Inorganic Polymers

Silicones

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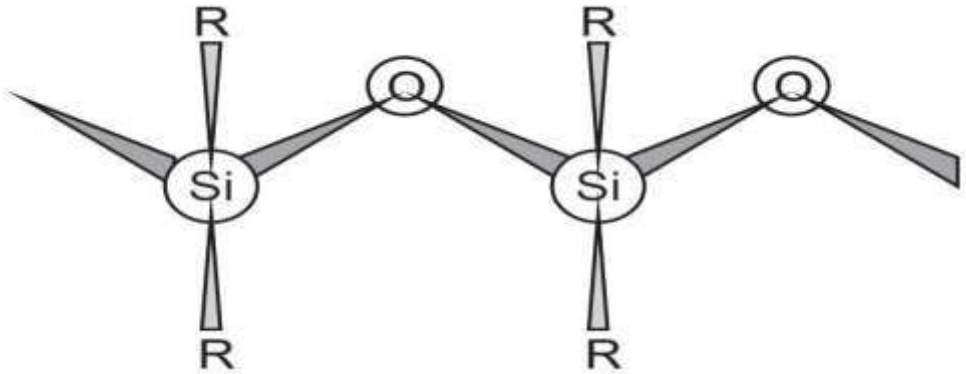
Introduction

- Silicones are also known as Polysiloxanes.
- They are polymers made up of repeating units of **siloxane**, which is a chain of alternating silicon atoms and oxygen atoms, frequently combined with carbon and hydrogen.
- Silicones exist in many forms like silicone oil, silicone grease, silicone rubber,
  - silicone resin, etc.
- Silicone is sometimes mistakenly referred to as **silicon**, which is chemical element and a crystalline metalloid widely used in computers and other electronic equipment. And they have totally different physical and chemical properties.

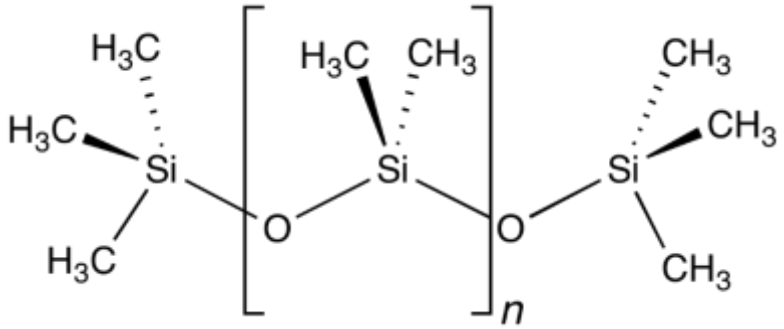
Silicones / Polysiloxanes

- Silicones consist of an inorganic silicon-oxygen backbone chain **(····-Si-O-Si-O-Si-O-····)** with organic side groups attached to the silicon atoms.
- These silicon atoms are tetravalent.



- Silicones have in general the chemical formula $[R_2SiO]_n$, where R is an organic group such as an alkyl (methyl, ethyl) or phenyl group.

- By varying the -Si-O- **chain lengths, side groups, and crosslinking**, silicones can be synthesized with a wide variety of properties and compositions.
- They can vary in consistency from liquid to gel to rubber to hard plastic.
- The most common siloxane is **linear polydimethylsiloxane** (PDMS), a silicone oil.



- The second largest group of silicone materials is based on silicone resins.
- Si–O bonds are much stronger than a typical C–O single bond. (809 kJ/mol compared to 538 kJ/mol)

History of Silicones

- **F. S. Kipping** and **Matt Saunders** coined the word silicone in **1901** to describe **polydiphenylsiloxane** by analogy of its formula, Ph_2SiO (Ph - C_6H_5), with the formula of the **ketone benzophenone**, Ph_2CO (his term was originally silicoketone).
- Kipping was well aware that polydiphenylsiloxane is polymeric whereas benzophenone is monomeric.
- The discovery of the structural differences between Kippings' molecules and the ketones means that silicone is no longer the correct term (though it remains in common usage) and that the term siloxanes is correct according to the nomenclature of modern chemistry.

