



Overview of the Sol–Gel Process

2

Plinio Innocenzi

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Abstract

The first studies on sol–gel processing have been very much focused on the possibility of obtaining bulk gels and through these glasses from a low temperature route.

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With the time this first idea has been almost abandoned and sol-gel inorganic chemistry has become something different. Nowadays it is an almost ubiquitous process in nano-chemistry to prepare a variety of different materials in the form of films, membranes, nanoparticles, aerogels, mesoporous and microporous materials, self-assembled materials, etc. This change of perspective has brought to an unexpected success of inorganic and hybrid sol-gel chemistry which is now a very popular tool for nano-science. At the same time, part of the interest in the basic chemistry of the process has been lost which has also made many people unaware of the fundamental scientific background. The complexity of sol-gel chemistry represents a natural limitation to our capability of giving very detailed and fine descriptions of complex processes.

In this chapter, some basic elements of sol-gel chemistry would be introduced with the purpose of giving a general overview and describing the main properties of sol-to-gel transition which is the physical-chemical phenomenon that characterizes the process.

Keywords

Sol-gel · Sol-gel transitions · Hybrid materials · Alkoxides · Organosilanes

2.1 Introduction

The formation of inorganic or hybrid organic-inorganic materials through a sol–gel process is the result of chemical reactions which transform the sol phase into a solid. Interestingly we define the sol–gel materials not on the basis of their structure and composition but by the process, which is the conversion of a sol into a gel. This synthesis can be included in the general definition of solution-based processing of inorganic materials which consist of several different methods such as for instance nonaqueous metallo-organic

decomposition, hydro-solvothermal synthesis, hot injection, and microemulsion routes. These methods do not show, however, the peculiarity of the sol to gel transition, which is a very distinctive process [1].

The sol–gel transition is quite a ubiquitous phenomenon which is commonly observed in many different systems, in particular organic polymers [2]; the definition of sol–gel materials is, however, mostly used in a very peculiar way to indicate oxides (both glassy and crystalline oxides), hybrids, aerogels, and mesoporous materials which are produced employing a sol–gel chemistry. In general, a sol to gel transition can be due to physical or chemical gelation, with the formation of entanglements or chemical bonds, respectively, which guides the process. In sol–gel materials the formation of a growing spanning interconnected network through hydrolysis and condensation reactions is at the ground of the sol to gel transition that with few exceptions is an irreversible process.

2.2 A Sol and a Gel: A Definition

The definition of *sol* given by IUPAC (International Union of Pure and Applied Chemistry) is: “A fluid colloidal system of two or more components, e.g. a protein sol, a gold sol, an emulsion, a surfactant solution above the critical micelle concentration” [3]. This definition is, however, not self-consistent, because it is necessary also to explain what is a fluid colloidal system (IUPAC [4]): “. . . a state of subdivision, implying that the molecules or polymolecular particles dispersed in a medium have at least in one direction a dimension roughly between 1 nm and 1 μm , or that in a system discontinuities are found at distances of that order.” A sol should, therefore, form by two components, one is a fluid while the second one is defined by the dimension instead of any specific property. Approximately 1 μm has been chosen as a reference dimension to be sure that within this limit the equilibrium of the system is governed by Brownian motion. Beyond 1 μm the gravity force can be predominant over short-range forces and pushes the particles to sediment. Putting the limit of 1 μm we implicitly assume that the sol should be stable, and it is not necessary to specify this property in the definition.

It remains to define what a gel is; in general if the reactions do not stop when the colloidal dimension has been reached, the further growth of the solid phase can form a continuous phase expanded throughout all the container. This is basically how a gel is defined by IUPAC: “Non-fluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid” [5]. The continuity in a gel is very important to define the nature of this state of the matter which is actually composed by two phases, a liquid and a solid, which extend from one side to the other of the

container. The coexistence of two phases, a continuous solid one (the spanning macromolecule) and the liquid component (the residual sol) makes, however, quite difficult to obtain a more precise definition of a gel. This difficulty [6] has been well described by Hench [7]: “A gel, for instance, has been defined as a ‘two-component system of a semi-solid nature rich in liquid’ and no one is likely to entertain illusion about the rigor of such a definition.”

The mechanical resistance developed by a system which is transforming into a gel is an important macroscopic parameter to monitor the gelation process and the resistance to a shear stress and an elastic deformation is taken as an indication of a sol to gel transformation. The development of an elastic response can be therefore used to give a more precise definition of gel (Encyclopædia Britannica): “. . . Gels are colloids in which the liquid medium has become viscous enough to behave more or less as a solid.” [8]. The “more or less,” however, does not help to define in a very precise way what a gel is but at least the rise of a mechanical resistance is an indication of a transition which has been realized within the material from a fluid to a semisolid material.

Another important point to stress is that a gel is a disordered biphasic structure and does not exhibit any significant local order; in the case of silica, the gel is an intermediate state to obtain a glass. After drying (removal of residual solvent) and firing the final product is a high purity silica glass which cannot be distinguished by the structure from a glass of similar composition which has been prepared from a melt in a furnace [9].

Several types of materials can be found in the gel state such as organic polymers, oxides, and organic-inorganic hybrids and the sol to gel transition is a very general phenomenon that can be observed in many different systems. The characteristic of the transformation from a sol to a gel is, therefore, the transition from the two states, the sol and the gel. This needs also to be defined (IUPAC): “Process through which a network is formed from solution by a progressive change of liquid precursor(s) into a sol, to a gel, and in most cases finally to a dry network” [10], with the additional note, “An inorganic polymer, e.g., silica gel, or an organic–inorganic hybrid can be prepared by sol-gel processing.” The sol–gel process is, therefore, the transformation from a colloidal to a gel system; the removal of the liquid in a gel through drying allows obtaining a final solid material. This is a general description of the sol–gel process but still remains to define the sol–gel transition by identifying the *gel point*: “Point of incipient network formation in a process forming a chemical or physical polymer network” [11], the change in mechanical properties is again used to measure the gel point: “The gel point is often detected using rheological methods. Different methods can give different gel points because viscosity is tending to

infinity at the gel point and a unique value cannot be measured directly.” The development of a mechanical resistance [12], in particular to a shear stress, is, therefore, a property that can be used not only to define a gel but also to measure the gel point.

2.3 From the Precursor to a Gel

With some cautions we can divide the sol to gel process into different stages [13]: the formation of a sol from a precursor through hydrolysis and condensation reactions, the sol to gel transition and the gel formation. The last stage is the production of a solid dried material by removal of the residual liquid phase which gives the final product [14].

2.3.1 The Chemical Precursors

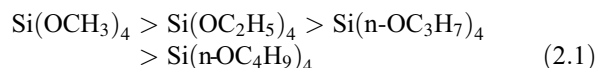
The choice of the chemical precursor is very important, not only because they clearly would control the composition of the final material but also because the chemistry can be very different even by changing only the alkoxy group. The most common precursors can be either *inorganic metal salts* (chloride, nitrate, sulfate, etc.) or *metal alkoxides* [15].

The alkoxides, in particular, are very popular precursors because they react easily with water and can be synthesized using different metals. Silicon and transition metal alkoxides show, however, a distinctive reactivity, and while the chemistry of silicon alkoxides is relatively easy to control, transition metal alkoxides (such as Ti, Al, Zr) are much more reactive and specific synthesis have to be designed to slow down and control the reactions.

2.3.2 Silicon Alkoxides

The silicon alkoxides (alkoxisilanes) are the most common precursors employed in the synthesis of silica based sol–gel materials and are characterized by covalent Si–O bonds, hydrophobicity, and immiscibility in water. Different alkoxysilanes are obtained by changing the alkoxy function; tetraethylorthosilicate (TEOS) ($\text{Si}(\text{OC}_2\text{H}_5)_4$) and tetramethylorthosilicate (TMOS) ($\text{Si}(\text{OCH}_3)_4$) are the most common. The properties of the silicon alkoxides change according to the dimension of the alkoxy; larger groups produce an increase in molecular weight, viscosity, and boiling point and a decrease in density of the alkoxides (Fig. 2.1).

