

Silicon, Silicone, Silicate, Aluminosilicate, Zeolites and Shape Selective Catalysis

What makes silicon unique and its chemistry the choice of a wide range of environmentally friendly industrial applications ?

High natural abundance and easy availability of starting material (Sand)
(silicon is the second most abundant element on the earth)

An easy purification process to pure silicon

A simple and cost efficient method for synthesis of organochlorosilanes and their polymerization to silicone polymers

Highly environmentally friendly end products with a diverse range of proven applications

Applications in steel refining & Semiconductor industry

Inorganic polymer industry based on Silicones

Industry based on piezo electricity of quartz

Industry based on aluminosilicates: from bricks, glass, cement to crockery

Zeolites as drying agents water softeners and unique catalysts

Taken from the earth : given back to the earth



Unique properties of silicon

- Silicon mostly forms tetravalent compounds and to a minor extent divalent compounds

- Silicon forms non-toxic organo derivatives and therefore finds use in a wide range of applications

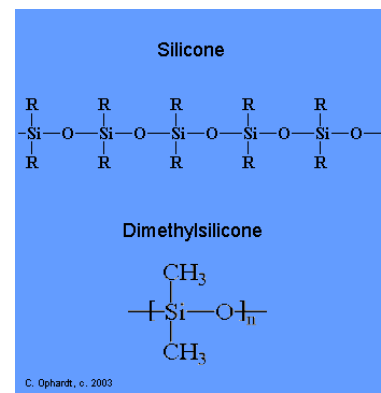
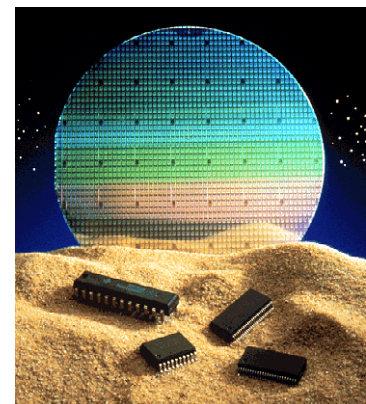
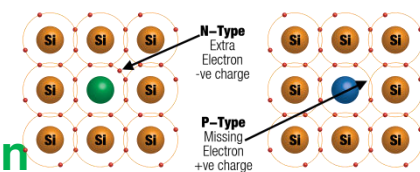
- Si-O bond is one of the strongest bonds based on silicon and silicone polymers having Si-O back bone are the most widely used inorganic polymers

- Silicon forms multiple bonds very rarely and to stabilize such bonds sterically bulky groups are required

- Silicon is a semiconductor and finds use in solar cell fabrication and electronics

- Unlike carbon, silicon does not form stable double bonds with oxygen (till 2014)

- Silicates, aluminosilicates and related compounds are highly environmentally friendly and many of them are naturally occurring.



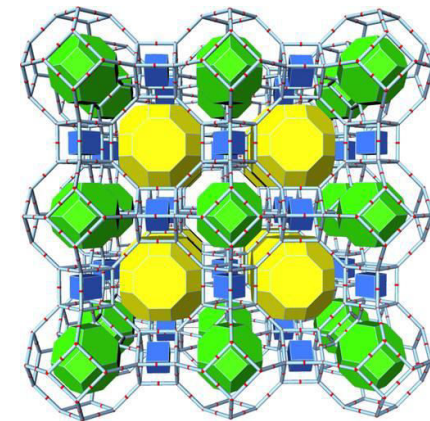
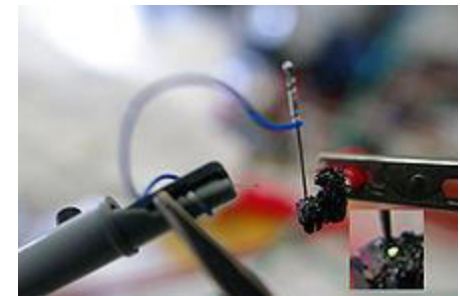
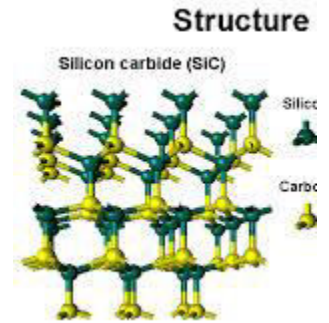
•Alumino silicates wherein a tetrahedral silicon is replaced by tetrahedral aluminum often have replaceable sodium counter-ions which make them excellent water softeners

•Zeolites are open framework alumino silicates and have pores and cavities of specific dimensions which can act as molecular sieves and bring about shape selective catalysis

•Quartz (silicon dioxide) shows piezo electric properties

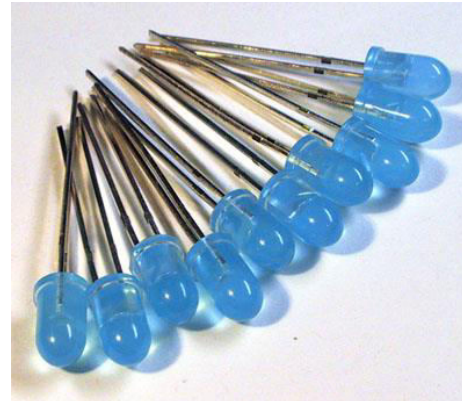
•Silicon carbide has been the first LED and is still used

•Trialkylsilyl groups are well known protecting units for functional groups in organic chemistry



Tough,
yet beautiful.

Gorilla glass

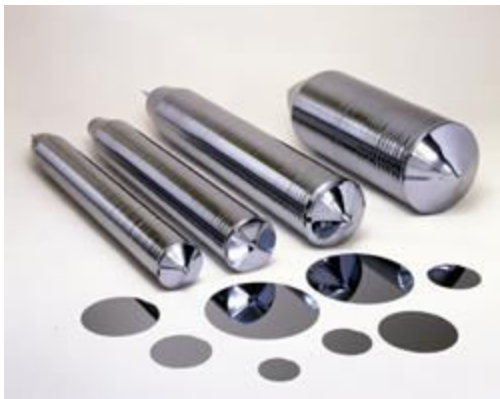
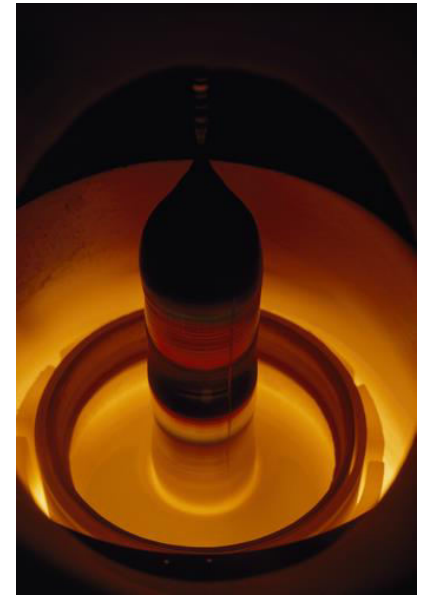


About the element

Silicon is a grey colored brittle solid having a melting point of 1414 °C and boiling point of 3265 °C.

It is a semiconductor and has a negative temperature coefficient of resistance as the number of charge carriers increases with temperature.

Naturally occurring silicon is composed of three stable isotopes, silicon-28, silicon-29, and silicon-30, with silicon-28 being the most abundant (92% natural abundance)



[Czochralski process of growing crystals of silicon](#)

Isolation and Purification of the Element

The first step in making pure silicon is reduction of silica to an impure form of silicon known as ferrosilicon. Ferrosilicon is an iron-silicon alloy that contains varying ratios of elemental silicon and iron.



Ferrosilicon accounts for about **80% of the world's production** of elemental silicon. Silicon has a high propensity to form bonds with oxygen and Ferrosilicon is primarily used by the steel industry to remove dissolved oxygen in steel melt.

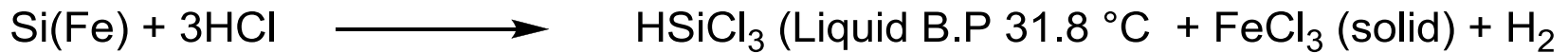
Ultrapure silicon for solar cells and electronics

For solar cell fabrication one requires silicon of much higher purity (+99.9%). For electronics grade the purity required is even higher (**99.9999999% ; known as 9 nines**)

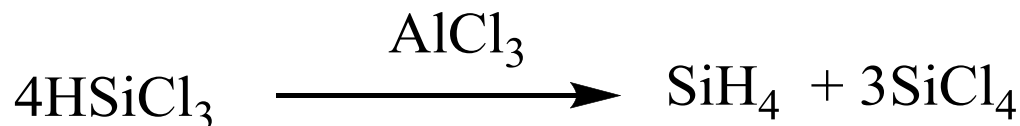
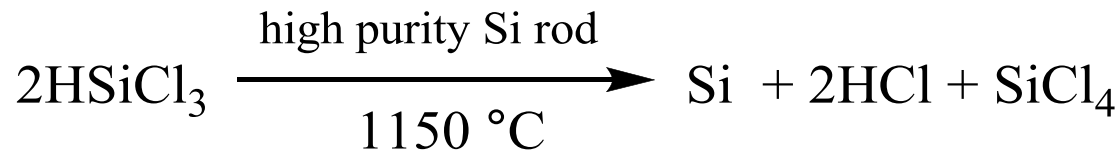
Although molten salt electrolysis of SiO_2 or zone refining of metallurgy grade silicon can be carried out for purification a more well known method and cost efficient is to convert the ferrosilicon to **SiCl_4 or HSiCl_3** . These two relatively low boiling liquids can be purified to a very high level of purity by repeated distillation