Production of silicon

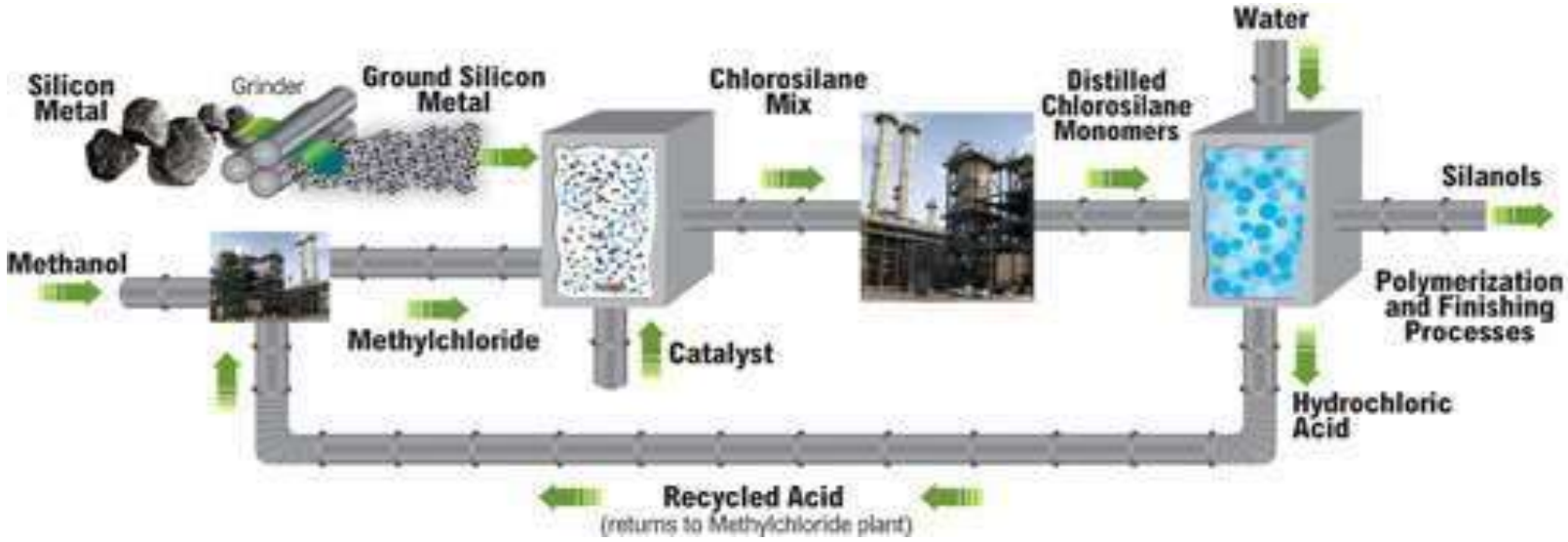
- Silicon does not exist on its own in nature. Most of it is bound with oxygen in materials like **sand, quartzite and granite rock**.
- Silicon producers reduce high-grade quartz sand to elemental silicon via a carbon-thermic smelting process.
- Silicon is typically produced in a submerged electric arc furnace via the carbothermic reduction of silicon dioxide (SiO_2) with a solid carbonaceous reducing agent such as coke, coal, or wood chips. The overall reduction reaction can be represented as

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

- This reaction occurs in an electric furnace at temperature greater than 1,400°C .

Preparation of silicones

- There are 2 methods for preparation of intermediates (Chlorosilane)
  1. **Grignard method**
  2. **Direct Process**



1. Grignard method

- In this method RMgX reacted with Silicon tetrachloride to give dimethyl silicone.
- where R is any alkyl or phenyl group and X is a halide.

$CH_3Cl + Mg \rightarrow CH_3MgCl$ (Grignard reagent)

$2CH_3MgCl + SiCl_4 \rightarrow (CH_3)_2SiCl_2 + 2MgCl_2$

$(CH_3)_2SiCl_2 + H_2O \rightarrow (CH_3)_2Si0 + 2HCl$

- **Advantage:**

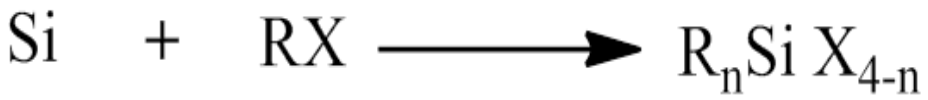
  Wide range of organic group can be attached.

- **Disadvantage:**

  Multiple steps involved and less economical.

2. Direct Process

- In this process, Si directly react with alkyl halide to get Chlorosilane.
- Catalyst used : Cu tube
- Temperature = 250- 280°C



- **Advantage:**

  More economical and less steps involve

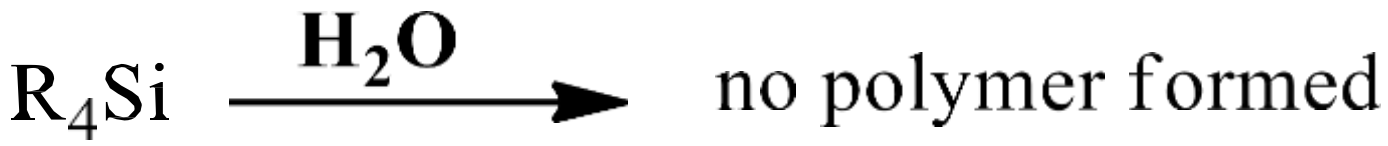
- **Disadvantage:**

Higher alkyl halide decompose at reaction temperature and give poor yield of desired product.