The reactivity depends on the nature of the alkoxy function; the hydrolysis of TMOS is almost six times faster than TEOS. As a rule of thumb the larger size of the alkoxy group is associated with a lower hydrolysis rate due to the steric hindrance. The reactivity follows the sequence (Eq. 2.1), with tetramethyl orthosilicate the most reactive alkoxide:



tetramethyl orthosilicate > tetraethyl orthosilicate
> tetra n-propylorthosilicate
> tetrabutyl orthosilicate

2.3.3 Exchange Reactions of Alkoxides with Alcohols

An important property of metal alkoxides is the capability of activating exchange reactions with alcohols. This has to be

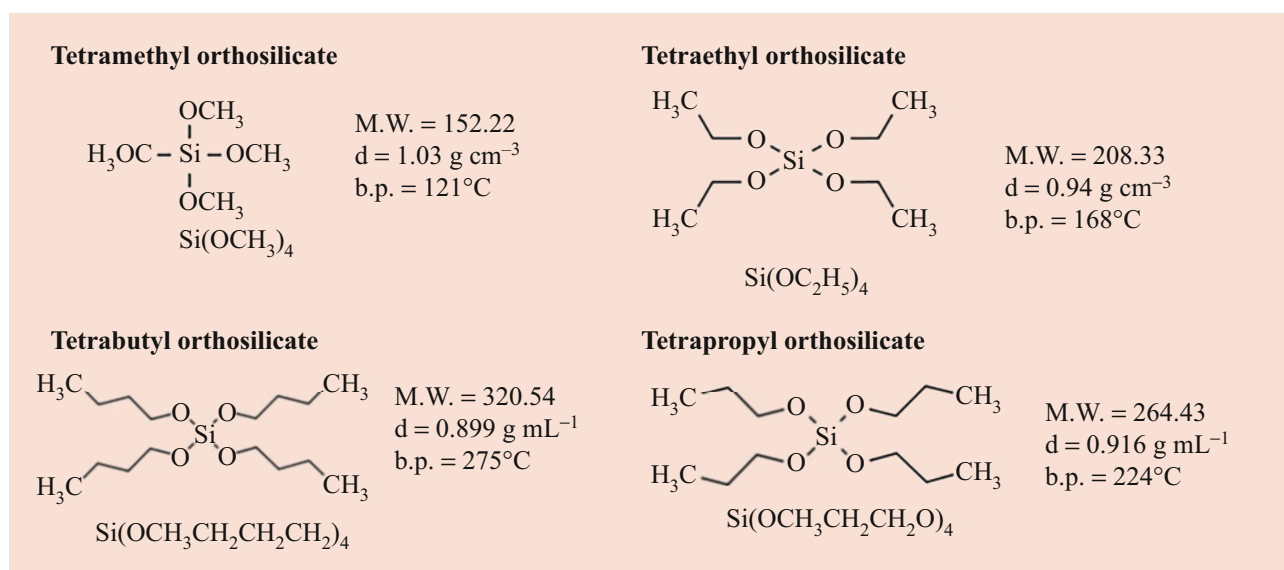
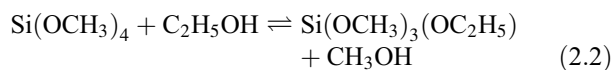


Fig. 2.1 The most common silicon alkoxides and their properties

taken into account during sol–gel processing, in fact, the presence of alkoxides with mixed ligands affects the hydrolysis and condensation reactions because they have a different reactivity and solubility. In general, mixing a metal alkoxide with a different alcohol produces almost immediately an exchange reaction with the formation of mixed ligands [16]. An example is the case of tetramethyl orthosilicate (TMOS); the equilibrium reaction with ethanol becomes (Eq. 2.2):



2.3.4 Hybrid Materials and Organically Modified Silicon Alkoxides

Another important family of silicon precursors is composed of the so-called organosilanes or organically modified alkoxides which are characterized by the presence of at least one Si–C bond [17]. This specific group of alkoxides has allowed the preparation of hybrid organic-inorganic materials through sol–gel reactions due to the presence of the non-hydrolyzable bond between silicon and carbon [18]. The chemistry and property of hybrids is dependent

on the different geometry, length, rigidity, and functionality of the organic functional groups.

The true nature of hybrid organic-inorganic materials synthesized via sol–gel processing is somehow difficult to define with clarity. In general, they are characterized by a direct covalent chemical bond which connects the inorganic and organic species. Incorporation of organic molecules into an oxide matrix, which can be easily done because of the synthesis of the material, is performed at low temperature route through solution processing, gives in most of the cases the formation of composites at molecular level [17] even if they are considered by some authors also a particular type of hybrid.

An example is the incorporation of fluorescent dyes [19], such as rhodamine 6G [20] or rhodamine B into a sol–gel matrix. The final material can be considered a composite at the molecular level because the host molecule does not change the chemical-physical properties. The surrounding chemical environment can affect the optical response but rhodamine B can be still clearly identified as a single molecule [21]. On the other hand, if rhodamine B is modified to form a silylated dye (Fig. 2.2), it can be directly used during the sol–gel reactions to form a hybrid where rhodamine B is covalently connected to the silica network and is a network modifier [22].

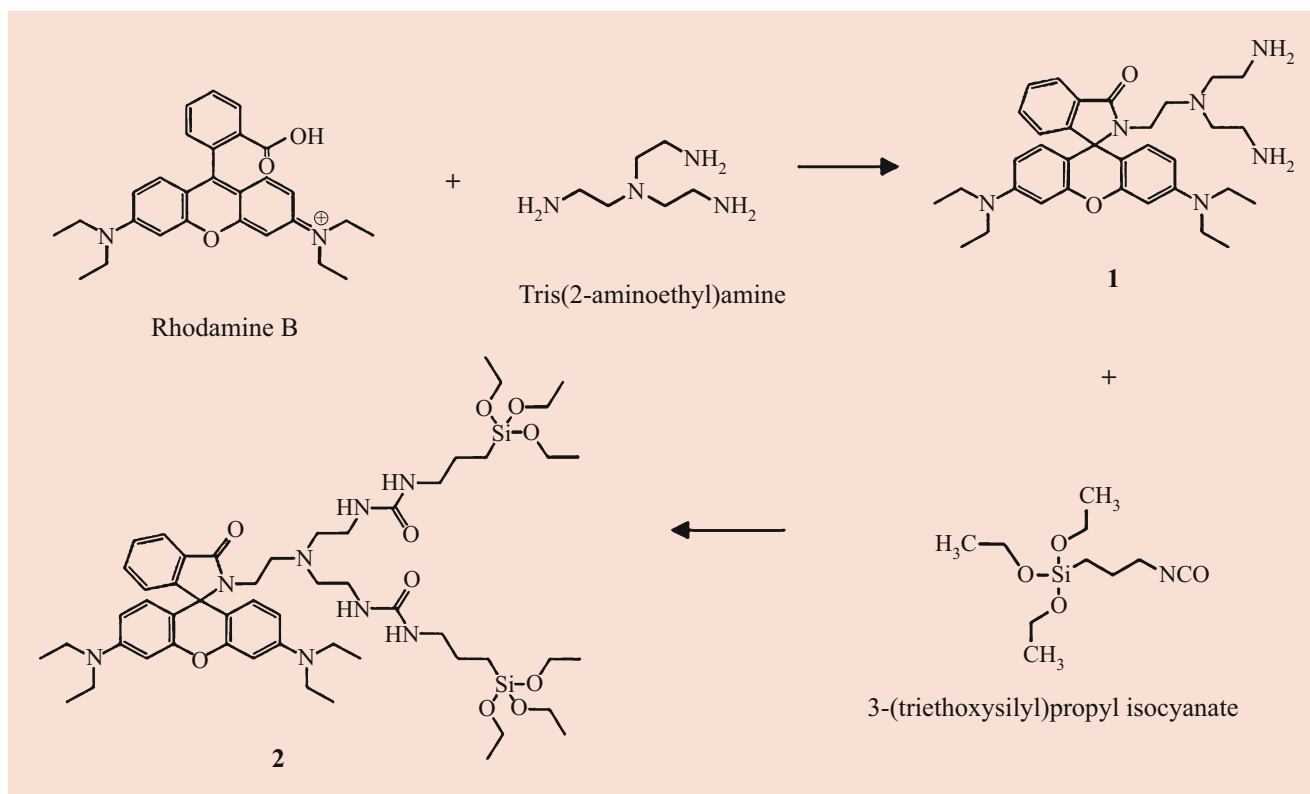
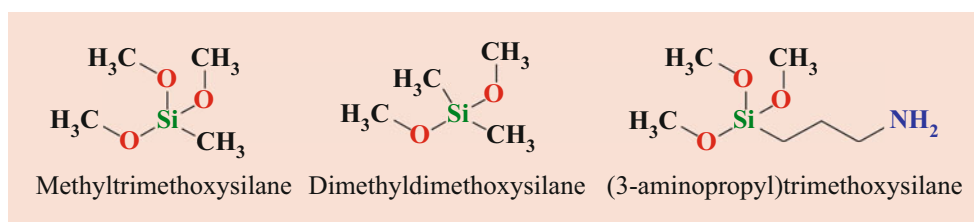


Fig. 2.2 Synthesis of a rhodamine B derivative as precursor of a hybrid functional material. Reaction of rhodamine B with tris(2-aminoethyl)amine gives the intermediate **1**, and further reaction with 3-(triethoxysilyl)propyl isocyanate allows forming the hybrid precursor **2**

Fig. 2.3 Silicon derivatives containing organic groups as modifiers



The identification of a hybrid organic-inorganic sol–gel material is, therefore, not always so straightforward, and a clear definition is difficult to achieve. Materials formed by interpenetrating organic and inorganic networks are another interesting example of hybrid composite. They can be obtained via sol–gel processing by independent polymerization of the organic and inorganic networks [23]. The possibility of forming a homogeneous composite depends on the capability of obtaining comparable rates of organic polymerization and inorganic polycondensation during the synthesis. When the organic polymerization is faster than the formation of an extended inorganic network via sol–gel reactions and vice versa, a heterogeneous structure with phase separation is observed.