Trichlorosilane is produced by treating powdered ferrosilicon with blowing hydrogen chloride at $300 \text{ }^\circ\text{C}$

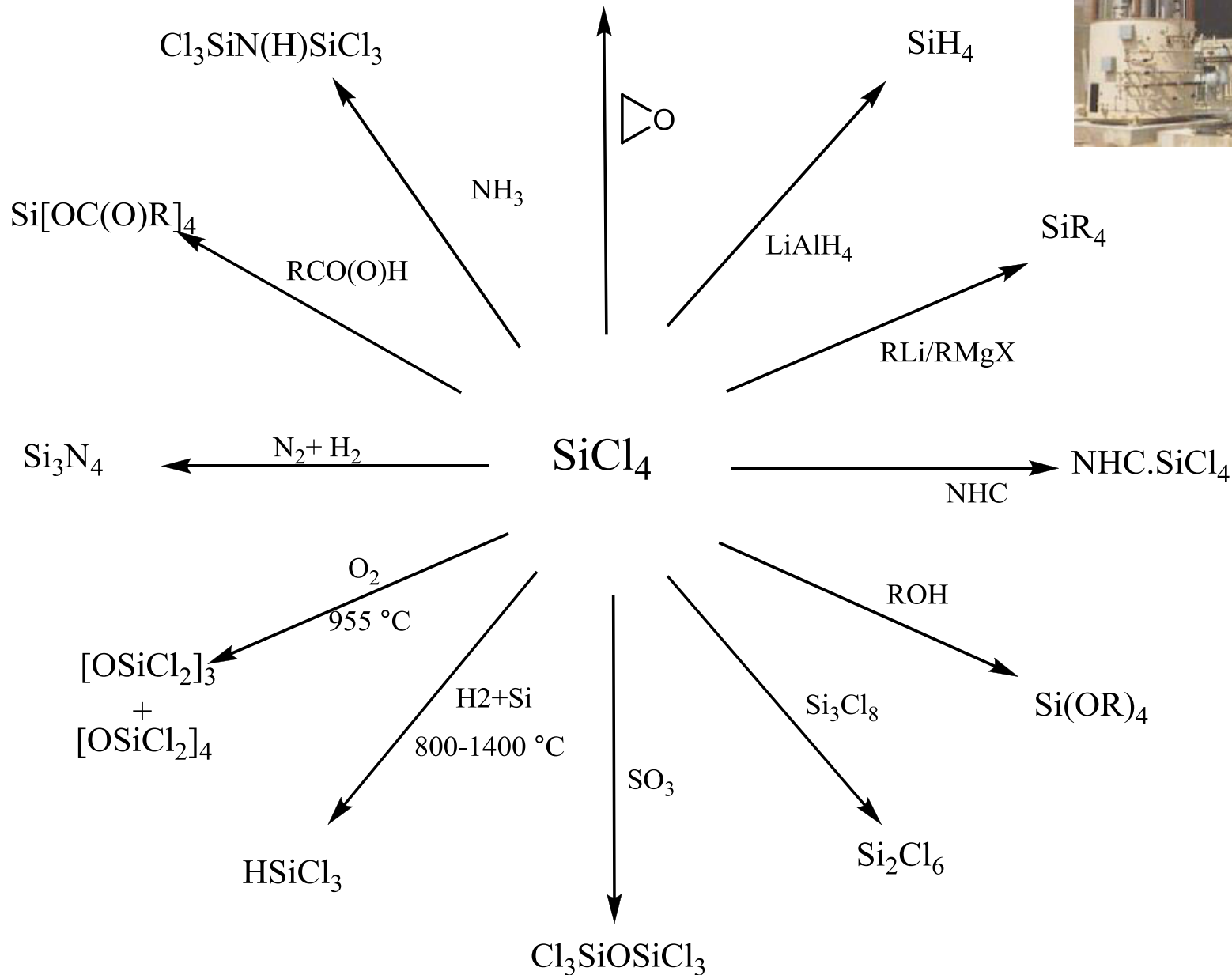
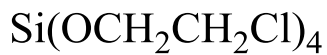


A convenient method to make ultrapure silicon has been the 'Siemens process' in which highly pure silicon rods are exposed at high temperatures to trichlorosilane. Polycrystalline silicon gets deposited on the silicon rod.

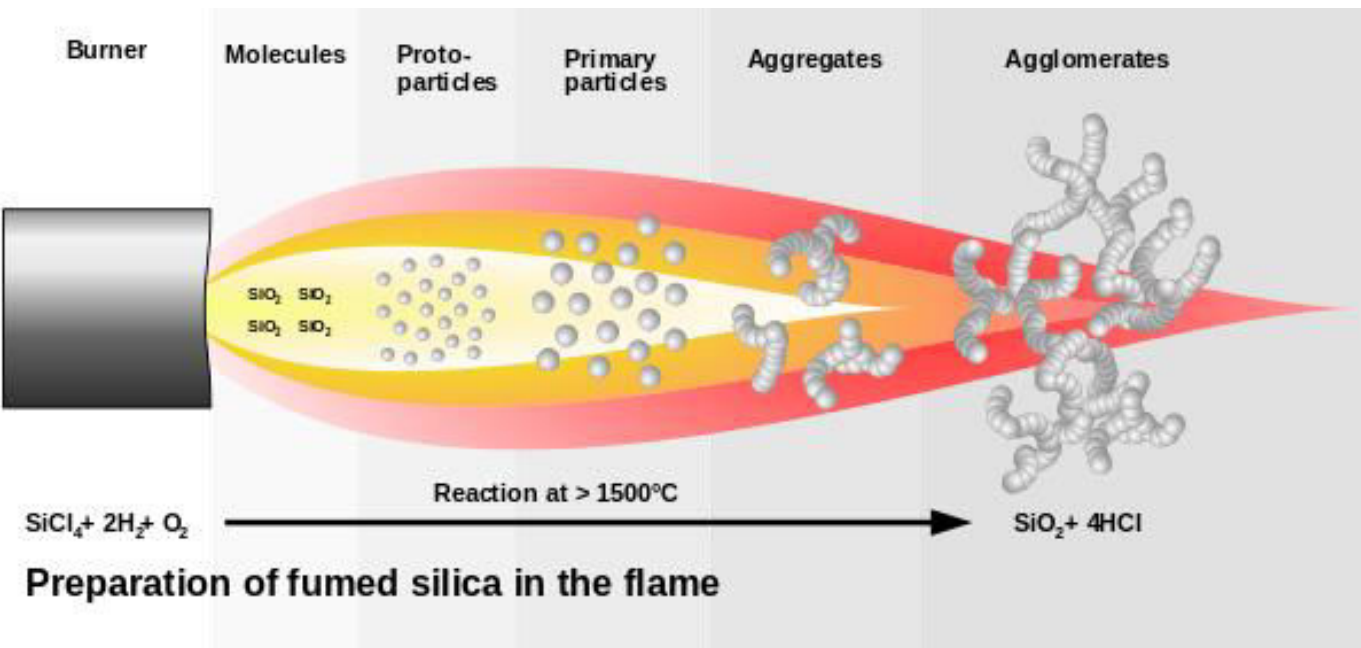


[Czochralski X'tal puller](#)

Silicon tetrachloride: A useful precursor



Fumed silica (pyrogenic silica) from SiCl_4 : A useful filler



Fumed silica is made mostly from flame pyrolysis of silicon tetrachloride

Fumed silica serves as a universal thickening agent and an anticaking agent (free-flow agent) in powders. Like silica gel, it serves as a desiccant. It is used in cosmetics for its light-diffusing properties. It is used as a light abrasive, in products like toothpaste. Other uses include filler in silicone elastomer and viscosity adjustment in paints, coatings, printing inks, adhesives and unsaturated polyester resins.

Comparing Silicon and Carbon in bond strengths

Compound	Bond energy, kJ/mol	
	X = Si	X = C
H ₃ X-H	378	439
H ₃ X-CH ₃	343	378
H ₃ X-OH	452	386
H ₃ X-F	565	460
H ₃ X-Cl	381	354
H ₃ X-SiH ₃	310	343



Si-O and Si-F bond strengths dominate: driving force for many reactions.
Si-O bonds cleaved by fluoride ions. However SiF₄ hydrolyses in water to give SiO₂

SiH₄ explosively reacts with air giving SiO₂. Si-H bonds adds to alkenes in the presence of platinum catalysts (Hydrosilylation)

Etching of glass: leaching away of surface silica by fluoride sources (HF, H₂SiF₆)

Me₃Si-SiMe₃ and Cl₃Si-SiCl₃ are oxygen scavengers converting to Si-O-Si bonds

Silyl ethers are hydrophobic while Alkyl ethers are hydrophilic

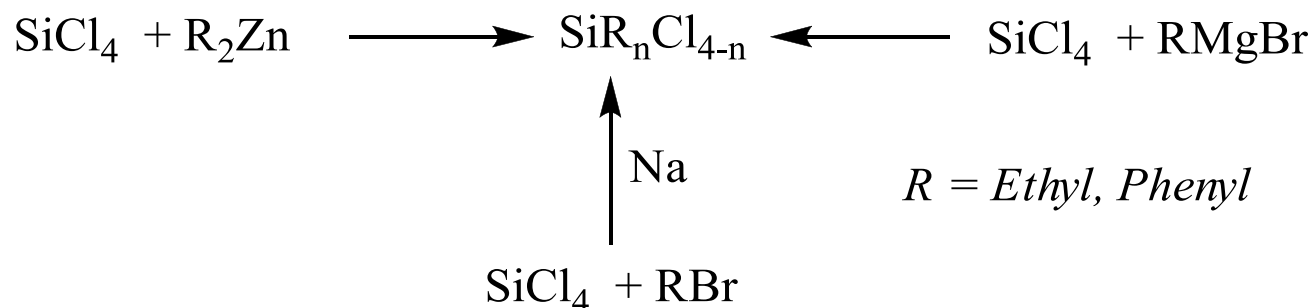
Early synthesis of organosilanes

First report 1863 Friedel and Craft using alkylzinc reagents



F. Stanley Kipping used first organozinc, followed by Wurtz coupling (Na) and later Grignard reagents to make organosilicon compounds.

