CHAPTER I

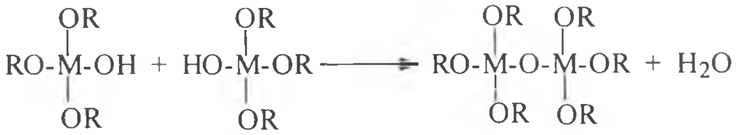
INTRODUCTION

Applications for sol-gel derived products are numerous. One of the largest application areas is for coatings and thin films used in electronic, optical, and electro-optic components and devices, such as substrates, capacitors, memory devices, infrared (IR) detection, and wave-guides. Moreover, the sol-gel method is also suitable for preparing catalytic materials. The term sol-gel was first coined in the late 1800s. The gel route to glasses and ceramics has been attractive in science and technology because of their diverse utilities (Turgay, 2000). Moreover, the sol-gel process offers new approaches to the synthesis of oxide materials. Starting from molecular precursors, such as metal alkoxides, an oxide network is obtained via inorganic polymerization reaction. Initiation is performed through the hydroxylation of metal alkoxides. As soon as hydroxyl groups are generated, propagation occurs through a polycondensation process. With an alkoxide (M $(OR)_n$) as a precursor, sol-gel chemistry can be described in terms of two classes of reactions: (David, 1995; Charles, 1994)

Hydrolysis: $-M(OR)_n + xH_2O \longrightarrow M(OR)_{n-x}(OH)_x + xROH$

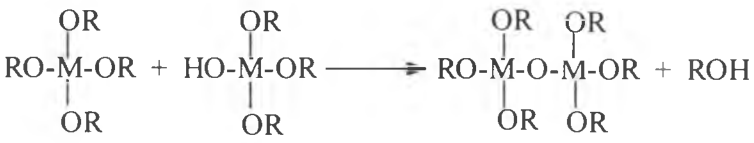
Condensation:

(a) Dehydration



$$RO\text{-}\underset{OR}{\overset{OR}{M}}\text{-}OH + HO\text{-}\underset{OR}{\overset{OR}{M}}\text{-}OR \longrightarrow RO\text{-}\underset{OR}{\overset{OR}{M}}\text{-}O\text{-}\underset{OR}{\overset{OR}{M}}\text{-}OR + H_2O$$

(b) Dealcoholation



$$RO\text{-}\overset{OR}{\underset{OR}{M}}\text{-}OR + HO\text{-}\overset{OR}{\underset{OR}{M}}\text{-}OR \longrightarrow RO\text{-}\overset{OR}{\underset{OR}{M}}\text{-}O\text{-}\overset{OR}{\underset{OR}{M}}\text{-}OR + ROH$$

In fact, sol-gel chemistry generally refers to a low temperature method using chemical precursors that can produce more pure and homogenous materials than conventional high temperature processes. The low temperature method leads to the formation of oxides with amorphous that are difficult to prepare by other methods.

Sol-gel chemistry of silicon alkoxides is rather simple, compared to that of complexes of transition metal alkoxides in which metal atoms may exhibit several coordination states. Molecular precursors of silicon alkoxides are always monomeric tetrahedral species $Si(OR)_4$. One of the usual starting materials for silica glasses is tetraethylorthosilicate (TEOS, $Si(OCH_2CH_3)_4$) (Turner, 1986). However, many other alkoxide precursors can be used to impart different properties to the gels. Recently, an inexpensive method of silica has been developed into precursors called glycolato silicate species, which produces refined powders. The advantages of these species are low cost, easy process and environmental friendly (Sun, 2000). By applying the sol-gel method, the resulting xerogel exhibited a different chemical properties, which is evidenced by the step-growth polymerization determined by solvent content, acid or base, aging time and temperature.