The organosilanes can be divided into two main groups: in the first one the organic function is a modifier of the oxide network which is formed via polycondensation reactions, the second one is polymerizable and can form an organic network by itself which would be covalently linked to the inorganic backbone [24]. In this last case the formation of the organic and inorganic networks, which are linked through a Si–C bond, is a competing process.

The family of organically modified alkoxides includes also some very peculiar precursors such as the silsesquioxanes [25] and the bridged polysilsesquioxanes which form hybrid organic–inorganic materials via polymerization of monomers with two or more trialkoxysilyl groups. Because of the presence of organic linear chains and the possibility of secondary bonds between adjacent molecules these precursors can easily form organic crystalline structures.

2.3.5 Modifiers

The most common group of organosilanes is formed by alkoxides that are bonded to one or more organic functional groups that modify the inorganic silica network. The organic species cannot react and do not participate in the sol–gel reaction even if the reactivity and solubility of the alkoxide are changed as a function of the type of functional group. They have the general formula $R'Si(OR)_3$ (with R' the organic modifying group) but can also substitute two ($R'_2Si(OR)_3$) or three (R'_3Si-OR) alkoxy functions. A very wide range of precursors with different functional groups such as amine, isocyanate, thiol, amide, and polyether and is now commercially available.

In this group of organosilanes are included some very common compounds that are largely employed for sol–gel hybrid chemistry such as methyltrimethoxysilane (MTMS, $CH_3-SiO(CH_3)_3$) [26] or (methyltriethoxysilane (MTES)) [27], and coupling agents or surface modifiers, such as 3-aminopropyl triethoxysilane (APTES, $H_2N(CH_2)_3Si(OC_2H_5)_3$) (Fig. 2.3). APTES is somehow a special type of precursor, because of the presence of a primary amine which can also easily react with many other organic species, such as epoxides, to form hybrid material of more complex structure [28].

This group of organosilanes can form a hybrid material by themselves via hydrolytic reactions but in general they are co-reacted with another alkoxide, such as TEOS to obtain the final hybrid material. This requires careful control of the kinetics of the reaction to obtain a homogeneous material without phase separation [29].

2.3.6 Organosilanes with Polymerizable Organic Groups

Another group of organosilanes which are common precursors for hybrid materials is formed by alkoxides modified to have polymerizable functions as the organic group, such as epoxy (3-glycidoxypropyltrimethoxysilane, GPTMS) [30, 31], vinyl (vinyltrimethoxysilane, VTMS), or methacrylate (3-methacryloxypropyltrimethoxysilane (MPTMS)) (Fig. 2.4). An important example is GPTMS which has an epoxy ring that forms upon controlled opening a poly(ethylene oxide) polymeric chain. Such as in the case of interpenetrating organic and inorganic networks the control of the kinetics is very important. In general, higher will be the condensation of the silica network and shorter will be the organic chains because of the smaller room for growth within the gel structure. The hybrids produced using this class of organosilanes may contain, therefore, an organic chain whose extent within the silica matrix depends on the synthesis conditions.

2.3.7 Silsesquioxanes

Cage-like structured organosilicon molecules with Si–O–Si bonds and silicon atoms at the tetrahedral vertices are another particular class of hybrid precursors. These compounds are

Fig. 2.4 Silicon derivatives modified with polymerizable organic functional groups

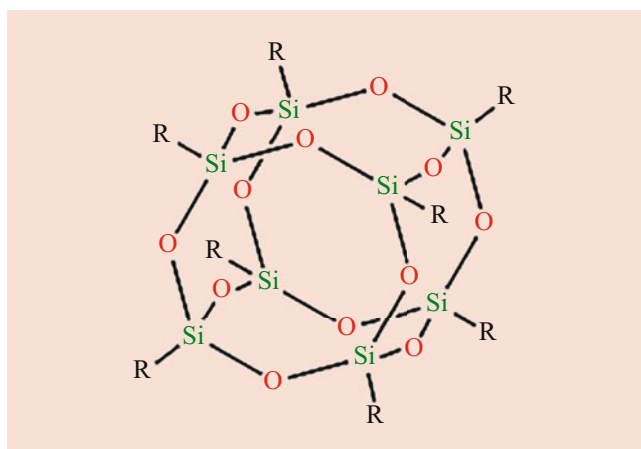
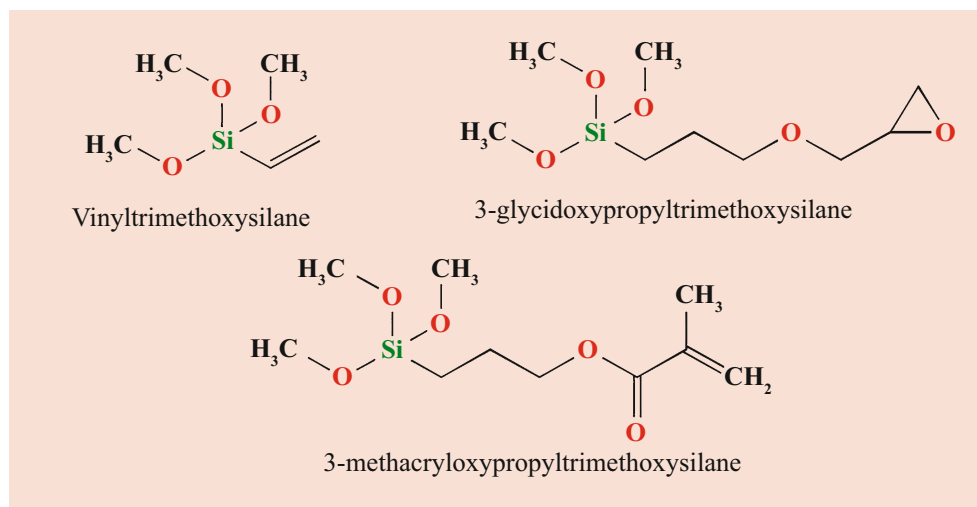


Fig. 2.5 The structure of a polyhedral oligomeric silsesquioxane (POSS)

characterized by a well-defined structural unit and silsesquioxanes may also have a polymeric structure with a ladder-like repeating unit [32] or random or open cage structures [25]. The general formula of silsesquioxanes is $(\text{RSiO}_{1.5})_n$ with the substituent $R = \text{H}$, alkyl, aryl, or alkoxy. The composition explains the name because every silicon atom is linked in average to one and a half (sesqui) oxygen atoms and to one hydrocarbon group (ane). The functional groups give the property of the silsesquioxanes and can be also hydrolyzed and condensed in the case of alkoxy, chlorosilanes, silanols, and silanolates. It is also possible to synthesize well-defined structures defined as polyhedral oligomeric silsesquioxanes (POSS) (Fig. 2.5).

2.3.8 Bridged Silsesquioxanes

A particular type of precursor for hybrid materials is composed by bridged silsesquioxanes organosilanes $(\text{R}'\text{O})_3\text{SiRSi}(\text{OR})_3$ [33, 34]. They are characterized by the presence of an

organic spacer bridging two or more silicon atoms (Fig. 2.6). If the nature of the organic spacer, R, and the synthesis are carefully designed, hybrid materials with a long-range structural order can be fabricated. The bridged silsesquioxanes organosilanes precursors have a higher number of available siloxane linkages. In the case of two silicon atoms bridged by the organic spacer, they become six instead of four. This property is reflected in a peculiar reactivity during the sol-gel reactions which favor the formation of closed ring structures.

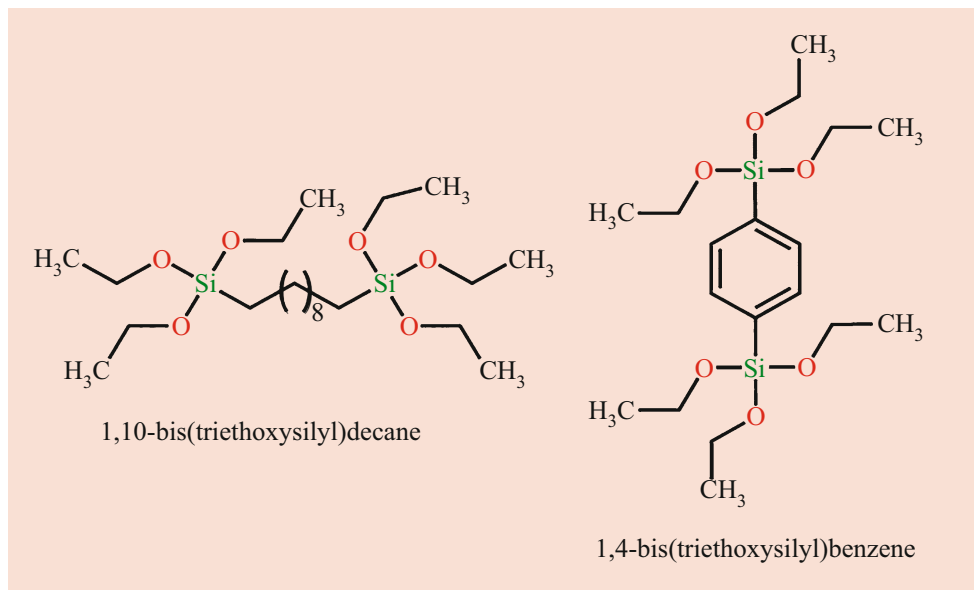
The organic spacers produce also favorable conditions to self-organization into a crystalline hybrid structure. This has been observed in bridged polysilsesquioxanes with different types of organic spacers; lamellar crystals [35] but even helical fibers have been observed to form during gelation of a bulk hybrid gel and in mesoporous hybrid silica materials. Bridged silsesquioxanes have been also widely used as precursors to obtain different types of aerogels [36].