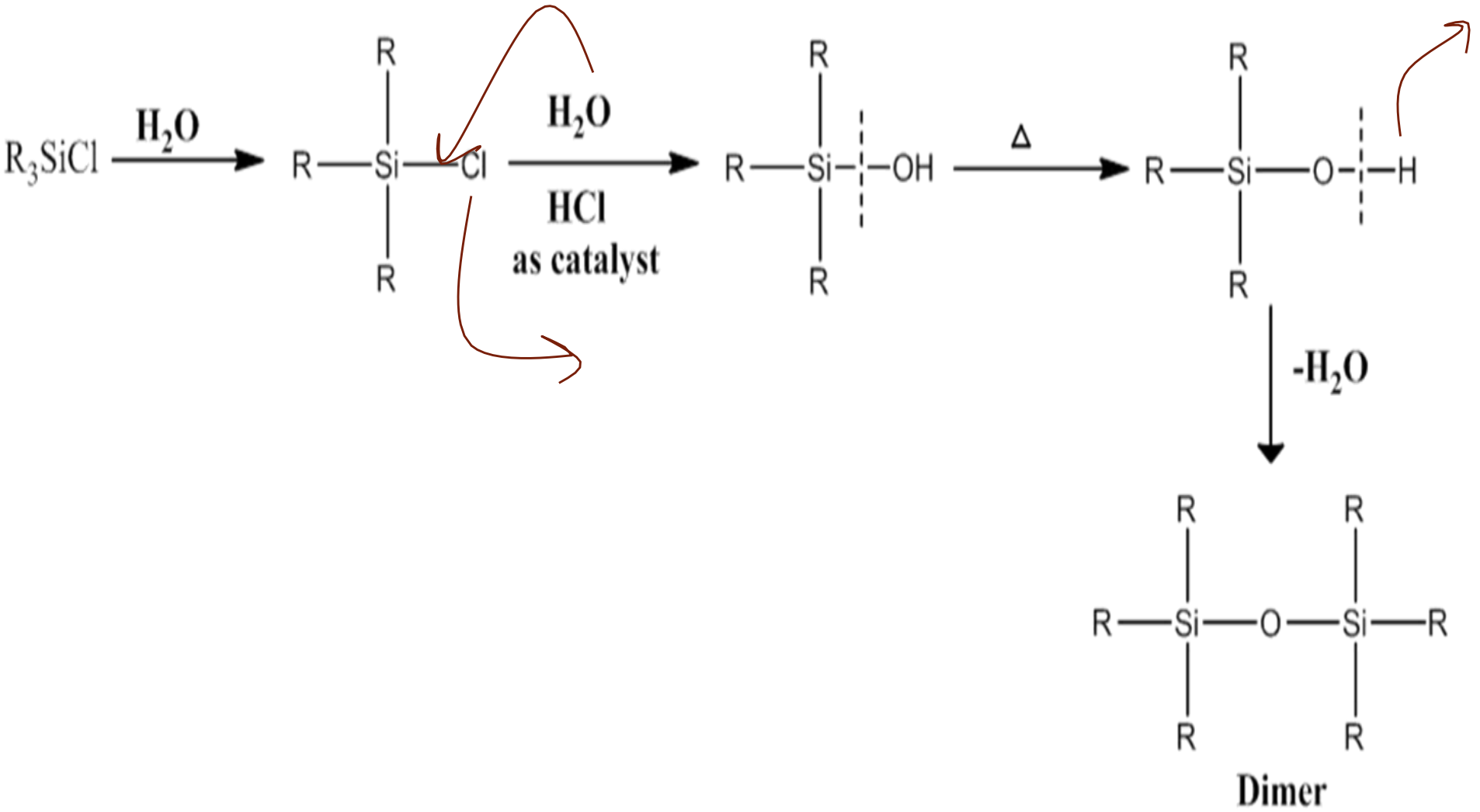
Reactions

- **General reaction :**

- **Now, when n = 4,**

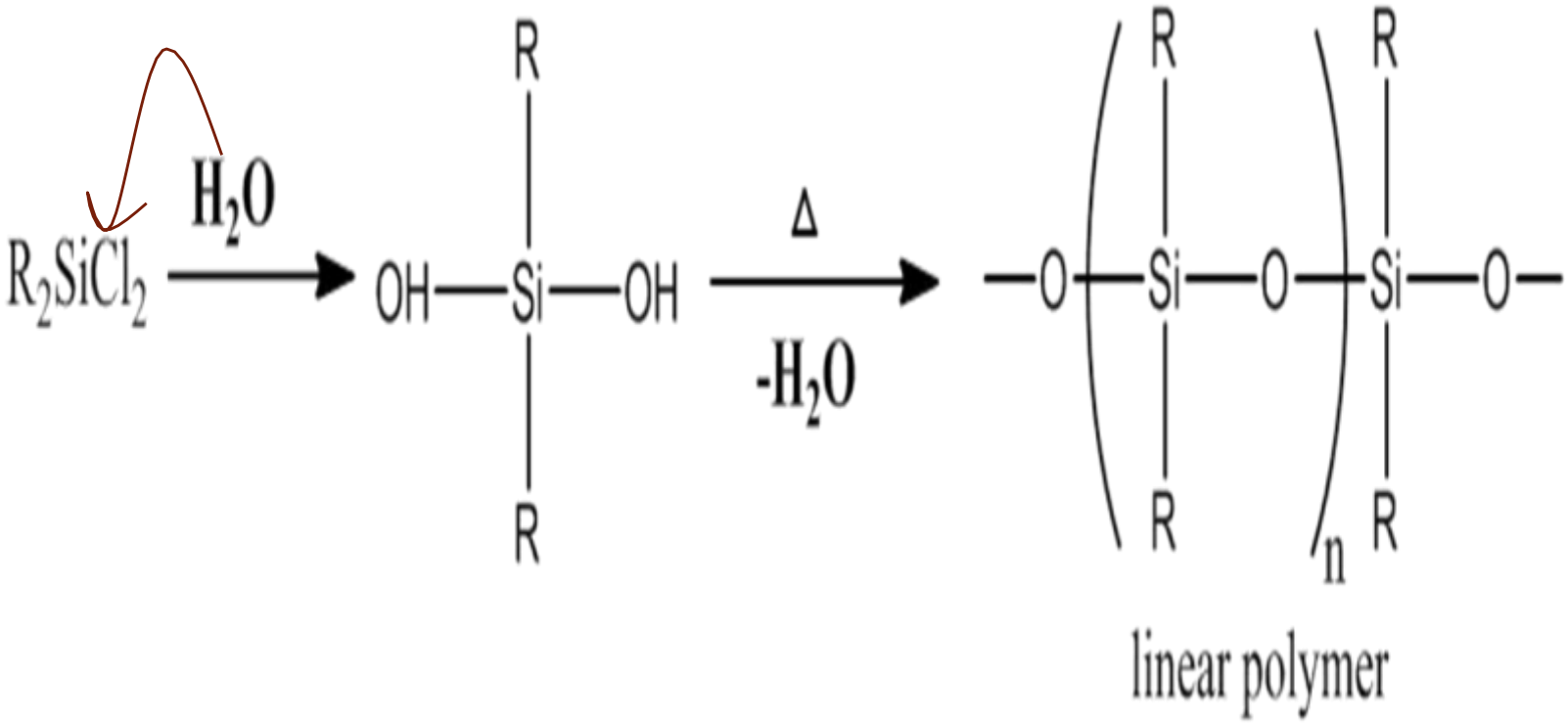