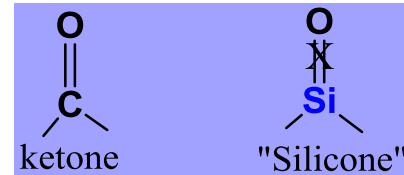
In 57 research papers Kipping created the basis of organosilicon chemistry. He made mostly ethyl and phenyl organochlorosilanes as methyl chloride is a gas difficult to handle. First examples of silicone polymers (having ethyl and or phenyl groups) was reported by Kipping in 1904 and he described the products of his reaction as “**sticky messes of no particular use!**”





F. Stanley Kipping

Silicone Polymers



Kipping coined the word silicone. In 1937, after 30 years of research, on the occasion of his retirement (Bakrerian lecture of the Royal Society) he said *"We have considered all the known types of organic derivatives of silicon and we see how few are their number, in comparison with the purely organic compounds. Since the few which are known are very limited in their reactions, the prospect of any immediate and important advance in this section of chemistry does not seem very hopeful."*

In 1943 Dow Corning company took up industrial production of silicone polymers

James Frank Hyde at Corning hydrolyzed Grignard derived organosilanes to industrially make silicones, He used ethylphenyl silicone along with glass fibres to make an excellent insulating material which during 2nd world war helped aircraft to fly at 35,000 ft upto 8hrs without having corona discharge (which affected aircraft communications with ground) and being flown directly to UK and north africa above Atlantic (earlier they were transported on ships).

Dow (Magnesium expertise) and Corning (silicon expertise) jointly started the company Dow Corning: the world leader in silicone chemistry and applications

First synthesis of a **silanone** -2014

World Silicone Demand, 2010
(\$12.4 billion)

The Direct synthesis: Rochow-Mueller Process (1940)

*The economically viable alternative for Grignard method:
Modern synthesis of organochlorosilanes*

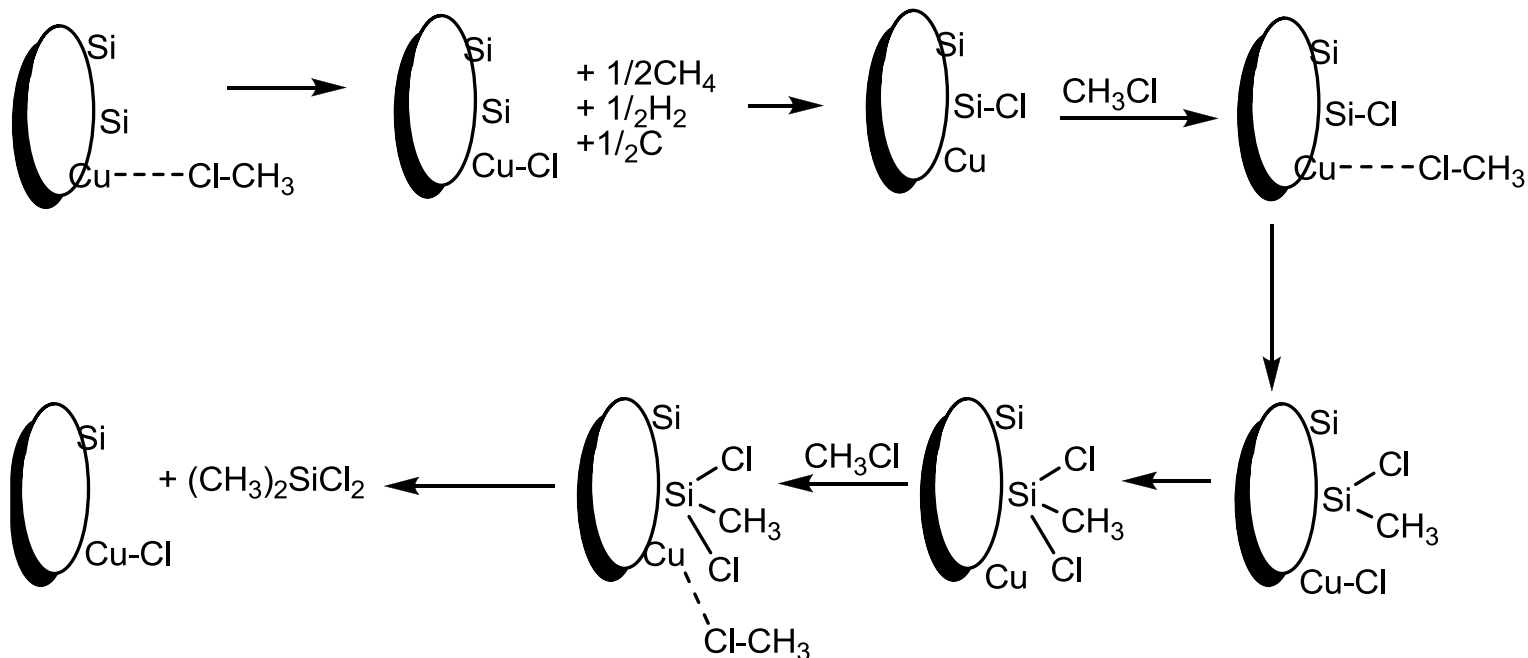
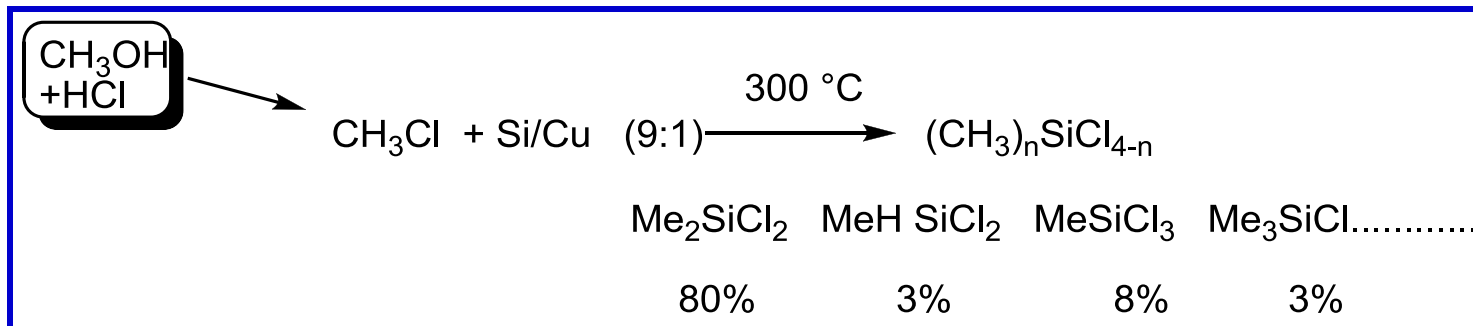
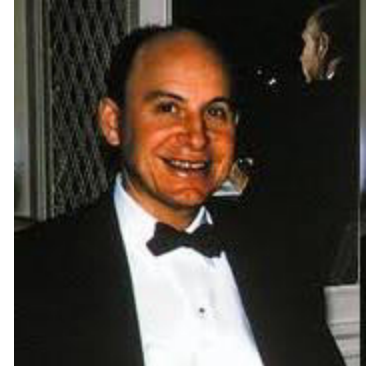


Table 1. Origin, functionality, and fields of application of silicon structural units

Starting compound	Structural unit		Application
	Symbol	Functionality	
(CH ₃) ₃ SiCl Monochloro-trimethylsilane	M	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{Si}-\text{O}_{0.5} \\ \\ \text{CH}_3 \end{array}$ monofunctional	chain end in silicone fluids, trimethylsilyl protecting groups
(CH ₃) ₂ SiCl ₂ Dichlorodi-methylsilane	D	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{Si}-\text{O}_{0.5} \\ \\ \text{O}_{0.5} \end{array}$ difunctional	linear siloxane polymers, silicone fluids, rubbers, elastomers
CH ₃ SiCl ₃ Trichloro-methylsilane	T	$\begin{array}{c} \text{O}_{0.5} \\ \\ \text{H}_3\text{C}-\text{Si}-\text{O}_{0.5} \\ \\ \text{O}_{0.5} \end{array}$ trifunctional	silicone resins for paints, impregnating agents, masonry protection
SiCl ₄ Tetrachloro-silane	Q	$\begin{array}{c} \text{O}_{0.5} \\ \\ \text{O}_{0.5}-\text{Si}-\text{O}_{0.5} \\ \\ \text{O}_{0.5} \end{array}$ tetrafunctional	silicone resins

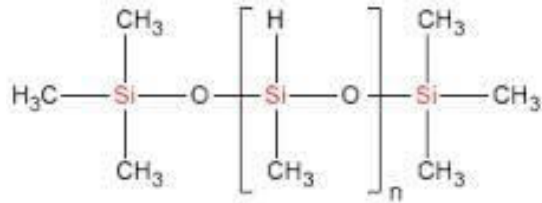
Table 1: Typical ²⁹Si NMR Chemical Shifts