2.3.9 Transition Metal Alkoxides

The chemistry of transition metal alkoxides is much different from that of silica; silicon is in fact tetrahedrally coordinated to oxygen, while metals have usually an octahedral coordination [37, 38]. The tetrahedral structure of silica is much more flexible than octahedras and is able to form “polymeric” structures of different types.

Transition metals, such as Ti or Zr, are generally more electropositive than silicon and this makes titanium (and the other transition metals) more prone to nucleophilic attacks [39]. Non-silicate metal alkoxides are, therefore, very reactive with water because they are salts of alcohol or acids and react as strong bases. The hydrolysis rate of

Fig. 2.6 Examples of bridged polysilsesquioxanes: 1,4-bis(triethoxysilyl)benzene and 1,10-bis(triethoxysilyl)decane



titanium alkoxide is generally up to 10^5 times faster than for the corresponding silicon alkoxide. The hydrolysis and condensation reactions must be, therefore, controlled by using complexing ligands such as acetylacetonate to inhibit condensation reactions and avoid precipitation. In general, a better control of the reactivity is obtained by forming complexes by replacing the alkoxy groups with diols, β -diketonates, carboxylic acids, amines, or other organic groups such as cyclooctatetraene.

The most common titanium alkoxides are: titanium ethoxide, $\text{Ti}(\text{OCH}_2\text{CH}_3)_4$ ($\text{Ti}(\text{OEt})_4$); titanium isopropoxide, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ ($\text{Ti}(\text{OiPr})_4$); and titanium butoxide, $\text{Ti}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$ ($\text{Ti}(\text{OBu})_4$) (Fig. 2.7).

2.4 Waterglass

Soluble silicates of alkali metals (sodium, potassium, or lithium), commonly known as *waterglass*, are another class of precursors for sol–gel processing. They are highly soluble in water which is also used as solvent of the reaction and this is, besides the much lower cost, the difference with silicon alkoxides, which are instead immiscible in water and require in general an alcohol as co-solvent for the reaction. Another difference is that in waterglasses the process is initiated by a pH change while in the alkoxides by the addition of water and the catalyst. The silica glass precursors have the general formula (Eq. 2.3):

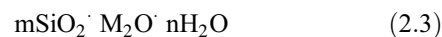
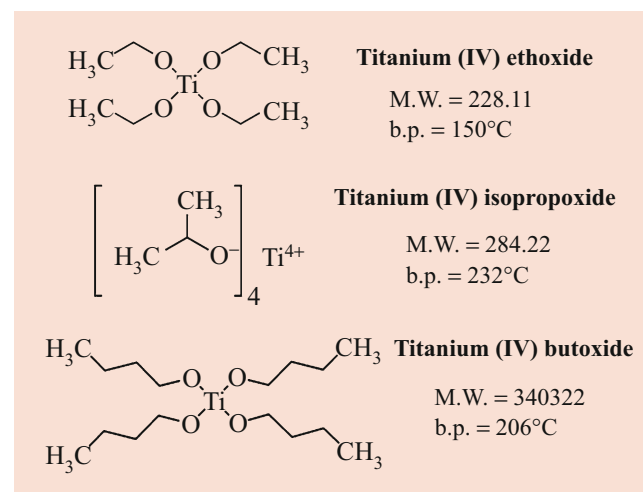


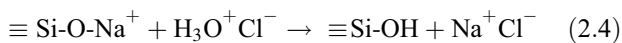
Fig. 2.7 Titanium alkoxides are most commonly employed in sol–gel synthesis



with M the alkali metal and m the molar ratio which defines the number of silica moles per oxide metal (M_2O).

The average composition of silicate species in waterglass solutions is M_2SiO_3 (with $\text{M} = \text{Na}$ or K); the solutions of waterglass are formed by mixtures of monomeric and oligomeric silicates with negatively charged non-bridging oxygen.

In the case of sodium silicate (Na_2SiO_3), for instance, the hydrolysis reactions are initiated by addition of hydrochloric acid (Eq. 2.4):

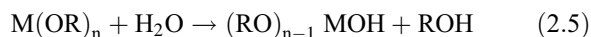


and the condensation by reaction of two silanols.

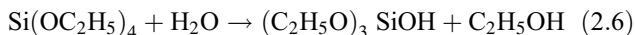
The stability of waterglass solutions is reached only in strongly basic conditions when the anionic species repeal each other. On the other hand even if the equilibrium of waterglass solutions depends on several parameters, such as temperature, concentration, and pH, the higher complexity chemistry makes the silicon alkoxides a much more flexible precursor for sol-gel processing.

2.5 Hydrolysis

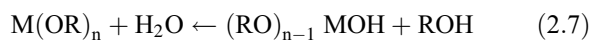
The beginning of the sol to gel conversion is the hydrolysis of the alkoxide. In general, because silicon alkoxides react slowly in a water-ethanol mixture the addition of a catalyst is necessary to start the reaction. During the hydrolysis the hydroxyl groups (OH) replace the alkoxide species (OR); the process produces the release of an alcohol molecule and the formation of a metal hydroxide, M-OH (Eq. 2.5):



with R the alkyl group, ROH the alcohol, and M the metal. The hydrolysis reaction in the case of TEOS becomes (Eq. 2.6):

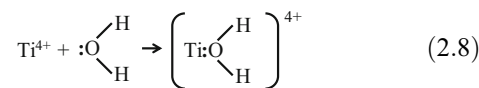


The reaction of alcohol with a hydrolyzed species can, however, change direction forming again a water molecule and an alkoxide ligand (esterification) (Eq. 2.7):

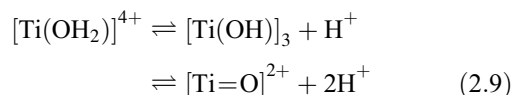


Alcohol has, therefore, an active role in sol-gel reactions, not only as solvent but a careful choice of the alcohol as a function of the reaction design has to be taken into account. Non-hydrolytic reactions are also possible and several synthesis routes, especially for transition metal alkoxides and mixed precursors, have been proposed [40, 41].

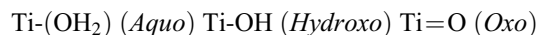
In the case of titanium, but it can be generally extended to other transition metals, the nucleophilic addition of water to the Ti center is the mechanism at the base of the hydrolysis. When titanium is dissolved in water as a salt the T^{4+} cations are solvated by the water molecules (Eq. 2.8):



This produces a charge transfer from the oxygen to the metal atom with a contemporary increase of the partial charge of hydrogen; this makes the water molecules coordinated with the metal ions more acidic than those not coordinated. The extent of hydrolysis is therefore depending on water acidity and the entity of the charge transfer up to reaching the equilibria (Eq. 2.9):



In non-complexing aqueous media, therefore, following Eq. 2.4, three types of different ligands would form [42, 43]:



Metal cation charge and pH are the two parameters that regulate the extent of the three domains, *aquo*, *hydroxo*, and *oxo*, as shown in Fig. 2.8:

Because condensation goes through the reaction of hydroxo groups with water elimination (Eq. 2.10):

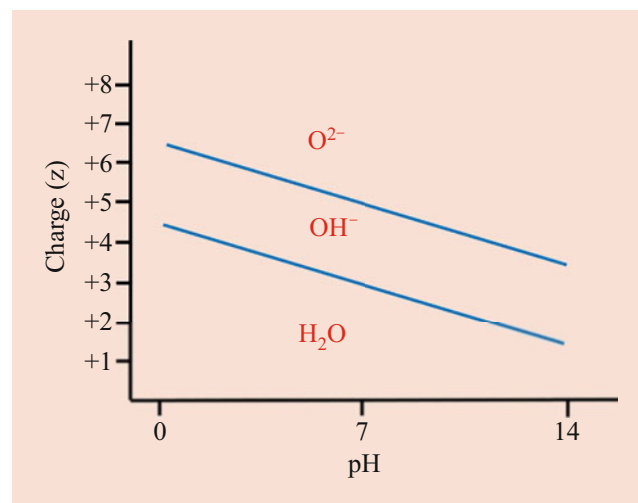
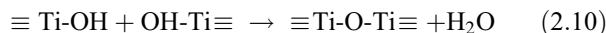


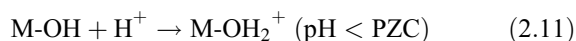
Fig. 2.8 The *aquo*, *hydro*, and *oxo* domains as a function of the charge and pH

Equation 2.5 has to be shifted to the Ti-OH region by controlling the pH.