Sol-Gel Process of Silica-Type Materials

Silicon containing materials are derived from the synthesis of oxides involving hydrolyzable alkoxides that undergo a sol-gel transition. The sol-gel transition represents a linking of nanometer-sized units, around 100A°, into an oxide network of infinite molecular weight. The process involves polymerization and branching, but a typical overall reaction may be written as eq 1.1

$$Si(OR)_4 + 2H_2O \longrightarrow SiO_2 + 4ROH \qquad (1.1)$$

Where the $Si(OR)_4$ organometallic species is typically TEOS. In this application, the organometallic compound is hydrolyzed, condensed to polymeric chains, the chain becomes more and more branched, and finally a highly swollen gel is formed. It is first dried at moderately low temperatures to remove volatile species, and then is fired into a porous ceramic object.

Advantages and Limitations of Sol-Gels

The advantages of the sol-gel process in general are (1) a higher purity of starting materials is obtained. (2) a relatively low temperature is required, reducing loss of volatile components. (3) the possibility of controlling the "ultra-structure" of the ceramic (to reduce the microscopic flaws that lead to brittleness) results, and (4) ceramic coatings can be formed.

The disadvantages of sol-gel processing include the shrinkage of the ceramics from removal of the solvents and the need for expensive high-purity alkoxides. This tends to limit the use of the process for bulk ceramics, but is a minor factor for specialty applications or those cases where conventional technology fails.

Polysiloxanes

The Si-O backbone of this class of polymers endows it with a variety of intriguing properties. The strength of these bonds gives the siloxanes polymers considerably thermal stability, which is important for their use in high temperature applications, for examples, as heat-transfer agents and high-performance elastomers. The nature of the bonding and the chemical characteristics of the side groups give the chains a very low surface energy and therefore, highly unusual and desirable surface properties.

Several structural features make the siloxane backbone one of the most flexible in all of polymer science. The reasons for this extraordinary flexibility can be seen in Figure 1.1. First, because of the nature of the bonding, the Si-O skeletal has a bond length of 1.64 A° which is significantly larger than that of the C-C bond (1.53 A°) found in most organic polymers.

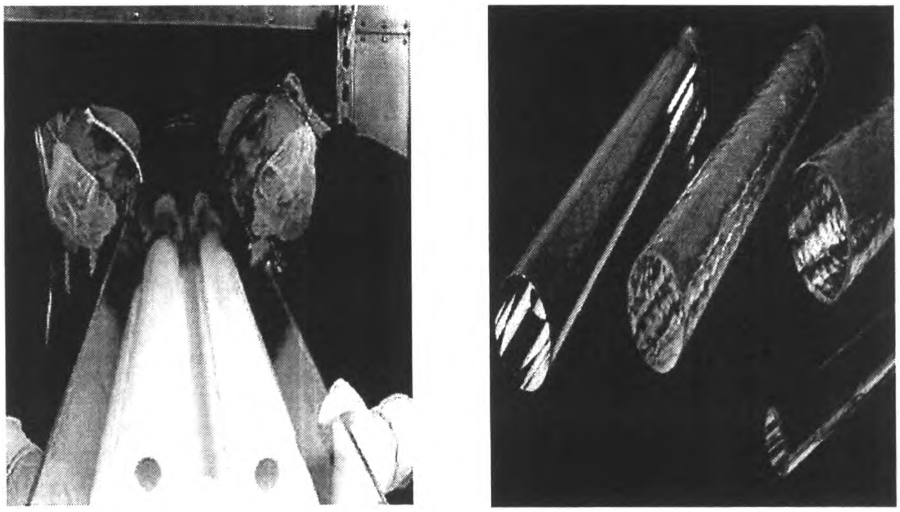


Figure 1.1 A monolithic glass shapes made using the sol-gel process.

As a results, steric interferences or intramolecular congestion is diminished. The oxygen skeletal atoms are also unencumbered by side groups, and still have the divalency needed to continue a chain structure. Finally the Si-O-Si bond angle (180-θ') of ≈ 143° is much more open than the usual tetrahedral bonding (≈110°), and torsional rotations can occur without incurring a serious energy penalty.

These structural features have the effect of increasing the dynamic flexibility of the chain (James, 1992).