<i>Unit Structure</i>	<i>Unit Type</i>	<i>Chemical Shift</i>
Me ₃ SiO _{1/2}	M	+ 7 ppm
Me ₂ SiO _{2/2}	D	- 22 ppm
MeSiO _{3/2}	T	- 66 ppm
SiO _{4/2}	Q	- 110 ppm
HOME ₂ SiO _{1/2}	M ^{OH}	- 10 ppm

Types of silicone polymers

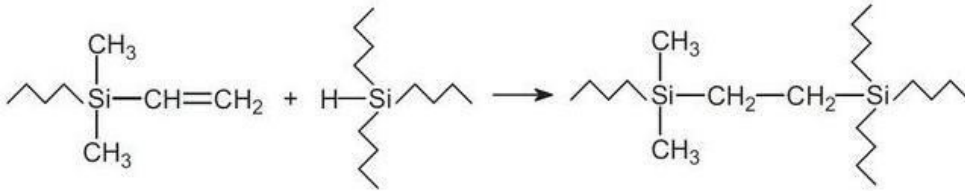
Silicone fluids:

Linear chain silicones with varying substituents on silicon

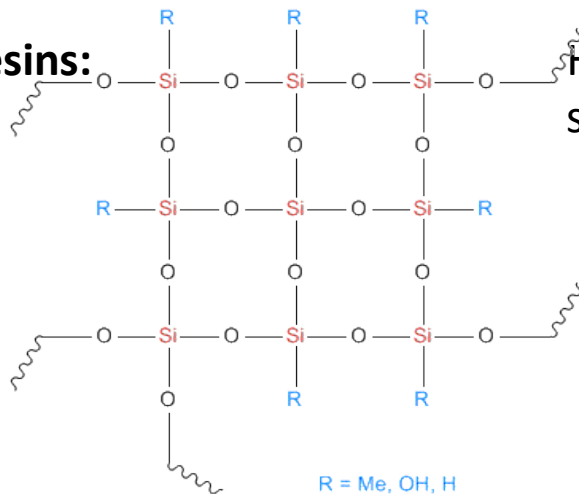


Silicone rubbers or elastomers:

Crosslinked silicone fluids with or without a filler



Silicone resins:



Highly branched containing significant T and Q units

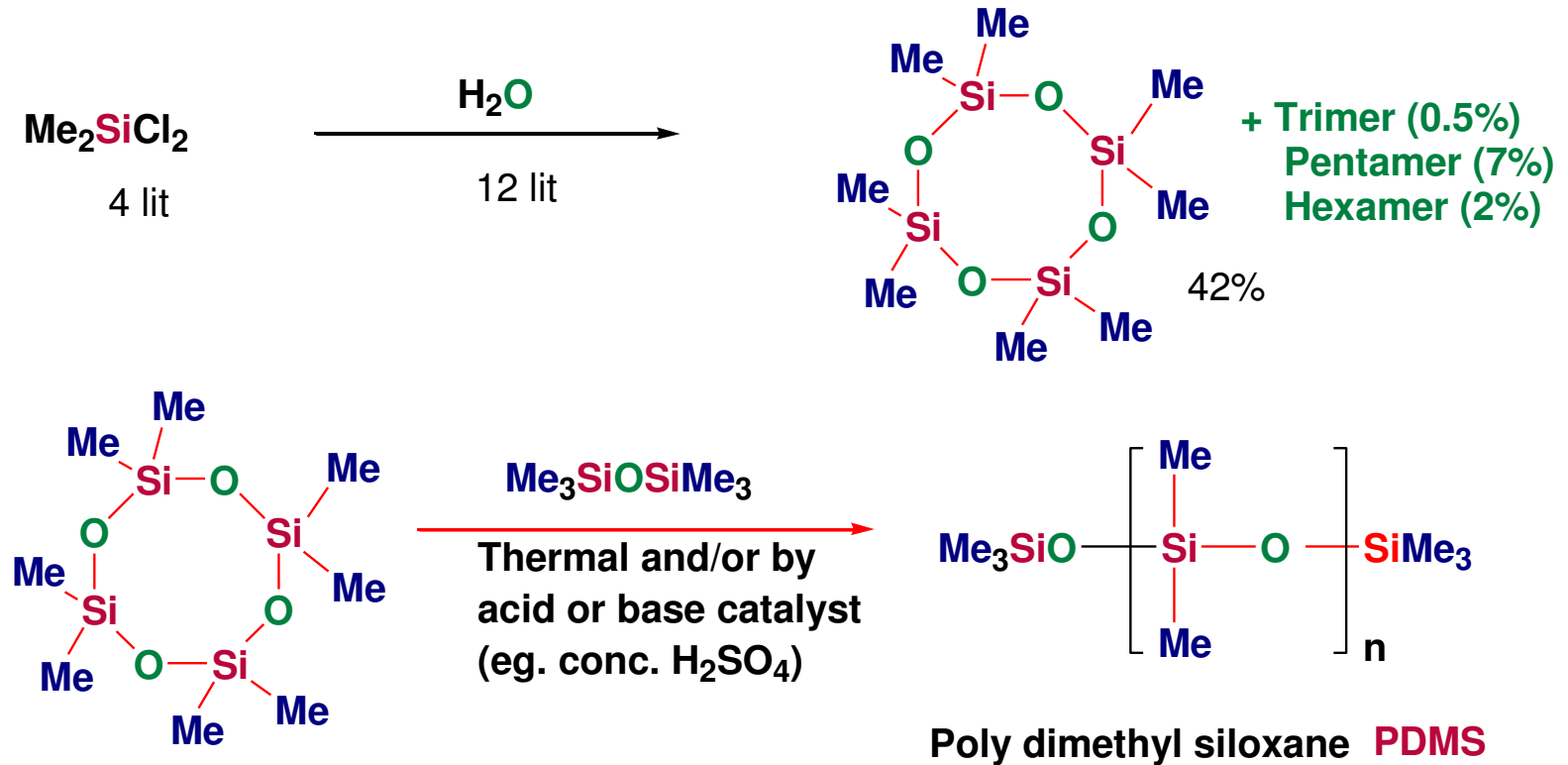
WEATHERCOAT
All Guard



Reverse the effect of rain with
SILICON
Keeps your house looking fresh, year after year.



Synthesis of silicone fluids : Polydimethylsilicone (PDMS)

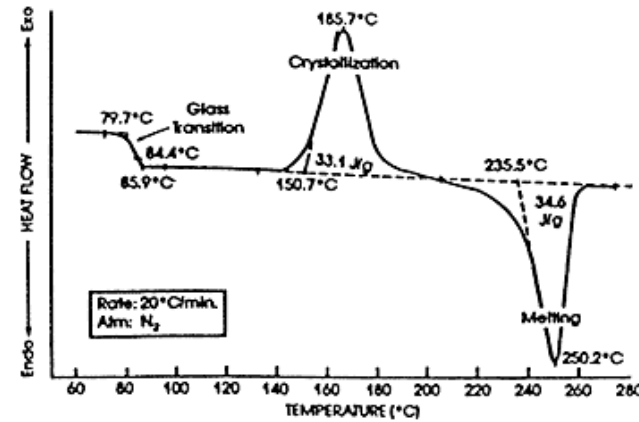
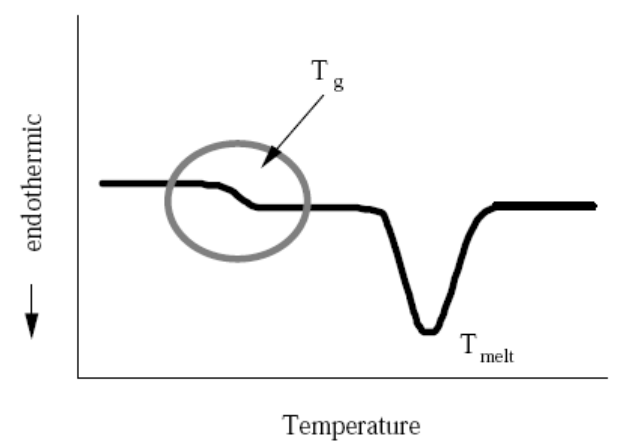
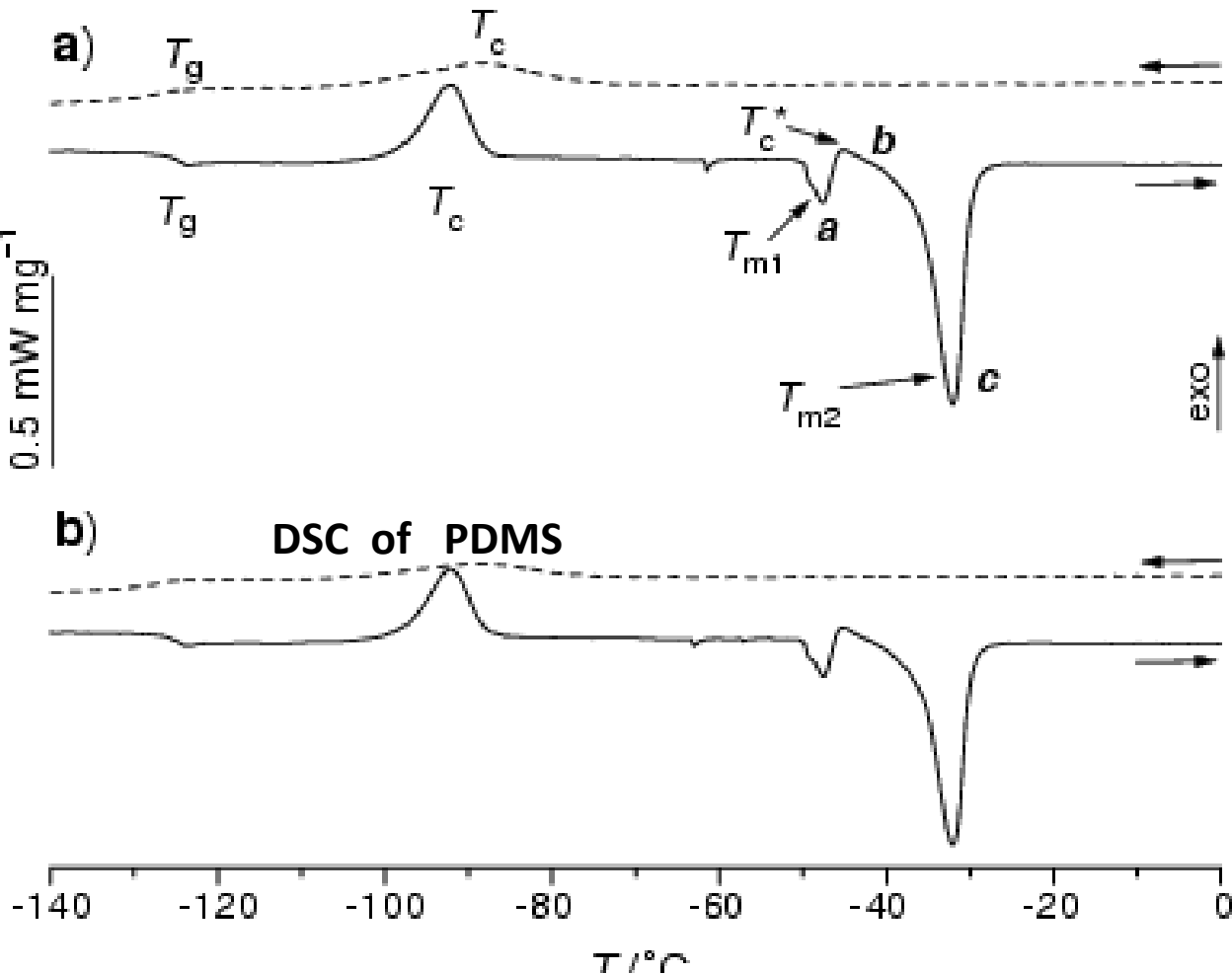


