Inorganic polymer

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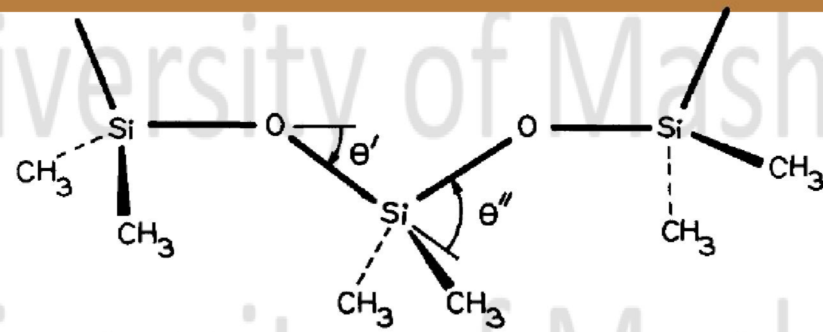
Structural Features



siloxane backbone is one of the most flexible in all of polymer.

The nature of the bonding

The Si-O (1.64 Å) > C-C (1.53 Å)

↓

steric interferences↓ and intramolecular congestion ↓

Oxygen skeletal atoms are unencumbered by side groups and they are as small as an atom can be and still have the di-valency needed to continue a chain structure.

Si-O-Si 143° > normal tetrahedral 110° → invert (little cost in energy)

Structural Features …

torsional rotations can occur without serious increases in energy

dynamic flexibility ↑ and *equilibrium flexibility* ↑

Elastomer Technology

Pure siloxane polymers are only rarely appropriate for use in technology

↓

Additives

reinforcing fillers, extending (non-reinforcing) fillers, processing aids, heat-aging additives, pigments, and curing agents (for example, end-linking agents with associated catalysts, or organic peroxides).

high surface area silica → by the fume process

↓

electrical insulation properties ← greatest reinforcement

Carbon black → reinforcement → interfere with some types of peroxide cures

Elastomer Technology …

silane coupling agents are used to improve the bonding between the reinforcing phase and the polymer

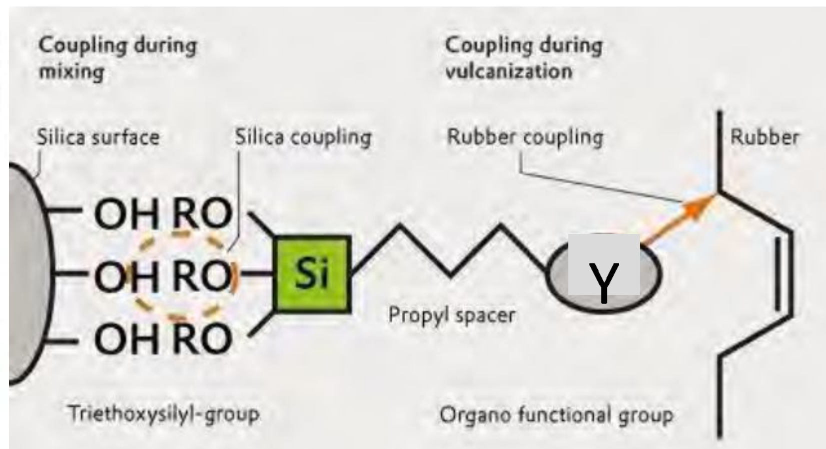
silane coupling agents : X_3SiY,

X : alkoxy group → hydrolyze → react with OH groups (surface of a filler)

Y : vinyl group → polymerized → reinforced

Amino-silanes couple fiberglass to phenolic or urea-formaldehyde resins

Vinylsilanes are used in PE and EPDM insulated wire and cable



extending (non-reinforcing) fillers

↓

reduce the cost of the compounded elastomer

kaolin, diatomaceous earth, minerals such as calcium carbonate.