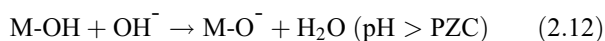
In the case of titanium alkoxides, and more in general transition metal alkoxides, because they are stronger Lewis acids than silicon, a nucleophilic attack is easier and this results in a higher hydrolysis rate. The condensation goes through the M-OH reaction which can be so fast that almost immediate precipitation can be observed upon addition of water [44].

2.6 The Point of Zero Charge

The hydrolysis reactions do not define a very specific stage of the sol–gel process because as soon as hydrolysis starts, the condensation reactions proceed. The pH of the solution strongly affects the species that are forming, and the final gel would have a different structure. The condensation reactions of silica are directly depending on the catalytic conditions that are employed. The *Point of Zero Charge* is very helpful to understand this point. The surface potential of hydroxides is given by the balance between H^+ and OH^- ions and the charge of the surface is pH dependent (Eq. 2.11):



$pH < PZC \rightarrow$ Surface positively charged



$pH > PZC \rightarrow$ Surface negatively charged

In the two extremes of pH, below 2 and more than 13, the hydrolysis is very fast while condensation is hindered or very slow; the sols tend to stabilize because the particles with the same charge repel each other. The pH and the PZC affect therefore the reaction rates and the gelation time. In an acid-catalyzed sol (TEOS, HCl with $H_2O/TEOS = 4$), the gelation time as a function of pH shows a response which looks like a Gaussian curve (Fig. 2.9). At $pH = 2.2$, which corresponds also to the PZT of the system, the sol is quiet stable with the longest gelation time. At higher pH the gel time quickly decreases such as at low pH.

2.7 From a Sol to a Gel: The Condensation

The condensation reactions begin through condensation of reactive $-OH$ to form M-O-M- units by realizing a water or an alcohol molecule. The reaction of two $-M-OH$ groups gives water as by-product (Eq. 2.13) while the reaction of $-M-OH$ with $-M-OR$ releases an alcohol molecule (Eq. 2.14):

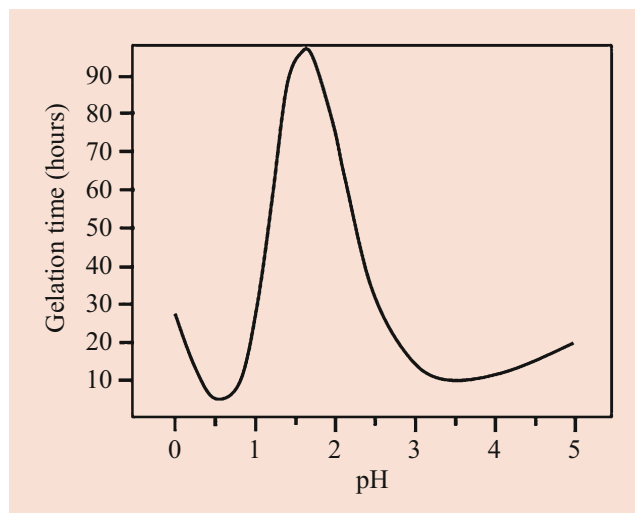
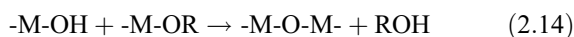
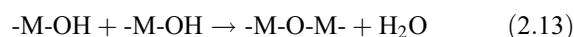


Fig. 2.9 Gelation time as a function of pH for a silica (TEOS) acid catalyzed (HCl) sol

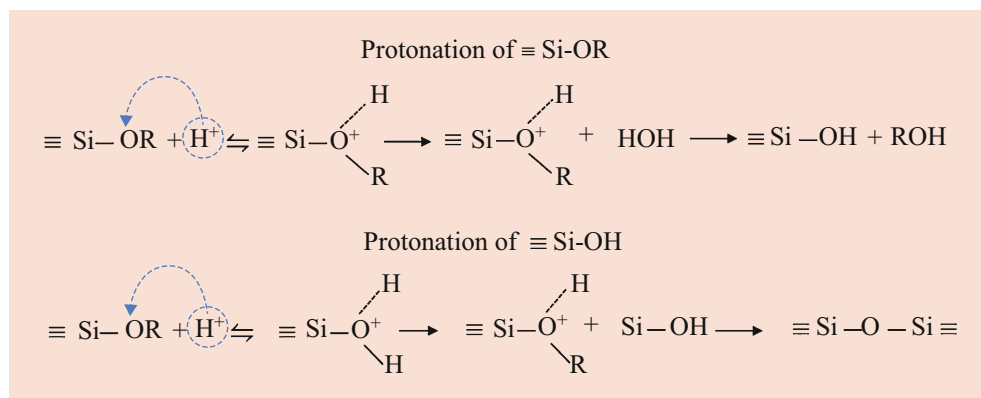


The polycondensation reactions allow forming an extended oxide network whose structure and growth depends on a set of synthesis parameters. Water alone cannot activate the hydrolysis and condensation reaction in absence of a catalyst. The choice of the catalyst is very important because the sol structure and the gel time are largely dependent on this selection [45].

2.7.1 Acid-Catalyzed Hydrolysis and Condensation

In an acid-catalyzed sol–gel reaction, the protons that are available in solutions will attack the oxygen atoms of the Si-OR groups to look for electrons. As a consequence the electronic cloud in the Si-O bond shifts from silicon to oxygen with an increase of the silicon atom positive charge. This makes silicon more electrophilic and more reactive to the attack from water in the hydrolysis or from silanols in the condensation reactions. The higher electrophilicity of silicon induced by the protonation has also the effect of changing its reactivity; the unreacted alkoxide ($Si-(OR)_4$) hydrolyzes faster than the partially hydrolyzed ($Si(OR)_{4-x}(OH)_x$) or condensed ($-Si-O-Si-$) species (Fig. 2.10). This means that the pH of the sol changes with the progress of the hydrolysis and condensation reactions. The silanol groups, in fact, become more acid with the increase of condensation when more

Fig. 2.10 Protonation of the different silica species in an acid-catalyzed reaction



Si-O-Si bonds are present; this is also reflected in a change of PZC with the increase of condensation.

2.7.2 Base-Catalyzed Hydrolysis and Condensation

The hydrolysis and condensation reactions, in the case of base-catalyzed sols, are promoted by the hydroxyl ions (OH^-) which have strong nucleophilicity and are strong enough to attack directly the silicon atom. Silicon in the alkoxide is the atom with the highest positive charge and becomes, therefore, the target of the nucleophilic attack from deprotonated hydroxyls (OH^-) or silanols ($\equiv \text{Si-O}^-$). In the base-catalyzed reaction OH^- and $\equiv \text{Si-O}^-$ species replace OR (hydrolysis) or $\equiv \text{Si-OH}$ (condensation), respectively. The associative mechanism involves the formation of a penta-coordinate intermediate (Fig. 2.11).

The condensation reaction can happen also for R at the place of H. These reactions in high basic conditions are also reversible via cleavage by OH^- .

2.8 The Role of Water

The different stages of the sol to gel transition are strongly dependent on the water/alkoxide ratio, r , and the amount of water available to start the hydrolysis affects the kinetic of the polycondensation process. The stoichiometric value of r is 4 means that four molecules of water are necessary for complete hydrolysis of a tetravalent alkoxide $\text{M}(\text{OR})_4$, while a ratio of 2 is enough for conversion of $\text{M}(\text{OR})_4$ into an oxide.

An increase in the amount of water available for hydrolysis should also increase the polycondensation rate. This is not actually the case because increasing the water content while keeping constant the amount of solvent produces a decrease

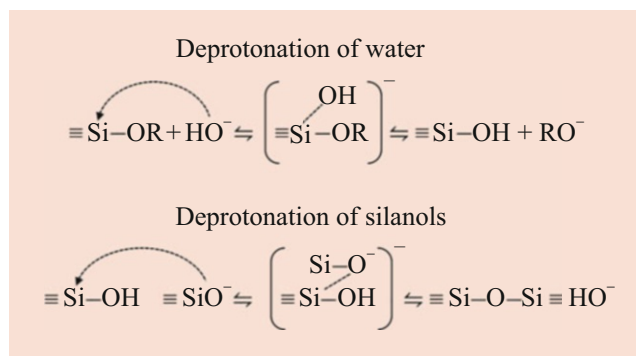


Fig. 2.11 Protonation of the different silica species in a base-catalyzed reaction

of the silicates concentration. This dilution effect changes the hydrolysis and condensation rate with an increase of the gel time.

The gel time changes as a function of the water/alkoxide ratio keeping constant the solvent content. An example of this effect is shown in Fig. 2.12, for a TEOS sol with ethanol used as the solvent. The response changes when water is present in substoichiometric amount, $r < 4$ (gray area), or higher, $r > 4$ (white area). As soon as the content of water increases, the gel time decreases, because more water is available for the hydrolysis; after around $r = 5$, however, the dilution effect is more effective and the gelation time increases quite quickly with the water content.

The gel time also increases with the amount of ethanol in the sol; the concentration of the oxide species is very important, more the sol is diluted longer will be the gel time. Another question that arises with the increase of water is that the system could potentially enter in an area of immiscibility in the ternary phase diagram water/TEOS/ethanol; the polycondensation reactions, however, also produce alcohol as a by-product which in most of the cases is enough to homogenize the system.