- When n = 3,



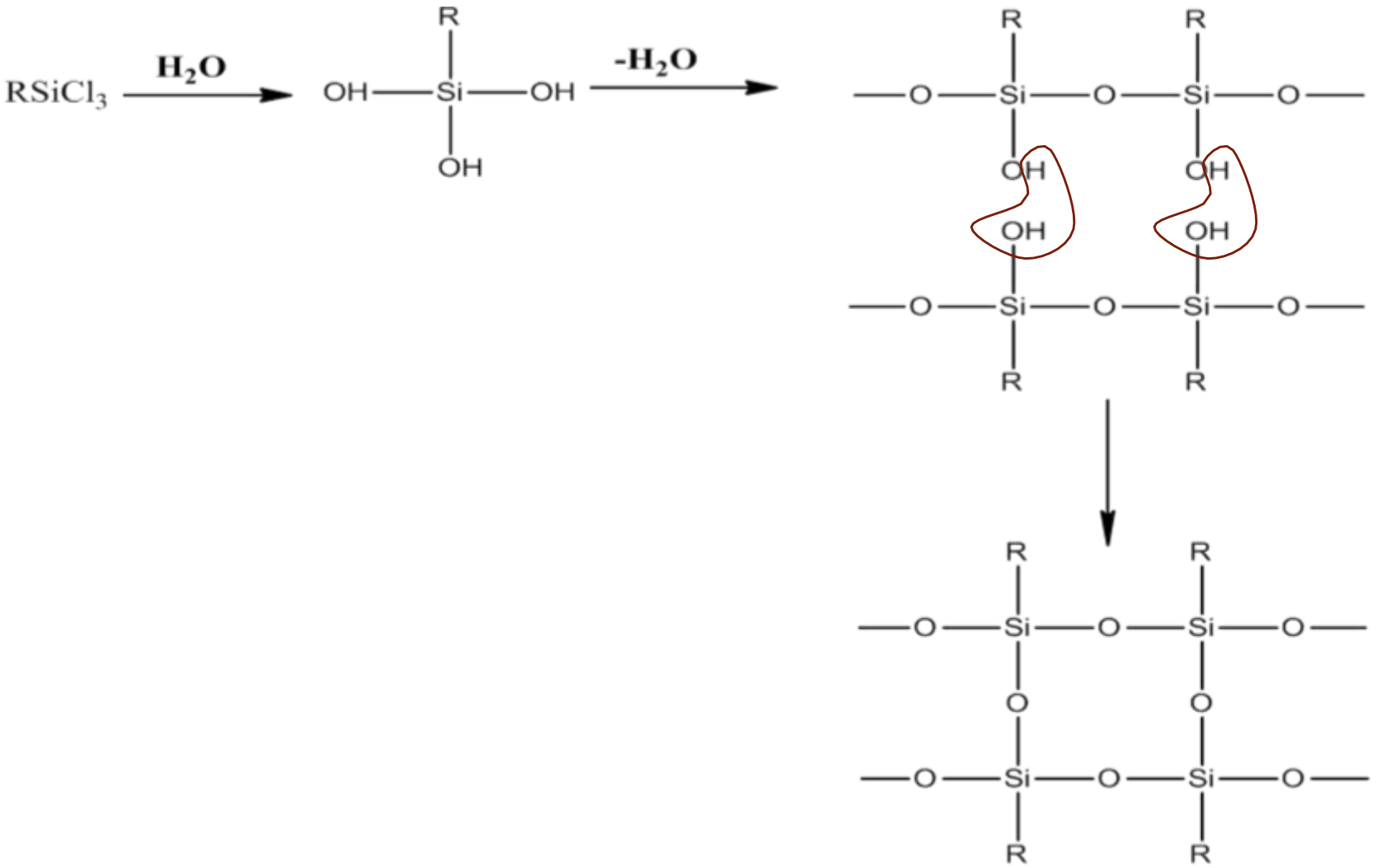
Here we get dimer of siloxane and by product HCl

