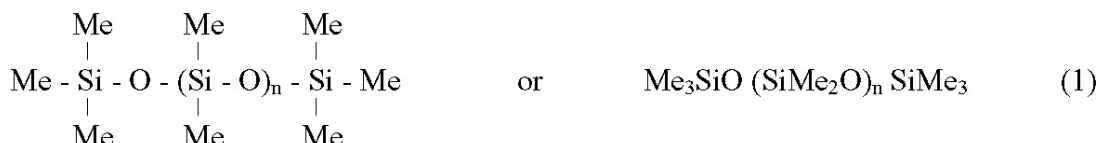


1. Introduction to Silicone Chemistry

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By analogy with ketones, the name “silicone” was given in 1901 by Kipping to describe new compounds of the brut formula R_2SiO . These were rapidly identified as being polymeric and actually corresponding to polydialkylsiloxanes. Among them, the most common are polydimethylsiloxanes (PDMS), trimethylsilyloxy terminated with the structure:

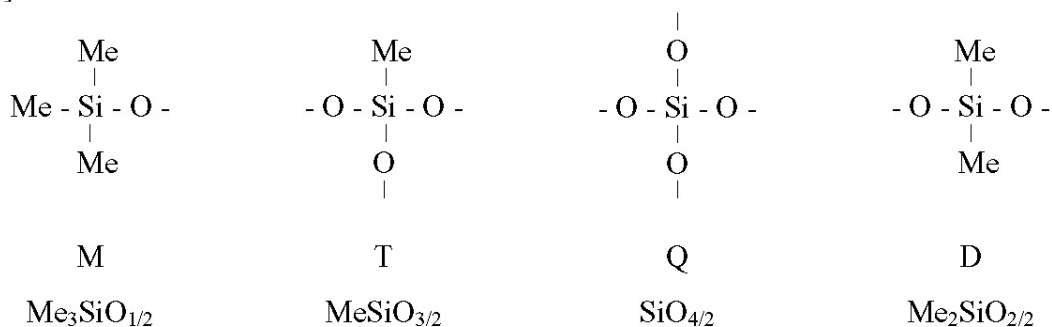


where $n = 0, 1, \dots$

The methyl groups along the chain can be substituted by many other groups (e.g., phenyl, vinyl or trifluoropropyl). The simultaneous presence of “organic” groups attached to an “inorganic” backbone gives silicones a combination of unique properties and allows their use in fields as different as aerospace (low and high temperature performance), electronics (electrical insulation), health care (excellent biocompatibility) or in the building industries (resistance to weathering).

Nomenclature

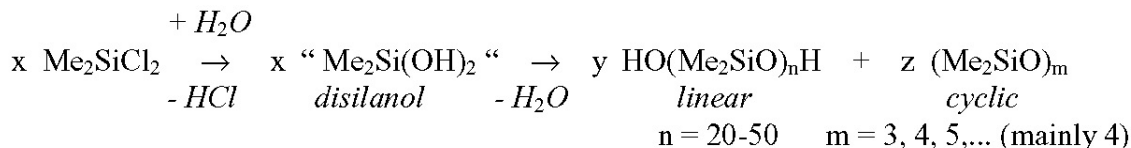
The main chain unit in PDMS, $-(\text{SiMe}_2\text{O})-$, is often shortened to the letter D because, as the silicon atom is connected with two oxygen atoms, this unit is capable of expanding within the polymer in two directions. In a similar way, M, T and Q units can be defined corresponding to [1]:



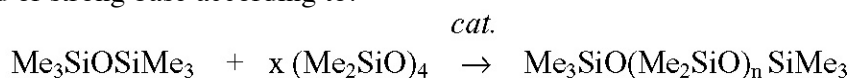
The above polymer (1) can also be described as MD_nM . This allows simplifying the description of various structures like $(\text{Me}_3\text{SiO})_4\text{Si}$ or tetrakis(trimethylsilyloxy)silane, which becomes M_4Q . Superscripts are sometimes used to indicate groups other than methyl (e.g., D^{H} for $\text{HMeSiO}_{2/2}$).



The synthesis of siloxanes has been described elsewhere [1, 2, 3]. In summary, PDMS is obtained from the hydrolysis of dimethyldichlorosilane Me_2SiCl_2 , which leads to a mixture of linear and cyclic oligomers:



Higher molecular weight PDMS is obtained after polymerisation, for example, of the above cyclics in the presence of an end-blocker such as hexamethyldisiloxane and catalysed by a strong acid or strong base according to:



Using other chlorosilanes, different end-blockers and/or different cyclics leads to many structures including polymers with various functional groups grafted on the polymer chain and/or at the polymer ends (e.g., vinyl, hydrogeno, phenyl, amino alkyl). These can be formulated into solvent-based, emulsion or solventless products.

Reactive polymers can be cross-linked into elastomers using:

- a peroxide-initiated reaction; in particular, if the silicone polymer carries some vinyl groups
- a condensation reaction; for example, between a hydroxy end-blocked PDMS and an alkoxy silane, in presence of tin salt or titanium alkoxide as catalyst
- an addition reaction; for example, between a vinyl-functional PDMS and an hydrogenomethyl dimethyl siloxane oligomer, in presence of an organic platinum complex

Such polymer, cross-linker and catalyst are formulated with various additives as one-part, ready-to-use products or two-part products to be mixed prior to use and to cure at room temperature or only at elevated temperatures.