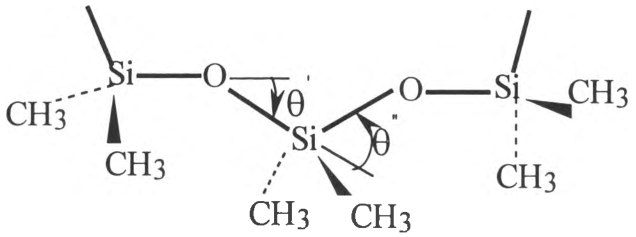


Figure 1.2 Sketch of poly(dimethylsiloxane)PDMS chain, showing some structural information relevant to its high flexibility.

Polycondensation of Polysiloxane

Polycondensation processes are often applied for the synthesis of both linear siloxane polymers and cyclic siloxane oligomers. A polysiloxane chain is most often formed as a result of two types of polycondensation; homofunctional polycondensation of silanediols and heterofunctional polycondensation involving the silanol group and another function. These reactions usually constitute the second step of the hydrolytic polycondensation of organosilanes having two hydrolyzable groups attached to silicon (eq 1.2)

$$n\mathrm{R_2SiX_2} \xrightarrow[\mathrm{-HX}]{\mathrm{H_2O}} \left[\mathrm{SiR_2O}\right]_n \quad \mathrm{X = Cl, OR, OC(O)R, NR_2, SR}\ \text{etc.} \qquad (1.2)$$

Both steps, hydrolysis and polycondensation, usually occur in one process. If the hydrolysis is much faster and an excess of water is used, then the silane is fully transformed into silanediol and the polymer is formed from the homofunctional silanediol polycondensation.

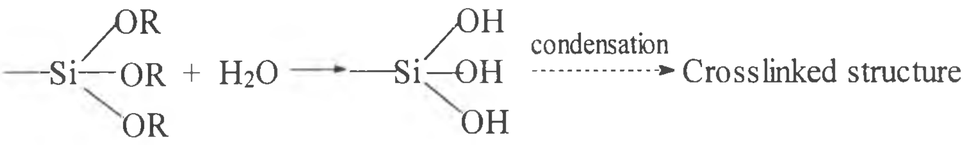
Heterofunctional polycondensation (eq 1.3) is favored in the process of eq 1.2 when the functional group is less reactive and a limited amount of water is used.

$$-R_2SiX + HOSiR_2- \longrightarrow -R_2SiOSiR_2- + HX \qquad (1.3)$$

Crosslinking using condensation reactions

The condensation of silanol to form siloxane bonds (eq. 1.4) is a reaction of considerable importance in industrial silicone chemistry. If it were feasible to extend this chemistry to molecules where more than one silanol group is attached to a single silicon atom, then this condensation reaction could be used to produce a three-dimensional crosslinked matrix with the desirable absence of any additional organic character, except siloxane bonds. The principle, however, has been harnessed successfully in room temperature curing systems. Molecules are synthesized (which contain $=Si(OR)_2$ or $-Si(OR)_3$ groups) as part of the siloxane chain and these groups, on exposure to atmospheric moisture, are spontaneously hydrolyzed and condensed to give a three-dimensional crosslinked network.

$$\equiv SiOH + \equiv SiOH \longrightarrow \equiv SiOSi\equiv + H_2O \qquad (1.4)$$



$$-Si(OR)_3 + H_2O \longrightarrow -Si(OH)_3 \xrightarrow{\text{condensation}} \text{Crosslinked structure} \qquad (1.5)$$

If we include the initial hydrolysis of the -OR functional group attached to silicon, then there are three possible reactions involved in the crosslinking process (Clarson, 1993).

$$\equiv \mathrm{SiOR} + \mathrm{H_2O} \longrightarrow \equiv \mathrm{SiOH} + \mathrm{ROH} \tag{1.6}$$

$$\equiv \mathrm{SiOH} + \equiv \mathrm{SiOH} \longrightarrow \equiv \mathrm{SiOSi} \equiv + \mathrm{H_2O} \tag{1.7}$$

$$\equiv \mathrm{SiOH} + \equiv \mathrm{SiOR} \longrightarrow \equiv \mathrm{SiOSi} \equiv + \mathrm{ROH} \tag{1.8}$$