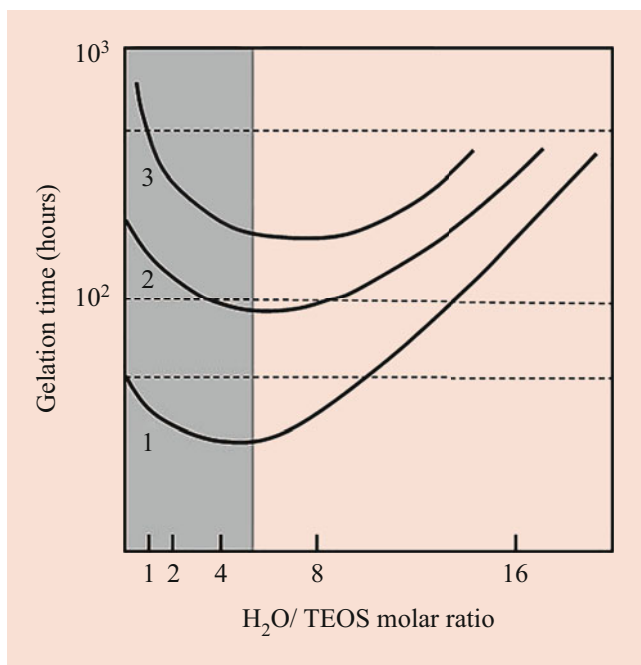
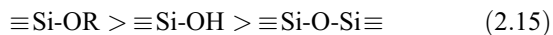


Fig. 2.12 The gel time as a function of the water/TEOS molar ratio. The three different curves show the change of gel time at different ethanol/TEOS ratios (1, 2, and 3) [46]

2.9 Hydrolysis Versus Condensation

During hydrolysis and condensation reactions the silicon alkoxides undergo a transformation through transition states; the electronic density of the silicon atom, as we have seen, depends also on the nature of the substituents and decreases with the progress of the reactions in the following order (Eq. 2.15):



The decrease in electron density of silicon during acid catalyzed reactions has the consequence that in acidic conditions also the reaction rates of hydrolysis and condensation increase with the electronic density; higher the electronic density (Si-OR), higher is the hydrolysis rate.

In acid-catalyzed systems, therefore, the hydrolysis is faster than condensation while in base-catalyzed sols a reverse trend is observed [47]. Besides the differences in the reaction rate the basic and acidic routes produce also a more subtle difference which is the structure of the silica clusters. In acid conditions, because of the higher reactivity of the electrophilic silicon atom with the growth of -Si-O-Si-bonds the formation of more chain-like structures is favored. On the other hand, in basic conditions branched and more connected silica structures are obtained.

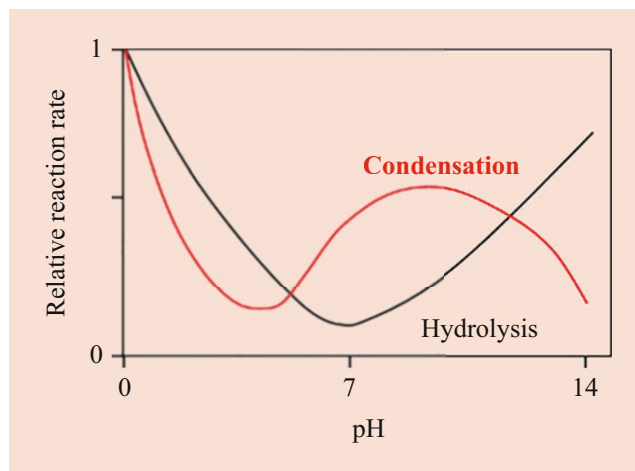
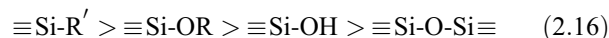
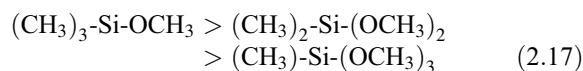


Fig. 2.13 Relative hydrolysis and condensation rates as a function of pH for a silicon alkoxide

The organically modified silicon alkoxides, $\text{R}'(\text{SiOR})_3$, have a higher electron density at the silicon atom and Eq. 2.14 can be rewritten:



this means that, in comparison with a silicon alkoxide, they have in acidic conditions a higher reactivity which increases with the number of organic substituent and in the case of $\text{R}' = \text{CH}_3$ (Eq. 2.16):



The reactivity of organically modified alkoxides depends also on the steric hindrance of the organic substituent groups and increases in the order (Eq. 2.18):



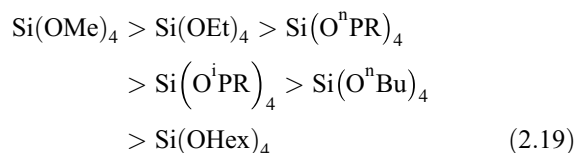
In basic conditions the reaction rates of hydrolyzed or partially hydrolyzed species are higher than the monomeric alkoxide, the opposite for what we have seen for acid catalysis. This is also true for the organically modified alkoxides which in basic conditions react slower than the corresponding silicon alkoxide.

The pH of the solution will trigger, therefore, the reaction rates of hydrolysis and condensation which remain competing reactions for all the sol to gel process.

The change of hydrolysis and condensation rates as a function of pH can be followed in Fig. 2.13. At pH lower than around 5 the hydrolysis rate is faster than condensation, in accordance with our expectations; the hydrolysis rate

decreases also with the increase of pH and reaches a minimum around 7. After this value it increases quite quickly with the alkalinity of the solution. The condensation rate, on the other hand, follows a similar trend and decreases with the increase of pH even if there is a lower reaction rate with respect to hydrolysis up to the value of around 5. After this pH value the condensation rate quickly rises up to around 10, and then decreases again. Why is this trend observed? Because we should always keep in mind that cleavage of silica bonds at higher pH values is quickly rising and condensation and hydrolysis are in competition.

Condensation and hydrolysis reactions are also depending on the size of the alkoxy group [48]; the reactivity of silicon alkoxides in fact decreases with the increase of the size of the alkoxy because of the steric hindrance. The reactivity of silicon alkoxides decreases when the size of the alkoxy group increases because of steric hindrance factors. The reaction rate order of silicon alkoxides with different alkoxy groups follows this order (Eq. 2.19):



To resume in acid conditions linear or weakly branched silica species are preferentially formed; they aggregate through entanglements which eventually cause gelation of the system. In basic conditions gelation occurs via formation of agglomerated silica clusters which condense to form a 3D network. The acid conditions give rise, therefore, to a final material which is denser with respect to the basic route which forms a material with a more porous network because of the free space between the particles. A dense silica material is obtained only after firing at high temperatures but in the gel or xerogel state the structural differences between acid and silica gels are still important.

2.10 The Gel Structure

The extent of hydrolysis and condensation reactions in the case of silicon alkoxides are essentially governed by the pH of the sol. The choice to use an acid or a base catalyst has also a direct effect on the structure of the final gel and in general an acidic route gives a more compact structure and a basic one a more open and porous (Fig. 2.14) [49].

This difference in the structure is due to the change in reactivity of the species which form upon the beginning of hydrolysis and condensation. In general, the acid-catalyzed silicon alkoxides have a higher reactivity with respect to the hydrolyzed or condensed species which favors the formation

of branched structures. In basic sols the reactivity shows a reverse trend and this gives rise to the formation of silica clusters and “spherical” particles.

The gel forms, therefore, through the growth of a branching macromolecule (acid conditions) or aggregation of silica clusters. In the last case a porous and less interconnected gel structure would form.

Another peculiarity of sol–gel reactions of silica is the formation of many different species from monomers to trimers and larger aggregates upon hydrolysis. Not only linear or branched macromolecules would form; cyclic species typically from threefold to sixfold rings are also commonly observed. The presence of cyclic molecules would also affect the gelation process because they could behave as local thermodynamic sinks reducing the condensation and growth process.

2.11 Modeling the Sol to Gel Transition

To describe the sol to gel transformation three main models have been used: the classic theory of a branching molecule, the percolation theory, and the fractal model. The classic statistical theory (or mean field theory) is based on three main assumptions: the reactivity of all the monomers remains the same during the polycondensation, the formation of cyclic species is not allowed, and the steric hindrance effects are negligible.

These assumptions do not work well for inorganic gelling systems because from the very beginning of the process they would form species which have a different reactivity while cyclization is also a common phenomenon especially in silica systems [50]. In general the models fail to be quantitative predictive but are helpful to reach a general understanding of the process.

The classic branching model predicts that the system would gel when around one-third of the available bonds have been formed. This value is far to fit with the experimental data because, as we have seen, the assumptions are too restrictive to be applied to the chemistry of sol–gel precursors.

The classic theory, however, allows obtaining a general prediction of the evolution of the weight fraction of the different reactive species (Fig. 2.4) [51].