Physicochemical Properties

The position of silicon, just under carbon in the periodic table, led to a belief in the existence of analogue compounds where silicon would replace carbon. Most of these analogue compounds do not exist, or if they do, they behave very differently. There are few similarities between Si-X bonds in silicones and C-X bonds [1-3]:

| <i>Element (X)</i> | <i>Bond length (Å)</i> | | <i>Ionic character (%)</i> | |
|--------------------|------------------------|--------------|----------------------------|--------------|
| | <i>Si - X</i> | <i>C - X</i> | <i>Si - X</i> | <i>C - X</i> |
| Si | 2.34 | 1.88 | -- | 12 |
| C | 1.88 | 1.54 | 12 | -- |
| H | 1.47 | 1.07 | 2 | 4 |
| O | 1.63 | 1.42 | 50 | 22 |



Between any given element and silicon, bond lengths are longer than for carbon with this element. The lower silicon electronegativity (1.8) vs. carbon (2.5) leads to a very polarised Si-O bond, highly ionic and with a large bond energy, 452 kJ/mole (108 kcal/mol). The Si-C bond has a bond energy of ± 318 kJ/mole (76 kcal/mol), slightly lower than a C-C bond, while the Si-Si bond is weak, 193 kJ/mole (46.4 kcal/mole). These values partially explain the stability of silicones; the Si-O bond is highly resistant to homolytic scission. On the other hand, heterolytic scissions are easy, as demonstrated by the re-equilibration reactions occurring during polymerisations catalysed by acids or bases. Silicon atoms do not form stable double or triple bonds of the type sp^2 or sp with other elements, yet the proximity of the d orbitals allows $d\pi-p\pi$ retro-coordination. Because of this retro-coordination, trialkylsilanols are more acid than the corresponding alcohols. Yet, the involvement of retro-coordination is challenged [4].

Another example of the difference between analogues is the tetravalent diphenyldisilanol, $(C_6H_5)_2Si(OH)_2$, which is stable, while its carbon equivalent, a gem-diol, dehydrates. The Si-H bond is weakly polarised, but here in the direction of a hydride, and is more reactive than the C-H bond. Overall, there are few similarities between a silicone polymer and a hydrocarbon polymer.

Silicones display the unusual combination of an inorganic chain similar to silicates and often associated with high surface energy but with side methyl groups that are, on the contrary, very organic and often associated with low surface energy [4]. The Si-O bond are strongly polarised and without protection should lead to strong intermolecular interactions. However, the methyl groups, only weakly interacting with each other, shield the main chain.

This is made easier by the high flexibility of the siloxane chain; rotation barriers are low, and the siloxane chain can adopt many conformations. Rotation energy around a CH_2-CH_2 bond in polyethylene is 13.8 kJ/mol but only 3.3 kJ/mol around a Me_2Si-O bond, corresponding to a nearly free rotation. The siloxane chain adopts a configuration that can be idealised by saying that the chain exposes a maximum number of methyl groups to the outside, while in hydrocarbon polymers, the relative backbone rigidity does not allow “selective” exposure of the most organic or hydrophobic methyl groups. Chain-to-chain interactions are low, and the distance between adjacent chains is also higher in silicones. Despite a very polar chain, silicones can be compared to paraffin, with a low critical surface tension of wetting [4]. Yet because of their low intermolecular forces, PDMS materials remain liquid in a much wider range of molecular weights and viscosities than hydrocarbons.

The surface activity of silicones is displayed in many circumstances [4]:

- Polydimethylsiloxanes have a low surface tension (20.4 mN/m) and are capable of wetting most surfaces. With the methyl groups pointing to the outside, this gives very hydrophobic films and a surface with good release properties, particularly if the film is cured after application. Silicone surface tension is also in the most promising range considered for biocompatible elastomers (20 to 30 mN/m).
- Silicones have a critical surface tension of wetting (24 mN/m), which is higher than their own surface tension. This means that silicones are capable of wetting themselves, a property that promotes good film formation and good surface covering.
- Silicone organic copolymers can be prepared with surfactant properties, with the silicone as the hydrophobic part (e.g., in silicone polyether copolymers).



The low intermolecular interactions in silicones have other consequences [4]:

- Glass transition temperatures are very low (e.g., 146 K for a polydimethylsiloxane compared to 200 K for polyisobutylene, the analogue hydrocarbon); cross-linked PDMS will be elastomeric at RT in the absence of any plasticizers.
- The presence of a high free volume compared to hydrocarbons explains the high solubility and high diffusion coefficient of gas into silicones. Silicones have a high permeability to oxygen, nitrogen and water vapour, even if in this case liquid water is not capable of wetting a silicone surface. As expected, silicone compressibility is also high.
- In silicone, the activation energy to the viscous movement is very low, and viscosity is less dependent on temperature compared to hydrocarbon polymers. Moreover, chain entanglements are involved at higher temperature and contribute to limit the viscosity reduction [4].

The presence of groups other than methyl along the chain allows modification of some of the above properties:

- A small percentage of phenyl groups along the chain perturbs sufficiently to reduce crystallisation and allows the polymer to remain flexible at very low temperatures. The phenyl groups also increase the refractive index.
- Trifluoropropyl groups along the chain change the solubility parameter of the polymer from 7.5 to 9.5 (cal/cm³)^{1/2}. These copolymers are used to prepare elastomers with little swelling in alkane or aromatic solvents.

Considering the above, many polymeric “architectures” can be prepared of different physical forms (volatile, liquid, viscoelastic, solid) with different functionalities, inert or capable of interacting or reacting with many other compounds. Formulation into convenient products leads to even more products. This explains the wide range of industries where silicones are used.



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