- When n = 2,



Here we get linear polydimethylsiloxane and by product HCl

- When n = 1,



Here we get a crosslinked silicone polymer and by product HCl

Types of basic silicones

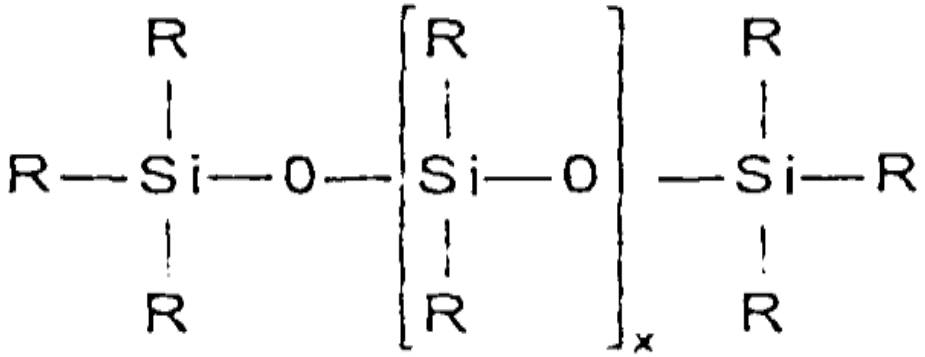
- **1. Silicone fluid**

- 2. Silicone resin

- 3. Silicone rubber

1. Silicone fluid

- Silicone fluids principally consist of chains of alternating silicon and oxygen atoms with two alkyl groups usually methyl groups, in special cases can also phenyl.
- General formula of silicone fluid :



PREPARATION

- Conversion of chlorosilanes involves three process:
  1. Hydrolysis
  2. condensation
  3. neutralisation (Hcl is used).

- Catalytic equilibration (to achieve a more linear polymer and also to stabilize viscosity by heating with catalyst such as HCl.)

- Devolatilization (volatile low molecular products are removed)

Properties of Silicone fluid

- HIGH ORDER OF THERMAL STABILITY :

  used as heat –exchange fluid in lab.

- WATER REPELLENCY:

  due to hydrophobic nature

- No color ,odour and low volatile in nature.
- Chemical resistance but are attracted by Conc. mineral acid and alkali.
- LUBRICATING and ANTI –ADHESION PROPERTY:

  used as electric grease and used in labs for lubricating stoppers and in high vacuum work.

Applications of Silicone fluid

- Used in laboratory for lubricating stoppers ,high vacuum work and in high temperature oppression.

- Used in laboratory as heat –exchange fluid.

- Used as electric grease for aircraft and car ignition system

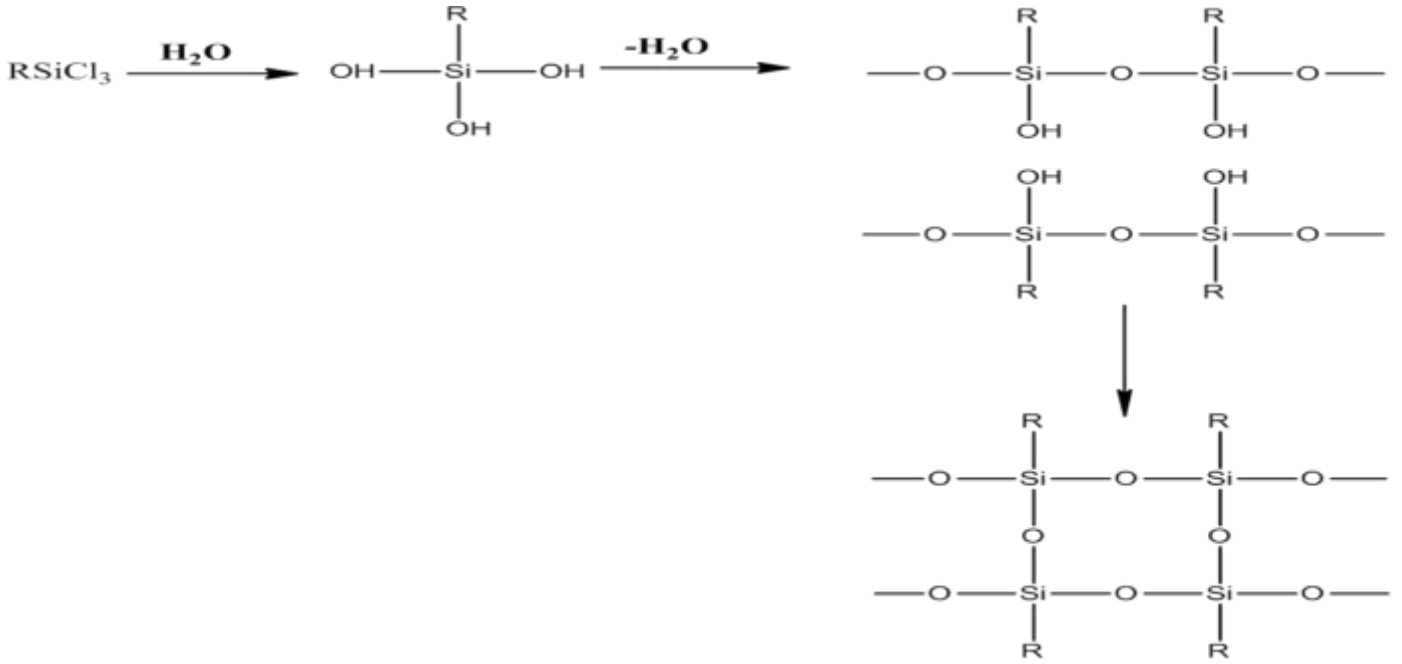
- Used as Hydraulic fluids in machinery where power is transferred.

- High molecular weight dimethyl silicone used in stationary phase in column chromatography.
- INSULATION and LAMINATION.

- Used as mould-release agent

2. Silicone resin

- Silicone resin is produced by hydrolysis of alkyl tri-chlorosilanes for the final product to be cross-linked.
- Cross-linking take place at elevated temp in presence of catalyst.