Figure 2.15 shows the change of reaction degree, p , as a function of the weight fraction, w_x , of the aggregates formed by x monomeric units (y axis, left) and of the weight fraction of the gel (y axis, right). At the gel point, p_c , the reaction degree according to the classic model is 0.33. At the beginning of the reaction most of the reactive species would be the monomers that quickly reduce to form dimers and larger aggregates. As soon as condensation proceeds the weight fraction of the aggregates ($x > 2$) would also decrease as soon as they become part of the large spaming cluster

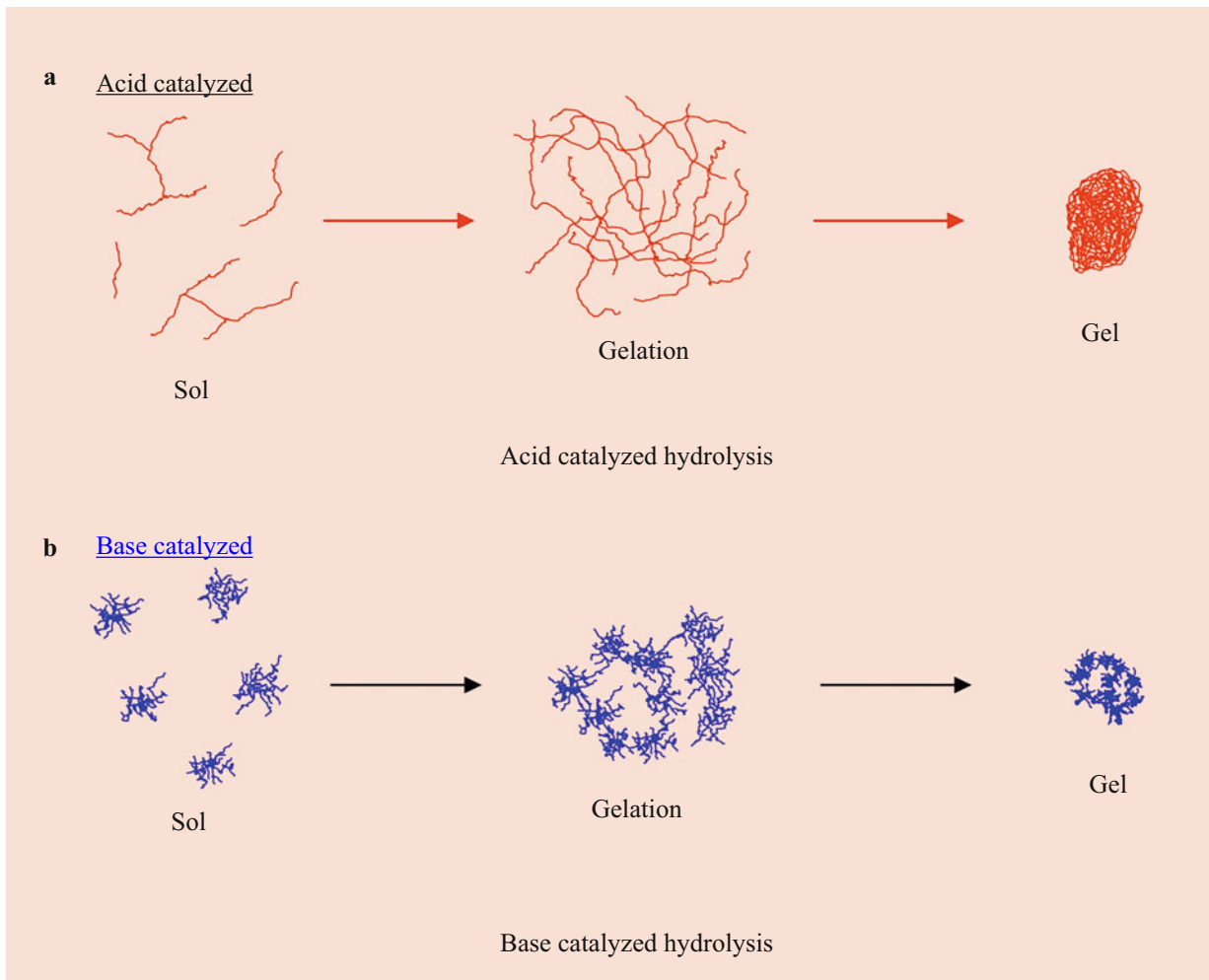
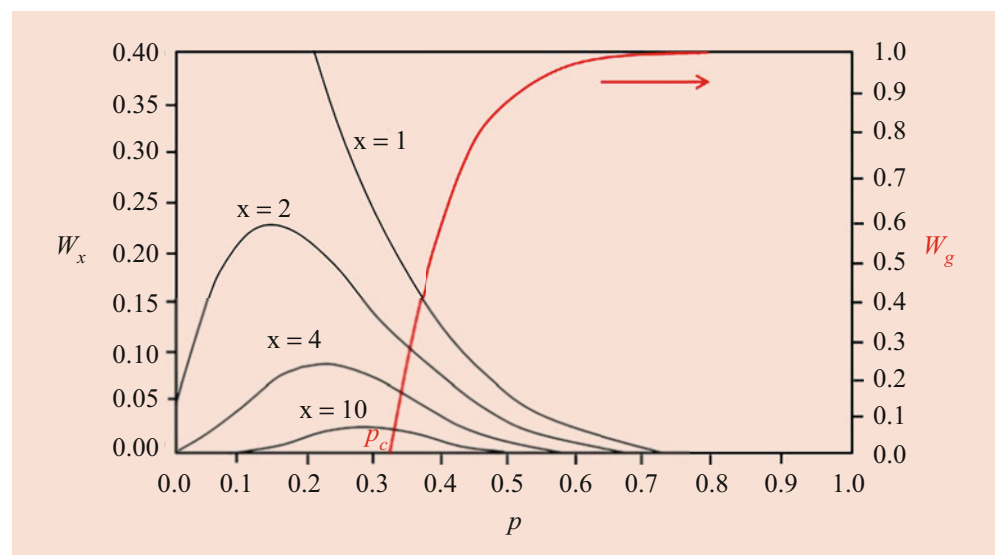


Fig. 2.14 Formation of a gel from an acid (a) or base (b) catalyzed hydrolysis, the change of inorganic structure from a sol to a gel

Fig. 2.15 Weight fraction (w_x) of aggregates formed by x monomeric units in a sol of tetrafunctional molecules as a function of reaction degree, p . w_g is the weight fraction of the gel. (Redrawn from Ref. [51])



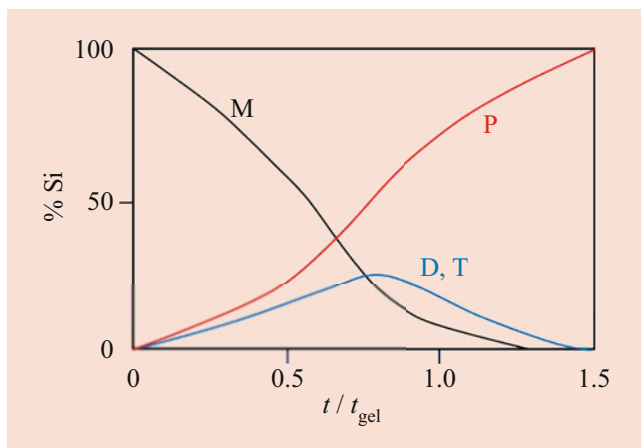


Fig. 2.16 Time evolution (t/t_{gel}) of monomeric (M), dimeric (D), trimeric (T), and higher branched (P) silicon groups. Data obtained by NMR and Raman analysis from a TMOS aging sol

which eventually would form the gel. At the gel point not all the molecules have reacted and the liquid phase would be composed by a sol with aggregates of different dimensions.

The theoretical data can be compared with the experimental results which show the change of the gelation time (t/t_{gel}) as a function of the content of monomers (M), dimers (D), trimers (T), and highly branched species. The data have been obtained by NMR and Raman spectroscopy analysis.

The experimental data qualitatively follow quite well the theoretical previsions as shown in Fig. 2.16. Dimers and trimers increase at expenses of monomers and around the gelation times they decrease to form higher branched, P, species. The similarities with the theoretical model in Fig. 2.15 are very striking.

Percolation theory [52] has been also applied to modeling the sol–gel transition in inorganic sol–gel systems [53]. In the percolation model the gel point is reached when a growing cluster is able to span over the whole sample region. The theory has no analytical solution and the gel point can be defined only on a statistical base. Without going too much in detail, we can use the theory to follow the change of the bond fraction, P , as a function of the size of the spanning cluster, s , and spanning length defined as the maximum distance between any bond center in a cluster (Fig. 2.17).

The percolation probability, $P(p)$, is the key function of the process and beyond the percolation threshold at p_c is correlated with the growth in volume of the network with the increase of the bond fraction. The average values of s and l , s_{av} and l_{av} , show singularities close to the percolation threshold.