Lowest glass transition temperature for any polymer , $T_g = -123 \text{ }^\circ\text{C}$

Glass Transition Temperature for Selected Polymers

Organic Polymer	T_g ($^{\circ}\text{C}$)	Organic Polymer	T_g ($^{\circ}\text{C}$)
Polyacenaphthalene	264	Polyhexamethylene sebacamide (nylon 6,10)	40
Polyvinyl pyrrolidone	175	Polyvinyl acetate	29
Poly- <i>o</i> -vinyl benzyl alcohol	160	Polyperfluoropropylene	11
Poly- <i>p</i> -vinyl benzyl alcohol	140	Polymethyl acrylate	9
Polymethacrylonitrile	120	Polyvinylidene chloride	-17
Polyacrylic acid	106	Polyvinyl fluoride	-20
Polymethyl methacrylate	105	Poly-1-butene	-25
Polyvinyl formal	105	Polyvinylidene fluoride	-39
Polystyrene	100	Poly-1-hexene	-50
Polyacrylonitrile	96	Polychloroprene	-50
Polyvinyl chloride	87	Polyvinyl- <i>n</i> -butyl ether	-52
Polyvinyl alcohol	85	Polytetramethylene sebacate	-57
Polyvinyl acetal	82	Polybutylene oxide	-60
Polyvinyl propional	72	Polypropylene oxide	-60
Polyethylene terephthalate	69	Poly-1-octene	-65
Polyvinyl isobutylal	56	Polyethylene adipate	-70
Polycaprolactam (nylon 6)	50	Polyisobutylene	-70
Polyhexamethylene adipamide (nylon 6,6)	50	Natural rubber	-72
Polyvinyl butyral	49	Polyisoprene	-73
Polychlorotrifluoroethylene	45	Polydimethyl siloxane	-85
Ethyl cellulose	43	Polydimethyl siloxane	-123

Experimental Determination of T_g : Differential Scanning Calorimetry



Difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature and plotted. When the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature.



Polydimethylsilicone (PDMS)

Industrial synthetic routes

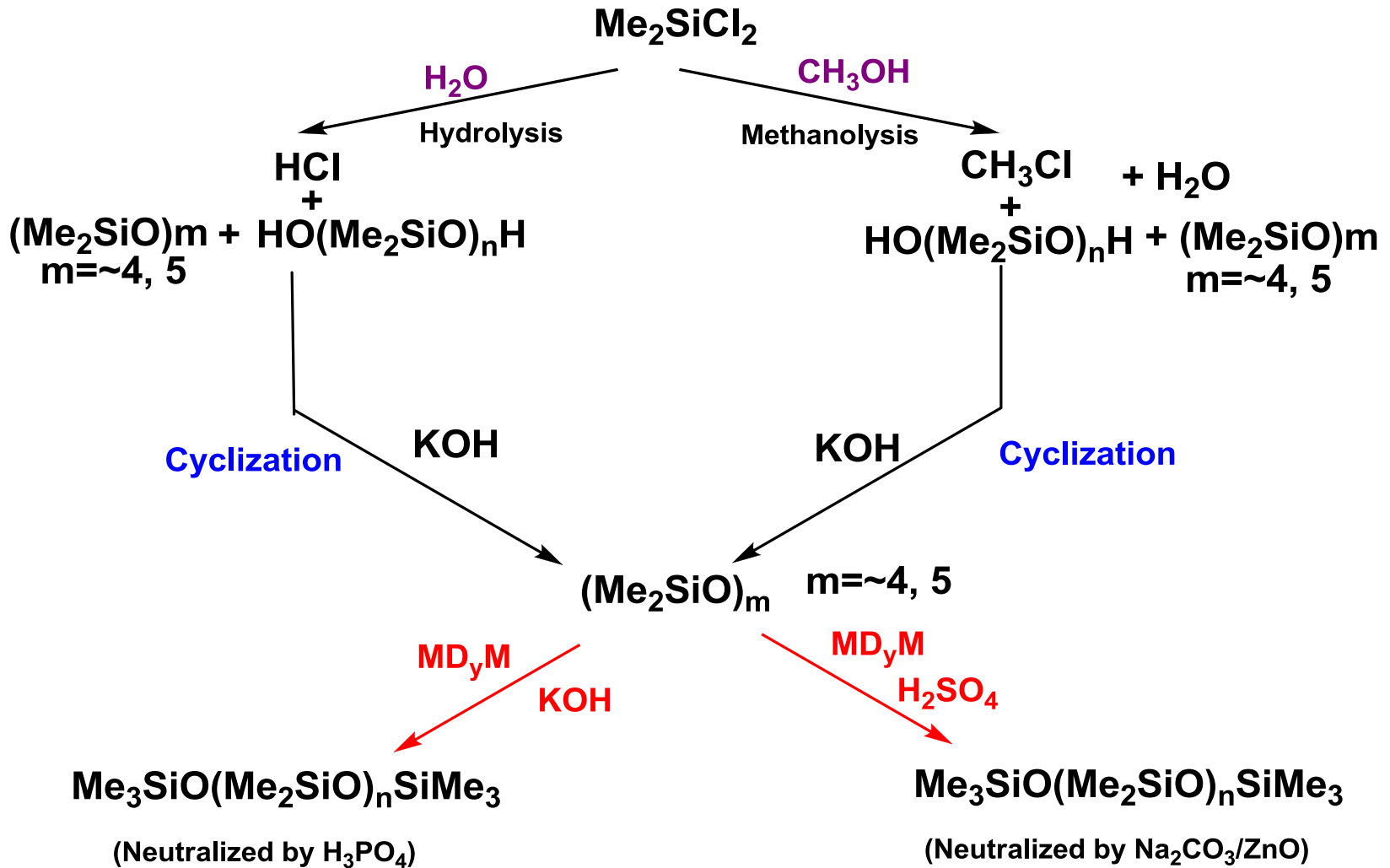
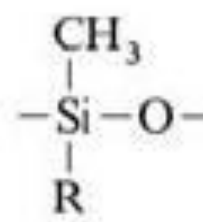
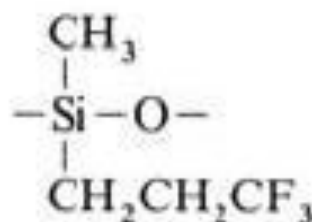
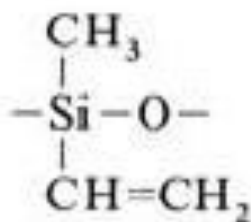
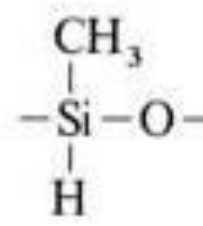
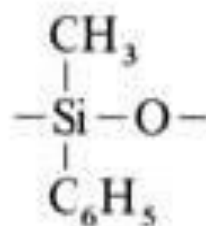
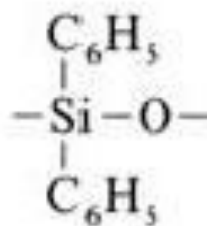


