 1–2, 32–41. Copyright (2003) Elsevier

concomitantly made, will permit the reticulation of the linear chains of polycarbosilane, leading to a three-dimensional system. This set of reactions occurs during a controlled pyrolysis which at $\sim 450^\circ\text{C}$ gives a viscous reticulum, which can be drawn into long fibers or be made into coatings for the protection and reinforcement of other materials. It is also possible to obtain composites with SiC or Si_3N_4 matrices containing reinforcement additives or fibers of another material. The last step is the ceramization of the material with the elimination of residual elements (essentially CH_4 and H_2).

The various stages of this reaction scheme have been optimized in order to increase the fiber yield and minimize the oxycarbides resulting from an ancillary oxidation quite difficult to avoid at the temperatures employed.²⁶

The Yajima and Verbeek processes constitute remarkable conceptual progress. The major inconvenience of the Yajima process is the use of an alkaline metal in stoichiometric amounts. We have described a much more handy catalytic preparation of polysilane using a catalytic polymerization of $\text{R}_1\text{R}_2\text{SiH}_2$ into $(\text{R}_1\text{R}_2\text{Si})_n$ discovered by Harrod and Samuel.^{27,28} The reaction in Equation (1.1) shows the direct polymerization of a hydrosilane in very mild conditions.

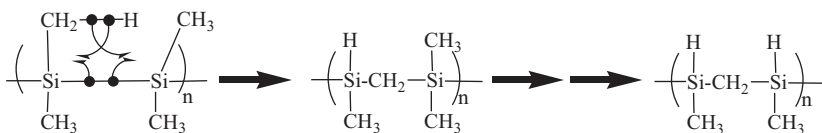
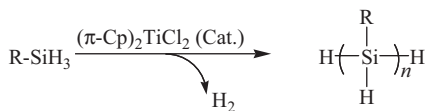
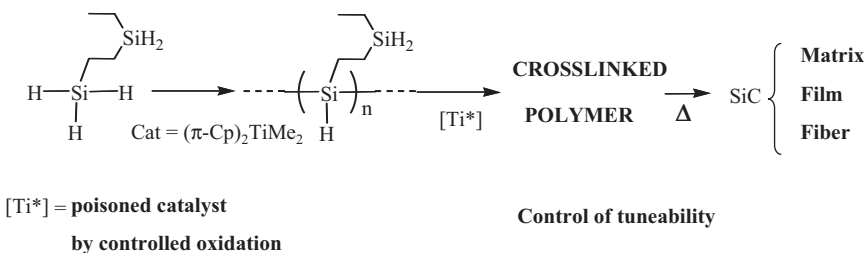


Figure 1.12 Mechanism of the Kumada rearrangement



Equation 1.1 Catalytic polymerization of polyhydrosilanes

The polycarbosilane is obtained in one step from pentahydrodisila-1,4-hexane, a molecular precursor which is directly polymerized and polycondensed in solution in the presence of the $(\pi\text{-Cp})_2\text{TiMe}_2$ catalyst (Figure 1.13).²⁹ The proposed mechanism for this reaction involves the reduction of the catalyst by the Si–H bonds, generating a complex of the $[\text{Cp}_2\text{Ti}]$ type. This complex catalyzes the formation of Si–Si bonds by oxidative addition and reductive elimination. The reticulation of the polycondensate (and by way of consequence, its viscosity) can be regulated by a carefully controlled admission of air, which provokes an oxidative poisoning of the catalyst. When the crosslinking of the chains reaches a suitable viscosity, one can proceed to the shaping and then the ceramization of the material. The poisoned catalyst is steadily regenerated *in situ* by reaction with the reducing Si–H bonds. This example nicely illustrates the flexibility of molecular chemistry: preparation of ceramic fibers or coatings is made in one single catalytic step leading directly to the easily shaped viscous material.



FILMS, FIBERS, MATRICES

Figure 1.13 Catalytic process for the control of tuneability of SiC. Reproduced with permission from *Journal of Organometallic Chemistry, Organosilicon Chemistry and Nanoscience* by Robert Corriu, 686, 1–2, 32–41. Copyright (2003) Elsevier

1.5 CONCLUSIONS

It is interesting to note that the works of Yajima and Verbeek – superb examples of the bottom-up approach – were realized long before the

concept of nanoscience was formulated by physicists. The studies on ceramic materials, using a combination of organic chemistry, polymer chemistry and catalysis, to surmount the difficulties of shaping an inorganic ceramic material, also show the unity of modern chemistry.

In conclusion, it is clear that chemistry possesses the essential synthetic and identification tools to contribute fruitfully to the advancement of nanosciences.

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