This model fits quite well with gelling silica systems which are characterized by a divergence of the viscosity close to the gel point (Fig. 2.18) [54]. During gelation the crosslinking reactions produce a constant increase of viscosity and the molecules gradually lose their mobility. In the

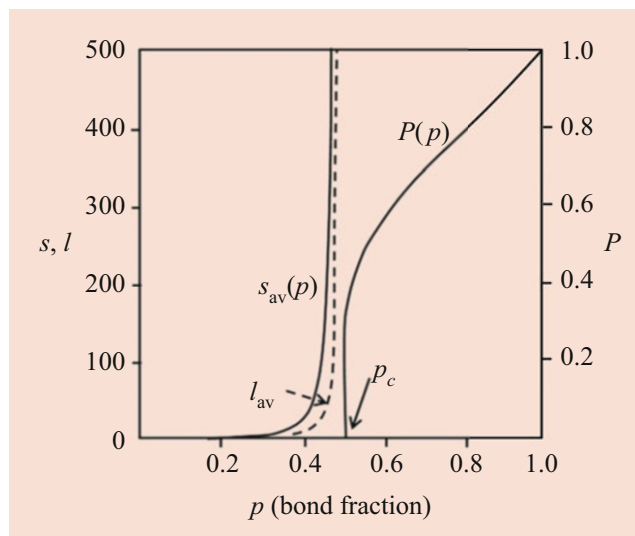


Fig. 2.17 Cluster size, s , spanning length, l , percolation probability, P , as a function of the fraction of the bonds which are formed in the system, p . (Redrawn from Ref. [54])

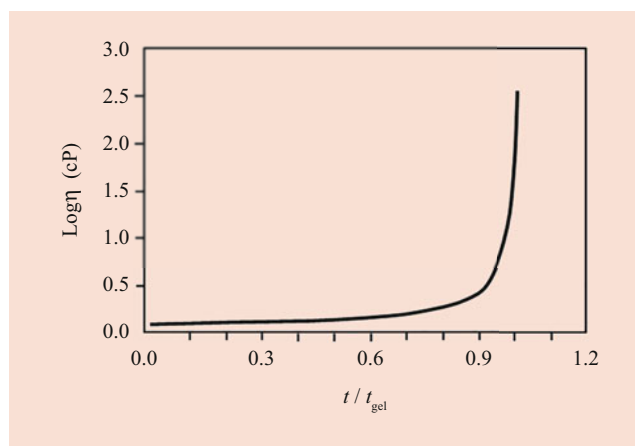


Fig. 2.18 Viscosity, η , of TMOS sols as a function of relative gelation time t/t_{gel}

proximity of the gel point the system enters in a viscoelastic regime and shows an elastic response to a shear stress.

The failure of the classic model of a growing branching system when applied to silica systems is basically due to the restrictive assumptions which do not take into account the specificity of the sol–gel chemistry. The minimum number of bonds necessary to observe gelation predicted from the theory results quite far from the experimental values. If we follow the transition of a TEOS sol to a gel, a much larger fraction of bonds forms at the gel point and around 83% of the available bonds are converted at longer reaction times (Fig. 2.19) [55].

The model of linear chains which randomly grow is not suitable, therefore, to describe the complexity of the

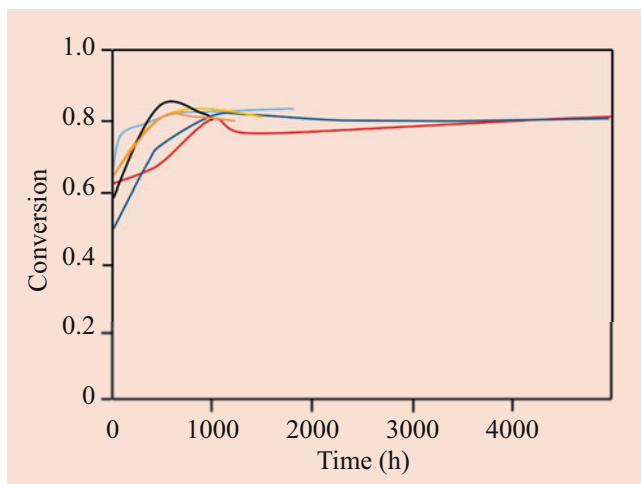


Fig. 2.19 Hydrolysis and condensation of TEOS: later in the reaction, conversions all slow down and converge to 83%. Gel times: (red line) 5064 h; (blue line) 4392 h; (light blue line) ~1700 h; (yellow line) ~1500 h; (black line) 1020 h; (orange line) 1200 h. (Redrawn from Ref. [55])

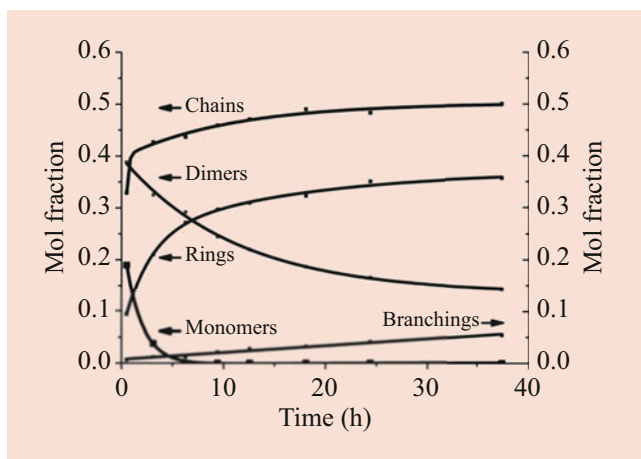


Fig. 2.20 Evolution of mole fractions of monomer and different types of oligomers in the R-0.7 sample (derived from Q^0 , Q^1 , and Q^2 signals in ^{29}Si NMR) and fraction of branching expressed as the fraction of Q^3 in totality of silicon atoms. Q^1 represents the fraction of silicon sites with different siloxane bonds (i) connected to other silicon atoms

composition of a sol and its transition to a gel. It is necessary to take into account the formation of different species with different reaction rates and the effect due to cyclization. NMR analysis has confirmed the complex interactions of the different species which form in the sol [56].

Monomers and dimers transform with the progress of the hydrolysis and condensation into linear chains and branching structures or give rise to cyclic species (Fig. 2.20). This works as a general rule, however, even small changes in the synthesis conditions can produce a totally different sol and gel structures.

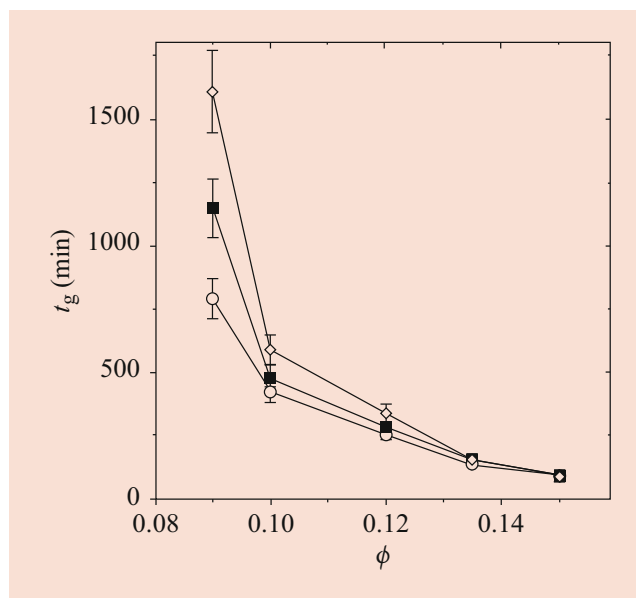


Fig. 2.21 Experimental dependence of the gel time t_g with the tetramethoxysilane (TMOS) volumic fraction Φ for different container sizes. Circles, squares, and diamonds correspond to container diameters of 10, 14, and 32 mm. The gels were prepared by hydrolysis of TMOS using a 0.05N ammonia-water solution. (Reprinted with permission from Ref. [58])

Using Dynamic Monte Carlo simulations, which consider the effect of the nearest-neighbors and cyclization of silica oligomers in an acid catalyzed sol, the calculated molecular weight distribution has been found to be in good agreement with the experimental values [57]. Extensive cyclization has to be taken into account to predict the distribution of species which give rise to a silica gel.

The control of experimental conditions is extremely critical and little differences in the synthesis can affect the sol to gel transition and the gel time. An interesting example is the effect of the size of the sol container which has been found to affect the gelation time [58]. The experimental values of the gelation time are longer with the increase of the container size. This effect has been experimentally observed only in base-catalyzed sols while the gel time remains size independent in neutral conditions when no catalysts are employed in the synthesis. Dependence on the container size has been also found in the case of acid-catalyzed sols [59] (Fig. 2.21).

2.12 Conclusions

In this brief overview the main features of a sol to gel transition in inorganic systems have been outlined. Silica has been taken as the main example because its sol–gel chemistry is well known and can be used to outline the main stages of the process. The sol to gel transition is a

continuous process and no thermodynamic variables can be used to identify the formation of a gel as difficult to measure and to define. It is a stochastic process which is randomly governed by the chemistry of the precursor sol. An exact prevision and measure of gelification, which means the exact moment when a growing macromolecule forms an interconnected continuous network spanning within the container, is difficult to obtain. In general, the models applied to sol to gel transitions in inorganic systems fail to give an accurate agreement with the experimental data. The divergence of some properties, such as the viscosity, close to the gel point well supports the general understanding of the process. The measure and definition of the sol–gel transition is still far from being rigorous and, especially in fast evaporating systems, such as thin films, is still elusive to measure.

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