Table 2. Polymerization processes

Starting material	D ₄	D ₄	HO[(CH ₃) ₂ SiO] _n H
Catalyst	KOH	H ₂ SO ₄	(PNCl ₂) _x
Amount of catalyst, ppm	5 – 20	100 – 1000	5 – 200
Polymerization time, min	10 – 90	15 – 30	10 – 20
Reaction temperature, °C	140 – 180	20 – 160	40 – 160
Volatile oligomers in the product mixture, %	13	13	2
Regulator	MD _x M	MD _x M	[R(CH ₃) ₂ Si] ₂ NH
Neutralization	H ₃ PO ₄	ZnO Na ₂ CO ₃	amines

Other types of
silicone fluids



R = C₂–C₁₄ alkyl

Silicone fluids are distinguished from common organic fluids by a number of unique properties:

1. Good thermal stability (150 – 250 °C)
2. Good low-temperature performance (< -70 °C)
3. Strong hydrophobicity
4. Excellent release properties
5. Antifriction and lubricating properties
6. Pronounced surface activity
7. Good dielectric properties
8. Very good damping behavior
9. Good radiation resistance
10. High solubility of gases
11. Physiological inertness
12. Low temperature dependence of physical properties

Silicone fluids

Property

High thermal stability

Good low temp performance

Low surface tension

Water repellency

Antifriction

Good dielectric properties

High water vapor permeability

Non toxicity

Tolerance to skin and physiology

Stability to UV

Application

Heat transfer media

refrigerant in cryostats

release agents

antifoams

antiflatulents

water proofing, polishes

waterproof textiles

lubricant

power transmission fluids

water repellent materials

medical

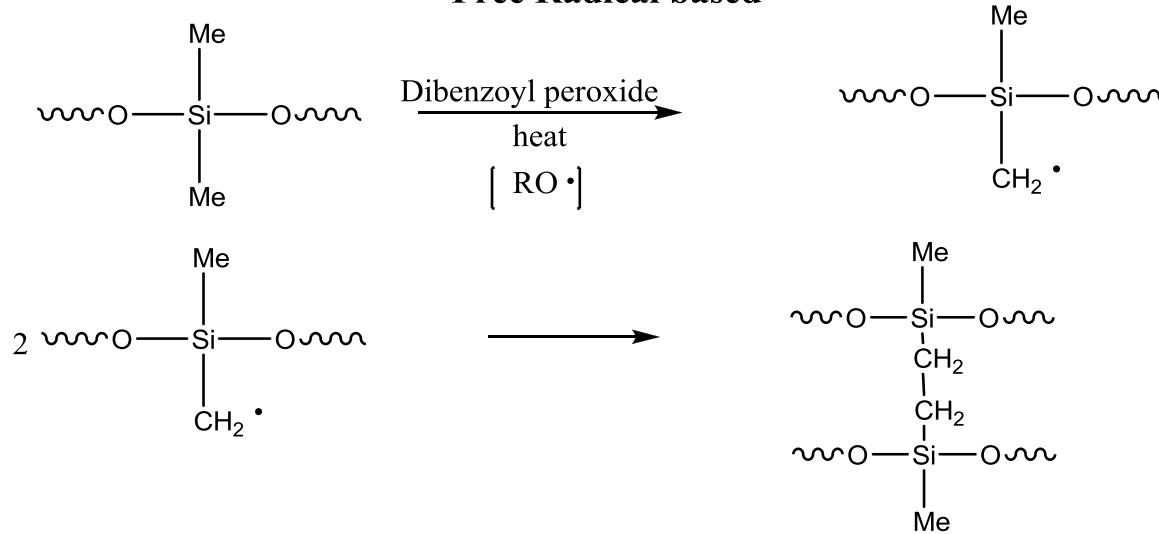
cosmetics, ointments

sunscreen, building

protection,

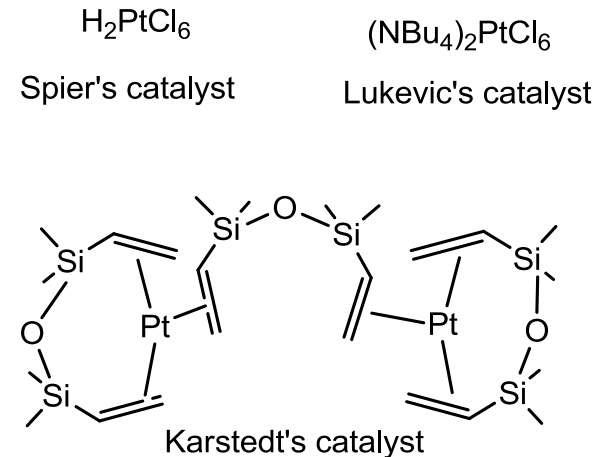
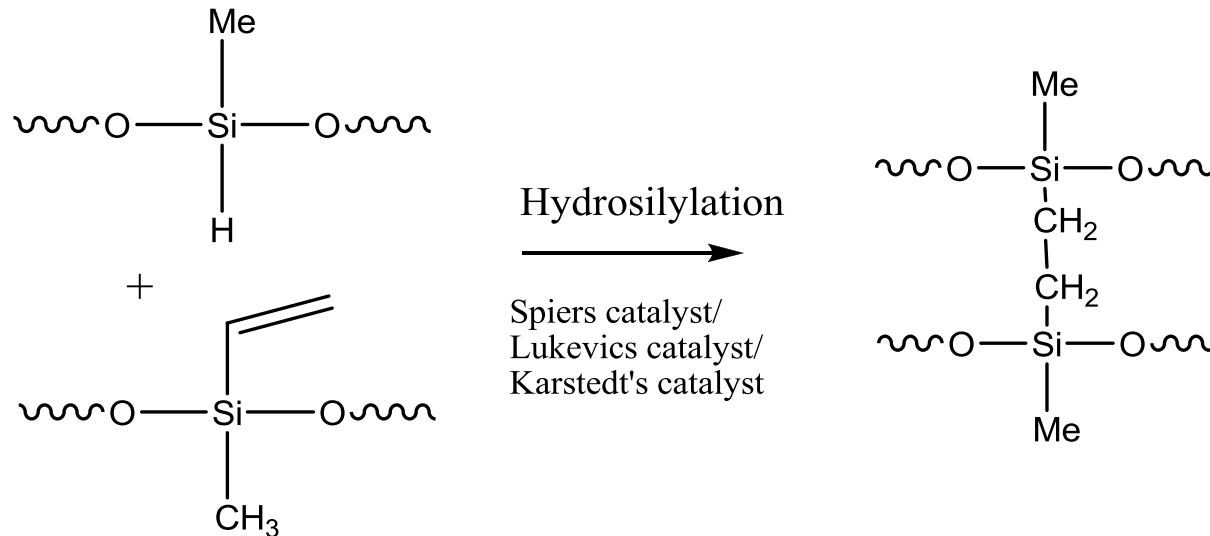
Silicone rubbers: Cross linking of chains

Free Radical based

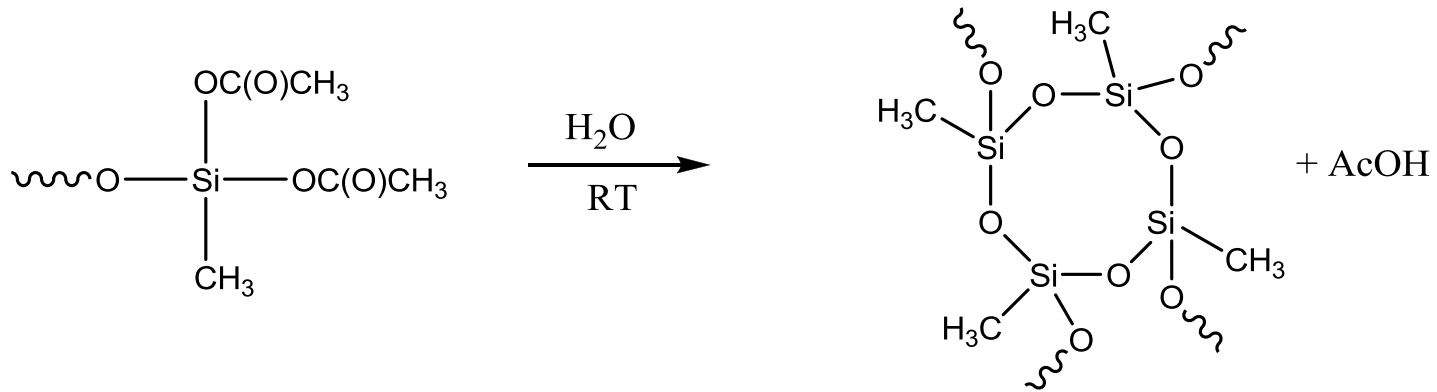


Very high Mol wt:
 $10^5 - 10^7$
 Reinforcing agent:
 fumed silica
 Vulcanized by
 crosslinking

Hydrosilylation based

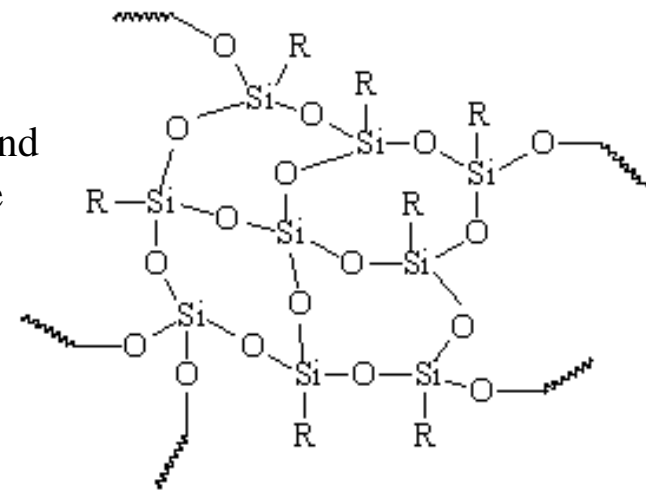


Oxygen based crosslinking – (T units)