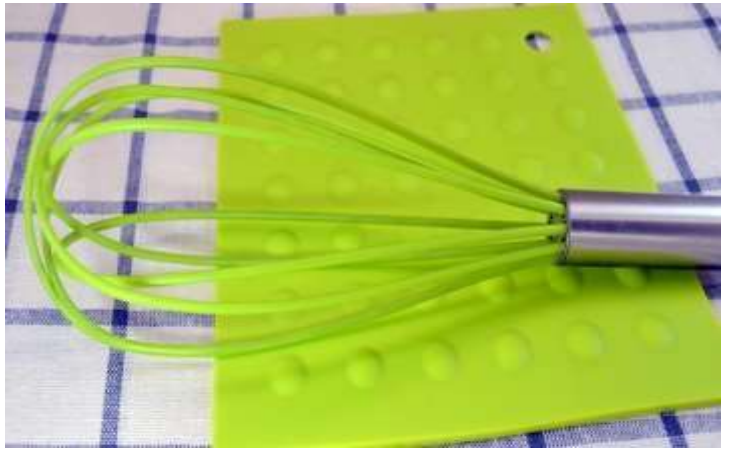


Properties of Silicone resin

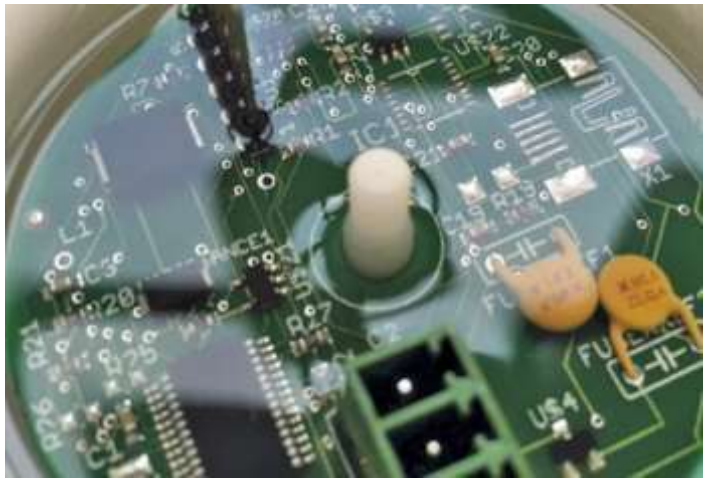
- **plastic.**
- **Highly water repellent**
- **Good insulator.**
- **High Flexibility and Low-temperature flexibility**
  - Good heat resistance but are mechanically much weaker than cross-linked organic
  - Silicone resins can resist temperatures up to +350 °C and have great oxidation resistance
  - Generally silicone glass cloth laminates are superior than PF & MF glass cloth laminates.

Applications of Silicone resin

- Used in cookware industry, particularly bakeware and kitchen utensils and as an insulator for heat resistance.



- Electronic components are sometimes encased in silicone to increase stability against mechanical and electrical shock