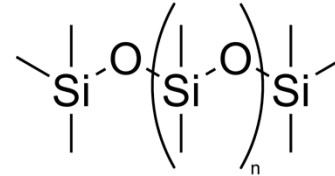
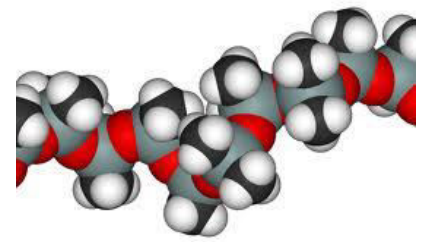
Silicone resins are a type of silicone material which is formed by branched, cage-like oligosiloxanes with the general formula of $R_nSiX_mO_y$, where R is a non reactive substituent, usually Me or Ph, and X is a functional group H, OH, Cl or OR. The most abundant silicone resins are built of **D and T units (DT resins)** or from **M and Q units (MQ resins)**, however many other combinations (MDT, MTQ, QDT) are also used in industry.

Silicone resins represent a broad range of products. Materials of molecular weight in the range of 1000-10,000 are very useful in **pressure-sensitive adhesives, silicone rubbers, coatings and additives for making water repellent paints.**



R = Me, OH, H.

Industrial success of Silicones



First human foot print on moon made with silicone soled shoes

Moon temperature
(-153 to +121 °C)



Glass transition temperature (T_g)

Material	T_g (°C)
Silicone	-123
Tire rubber	-70
Polypropylene (atactic)	-20
Polyvinyl fluoride (PVF)	-20
Polypropylene (isotactic)	0
Polyethylene terephthalate (PET)	70
<u>Poly(vinyl chloride)</u> (PVC)	80
Poly(vinyl alcohol) (PVA)	85
Polystyrene	95
Poly(methyl methacrylate) (atactic)	105
Polytetrafluoroethylene (PTFE)	115
Poly(carbonate)	145
Polysulfone	185
Polynorbornene	215



Buzz Aldrin and Neil Armstrong landed on the moon on July 20, 1969. They were wearing boots from silicon rubber soles developed by GE. Image Credit: NASA

The outer boot consisted of 12 layers of biaxially-oriented polyethylene terephthalate (boPET) – a polyester film (commonly called Mylar) made from stretched polyethylene terephthalate (PET). This footwear also included nonwoven ‘Dacron’ PET product and a fibreglass/polytetrafluoroethylene (PTFE) inner liner material. Requiring good flexibility under very low temperatures, the sole was made from silicone by the General Electric Company, and featured a ¼ inch tread. A fabric incorporating stainless steel was selected for the covering of the outer boot

Silicone Rubbers

The typical properties of silicone elastomers lead to their application in areas involving:

1. Electrical insulation or conduction
2. High and/or low temperatures
3. Weather and UV exposure
4. Oil and hot-air contact
5. Dynamic stress
6. Flame resistance, arcing resistance
7. Gas permeability
8. Contact with foods
9. Contact with living tissue
10. Adhesive surfaces
11. Transparent articles of high optical quality

World Silicone Demand, 2010
(\$12.4 billion)



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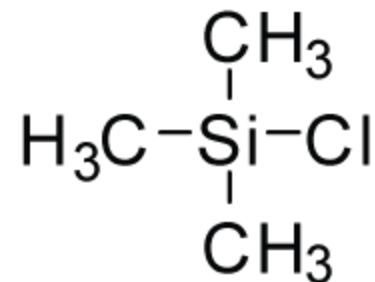
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Oral Drops For Infants
Antiflatulent

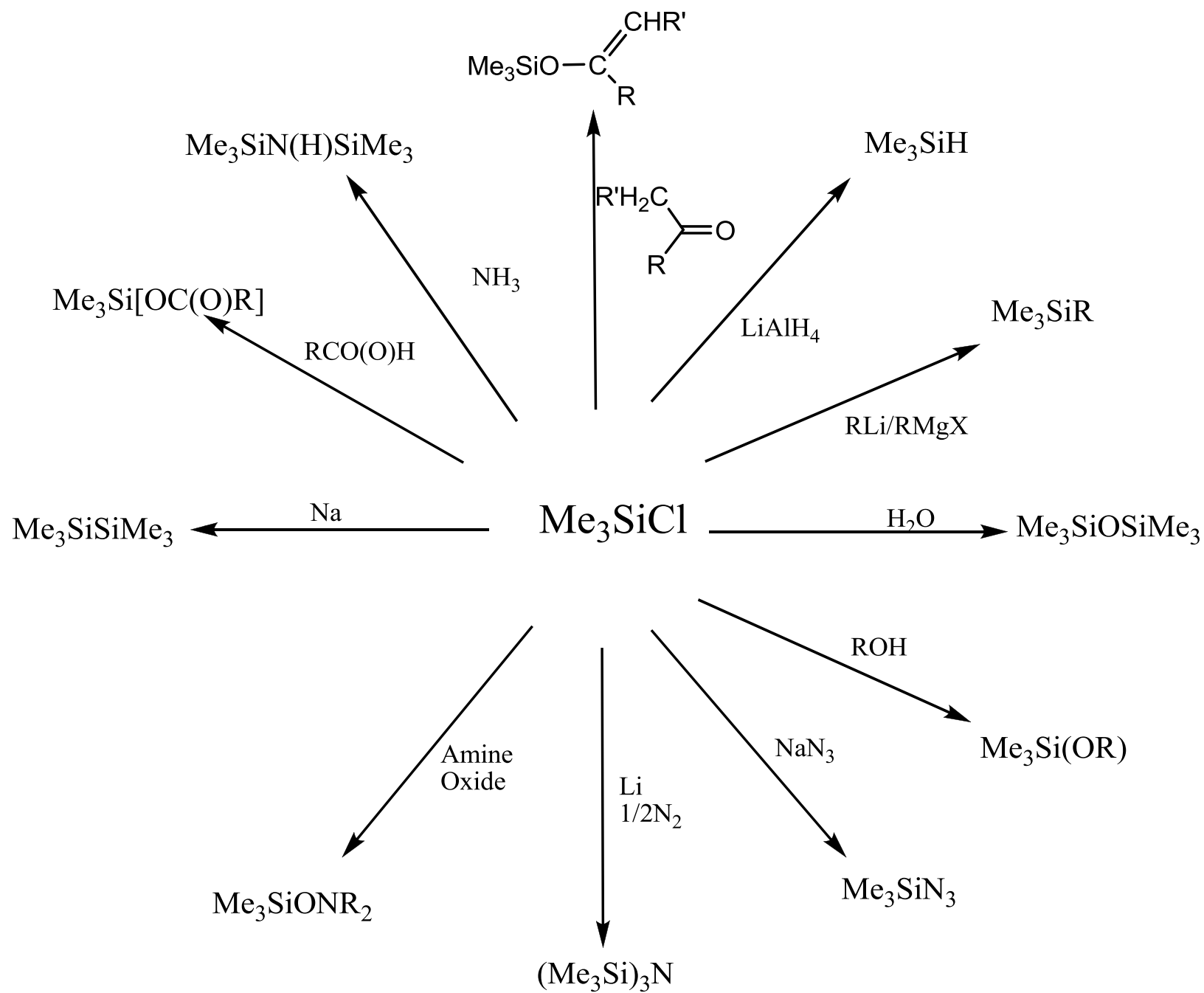
30 ml

AIMAIVA PHARM IND

Trimethyl chlorosilane

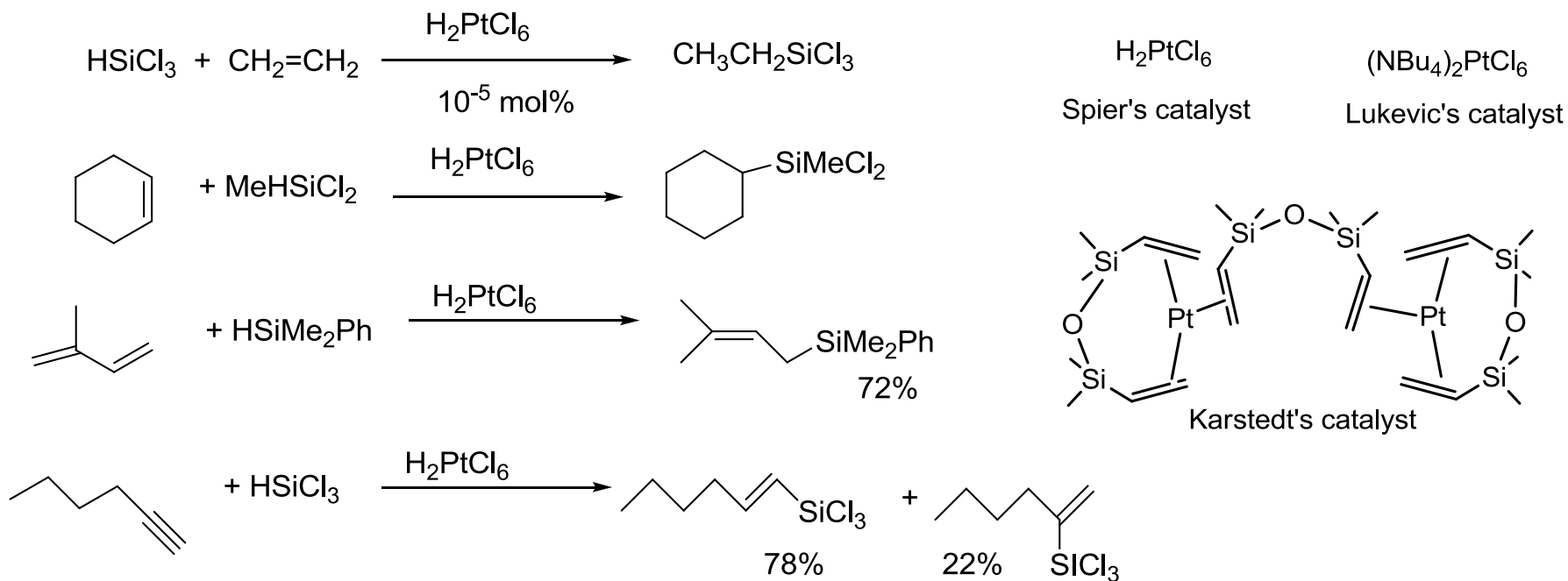


- Termed bulky hydrogen
- A well known protecting groups for alcohols, amines and alkynes
- Introduces hydrophobicity
- An alternative side product for HCl from many reactions which can be easily removed **b. p. 57 °C**
- Starting material for a host of organosilicon compounds



Hydrosilylation: Chemistry of the Si-H bond

Hydrosilylation is the addition of an Si-H bond across multiple bonds such as C=C, C≡C, C=O and C=N. Hydrosilylation was first reported using transition metal catalysts mostly based on platinum. Later rhodium palladium and recently even iron based catalysts have been found to bring about hydrosilylation.



Silicon carbide

Silicon carbide was accidentally discovered during an attempt to produce artificial diamonds, by E. G. Acheson in 1891. Acheson heated a mixture of clay and powdered coke in an iron bowl, with the bowl and an ordinary carbon arc-light serving as the electrodes. He observed bright green crystals formed on the carbon electrode and thought that he had prepared a new compound consisting of carbon and alumina from the clay. He called the new compound Carborundum since the mineral form of alumina is called corundum. He found that the crystals had hardness of diamond and applied for a U.S. patent. His early product was offered for the polishing of gems.



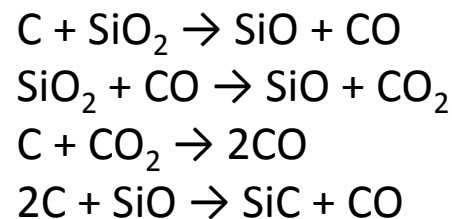
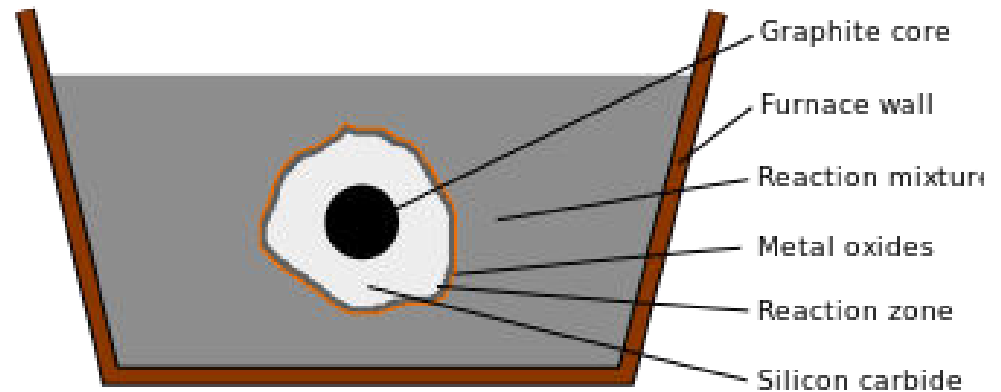
Nobel prize winner Henri Moissan, the father of fluorine chemistry while examining rock samples found in a meteorite in Arizona discovered a rare naturally-occurring SiC mineral. This mineral was later named in his honor as moissanite. Moissan also synthesized SiC by several routes, including dissolution of carbon in molten silicon, melting a mixture of calcium carbide and silica. Very pure silicon carbide is white or colorless; crystals of it are used in semiconductors for high-temperature applications. Grains of silicon carbide can be bonded together by sintering to form very hard ceramics that are widely used in applications requiring high endurance, such as **car brakes, car clutches and ceramic plates in bulletproof vests**. **Electronic applications of silicon carbide as light-emitting diodes (LEDs) and detectors in early radios** were first demonstrated around 1907, and today SiC is widely used in high-temperature/high-voltage semiconductor electronics

Synthesis of silicon carbide

The **Acheson process** is a process to synthesize graphite and silicon carbide, named after its inventor Edward Goodrich Acheson. The process consists of heating a mixture of clay (aluminum silicate) and powdered coke (carbon) in an iron bowl. Acheson, in 1890, originally attempted to synthesize artificial diamond, but ended up creating green crystals of silicon carbide. When heated to **4150°C**, the silicon is removed, leaving graphite. The process was patented by Acheson in 1896 which is the basis of most silicon carbide manufacturing today. Acheson developed an efficient electric furnace based on resistive heating for this purpose

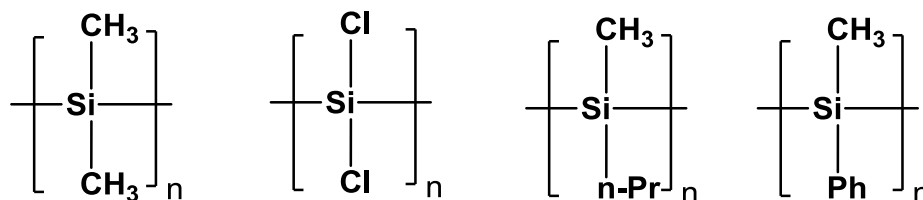


In the furnace, an electric current was passed through a graphite core, surrounded by sand, salt, and carbon. The electric current heated the graphite and other materials, allowing them to react, producing a layer of silicon carbide around the graphite core. The process gives off carbon monoxide.

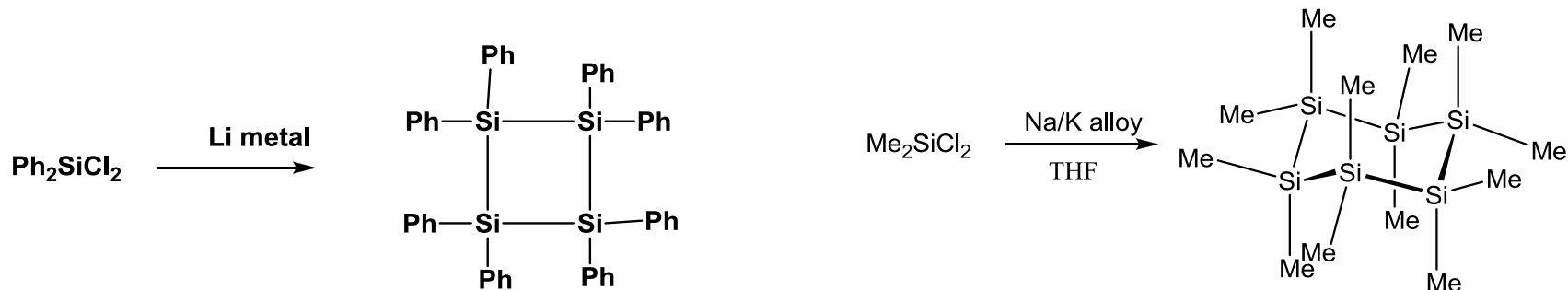


Polysilanes

Polysilanes are polymers with a linear Si-Si catenation in the main chain and with two organic substituents at each silicon atom: They show unusual electronic and photophysical properties. These properties result from electronic delocalization on the σ bonded chain which is a consequence of the lower ionization potential and greater electron affinity of silicon compared to carbon. Because of σ delocalization of electrons they show strong absorption in the range of 300-400 nm.

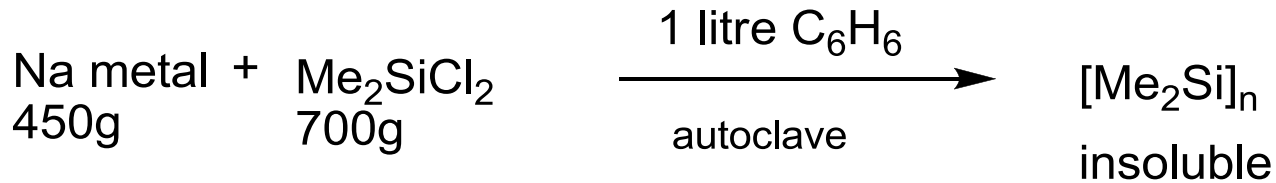


Initial work by Kipping indicated formation of cyclic oligomers having 4-6 membered rings. Polysilanes were obtained by opening up these rings or by using unsymmetrical or long chain R groups on the silicon atom.



Polysilanes to polycarbosilanes to SiC

Burkhard 1949



Burkhard in 1949 prepared polydimethyl silane, as an insoluble compound. Later Yazima and coworkers discovered that by heating this insoluble polymer at 450°C it can be converted to a polycarbosilane and which on further heating can be eventually converted to fibrous silicon carbide