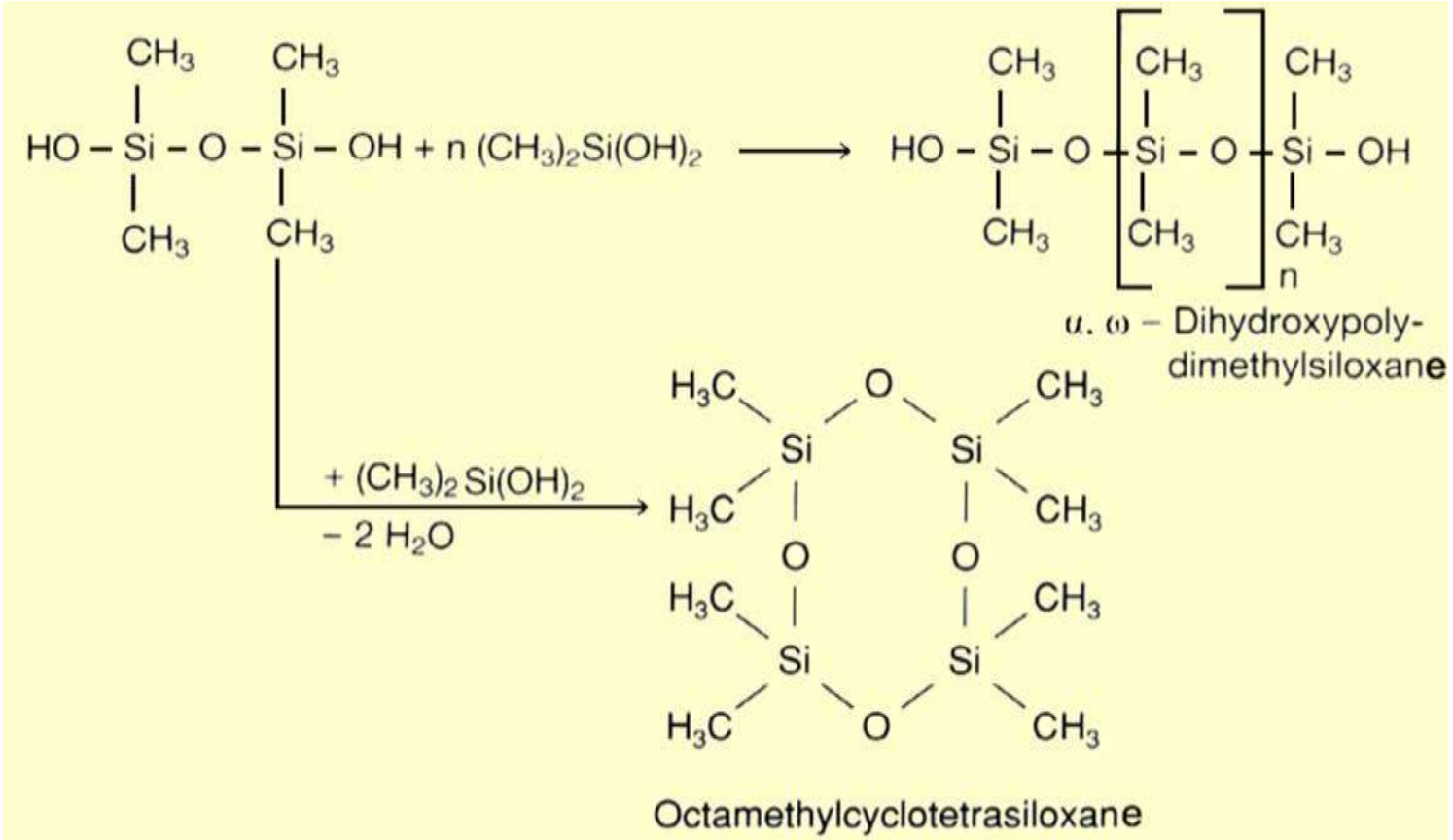


- Used in aircraft and automotive industry as sealants

3. Silicone rubber

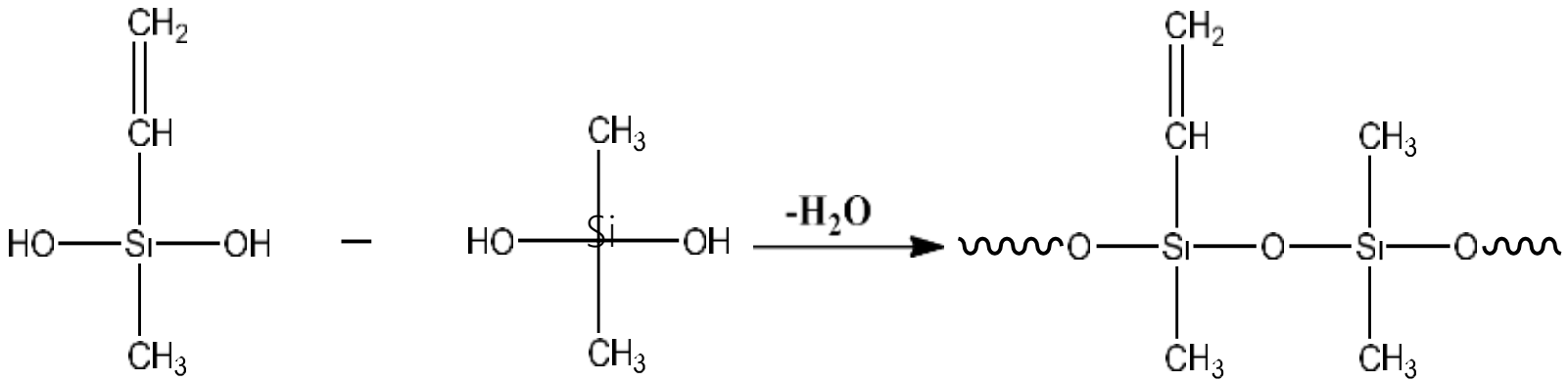
- Silicone rubber compound consist of long-chain polysiloxanes and various fillers, such as pyrogenic silica. They can be cured to form silicone elastomers.

- They are classified according to the curing method, the viscosity of the base polymer, and whether they cure at high or room temperature.

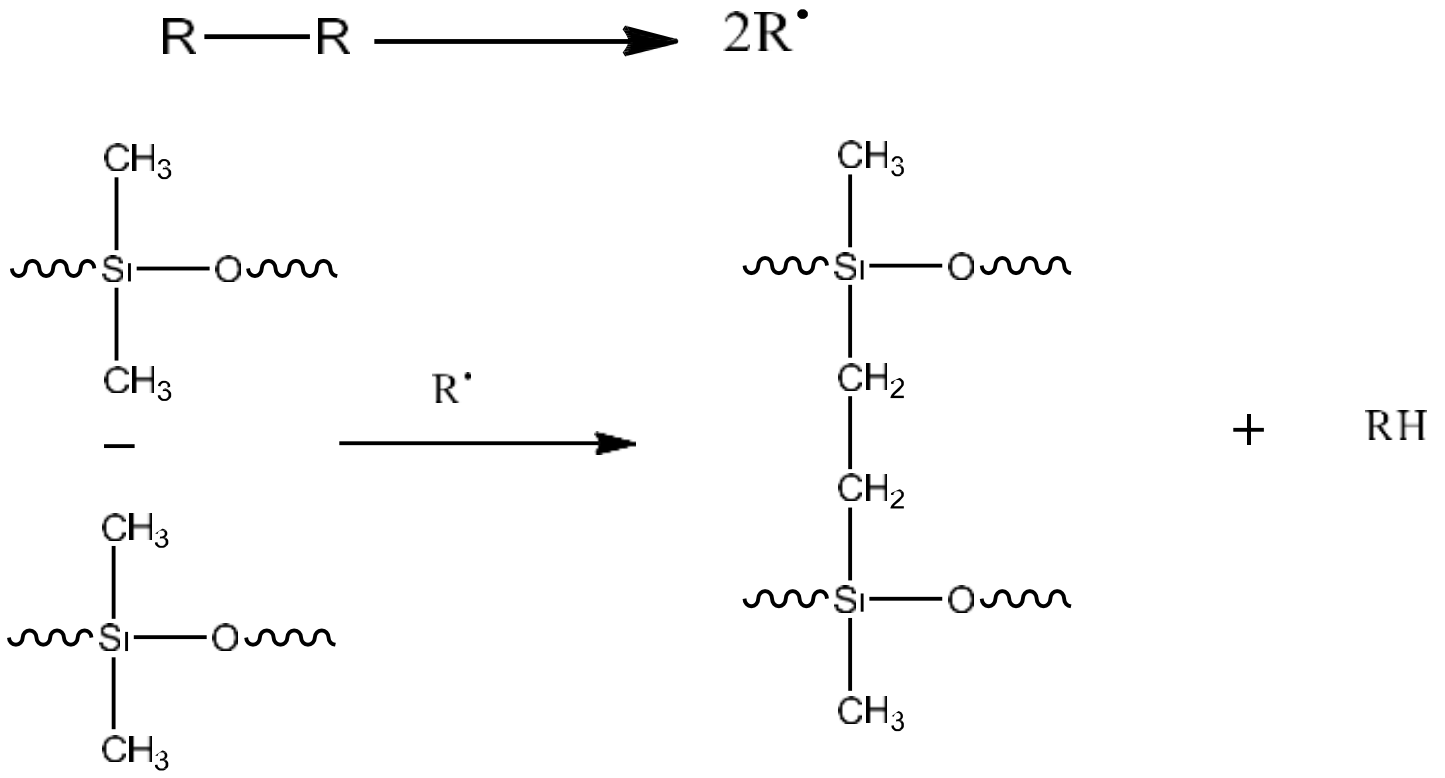

HO – Si – O – Si – OH + n (CH3)2Si(OH)2
α, ω – Dihydroxypoly-
dimethylsiloxane
+ (CH3)2 Si(OH)2
– 2 H2O
Octamethylcyclotetrasiloxane

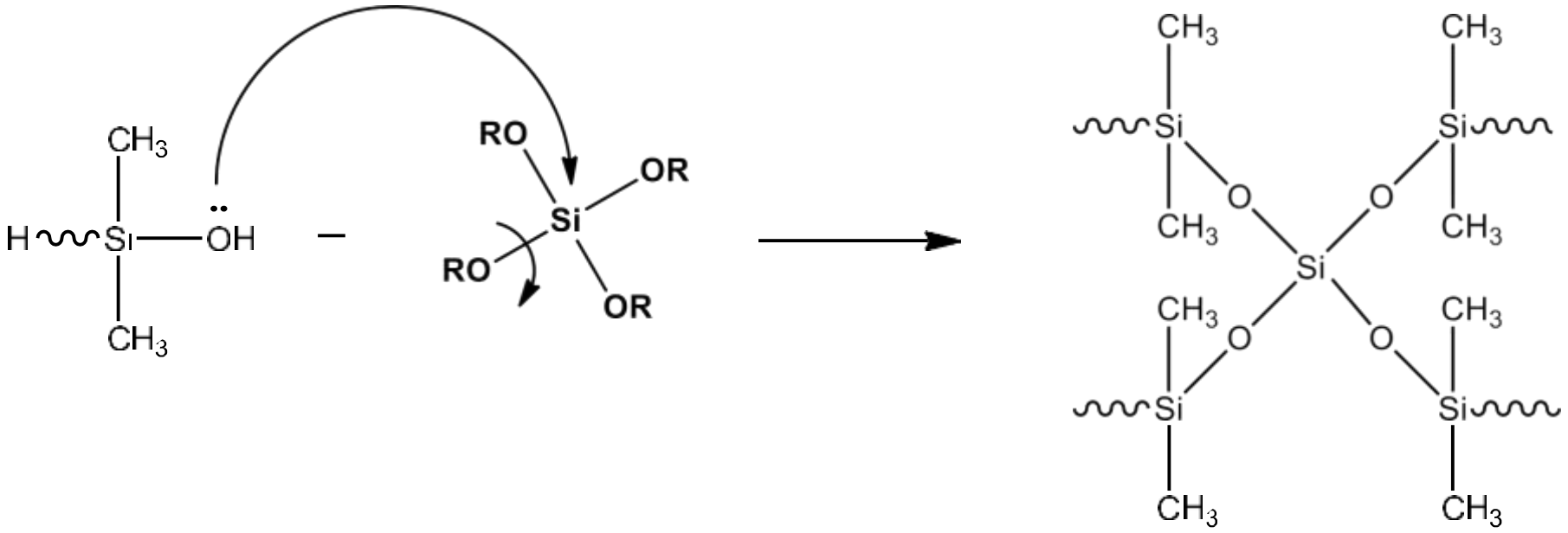
Cross-linking method

- Mixing of small amount of co-monomer containing vinyl group.



- Room temperature vulcanisation may tke place by following ways:
  - Radical formation




CH3
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CH3

Properties of Silicone rubber

- Good thermal stability, can operate from −100 to 300 °C
- Good UV resistance
- Highly inert and does not react with most chemicals
- Non toxic and can be used with food products and in medical applications
- Tensile strength is 11 N/mm^2
- Elongation at break is 100–1100% , which is great

Applications of Silicone rubber

- BIO-MEDICAL APPLICATION :

used in plastic surgery and cosmetic surgery and in pipes used for medical purpose.

- Used in cookware industry as ice cube trays, baby products, etc

- Used is day to day stuff like bands, mobile covers, keyboard protector ,etc