Coloring agents → organic or inorganic

inorganic colorants: oxides and salts of iron, chromium, cobalt, titanium, and cadmium

Processing aids: These fillers adsorb polymer chains so strongly to their surfaces that premature gelation can occur.

softening or plasticizing effect

curing (cross-linking) agents

↓

depends on the particular chemical reaction chosen for generating the cross-links

end-linking reactions → hydroxyl or vinyl units

oligomeric siloxane (reactive Si-H groups)

Tetraethoxysilane (TEOS) $[Si(OC_2H_5)_4]$

Aliphatic or aromatic peroxide

↓

reactions with vinyl side chains or even saturated alkyl groups.

bis(2,4-dichlorobenzoyl)peroxide, benzoyl peroxide, dicumyl peroxide, and di-t-butyl peroxide

Infrared and ultraviolet → determine the composition of siloxane copolymers

- vinyl groups introduced to facilitate cross-linking
- phenyl groups to suppress crystallization or to improve radiation resistance

-silanol end groups introduced during polymerization and used to determine number-average molecular weights, or for chemical reactions such as end linking.

Si-O-Si	1010 cm^{-1}
$Si(CH_3)_2$	800 cm^{-1}
$SiCH_3$	1260 cm^{-1}
Si-H	2200 cm^{-1}

Nuclear magnetic resonance (NMR)

Small-molecule characterization
^{1}H and ^{13}C NMR, ^{29}Si NMR

Characterize chemical composition, structural features, and conformational preferences, hybrid inorganic composites and silica-type ceramics

Chemical methods

chloride ions determination → silver salts titration
Si-H groups → hydrogen gas

Mass spectrometry
Gas chromatography
Liquid chromatography and
Gel permeation chromatography (GPC)

Average molecular weights :
dilute solution viscometry, osmometry, ultracentrifugation, light scattering intensity measurements

Molecular weight distributions :
fractional precipitations, gradient elutions, super-critical fluids

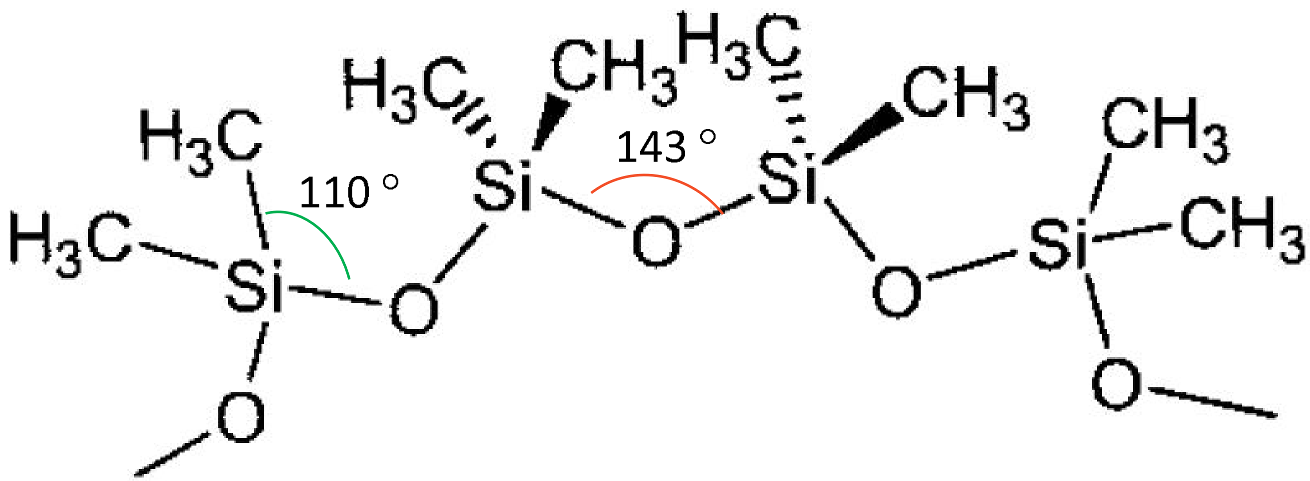
Transition temperatures, measurements of heats of fusion :

Differential thermal analysis (DTA)
Differential scanning calorimetry (DSC)
Thermogravimetric analysis (TGA) → Thermal stability

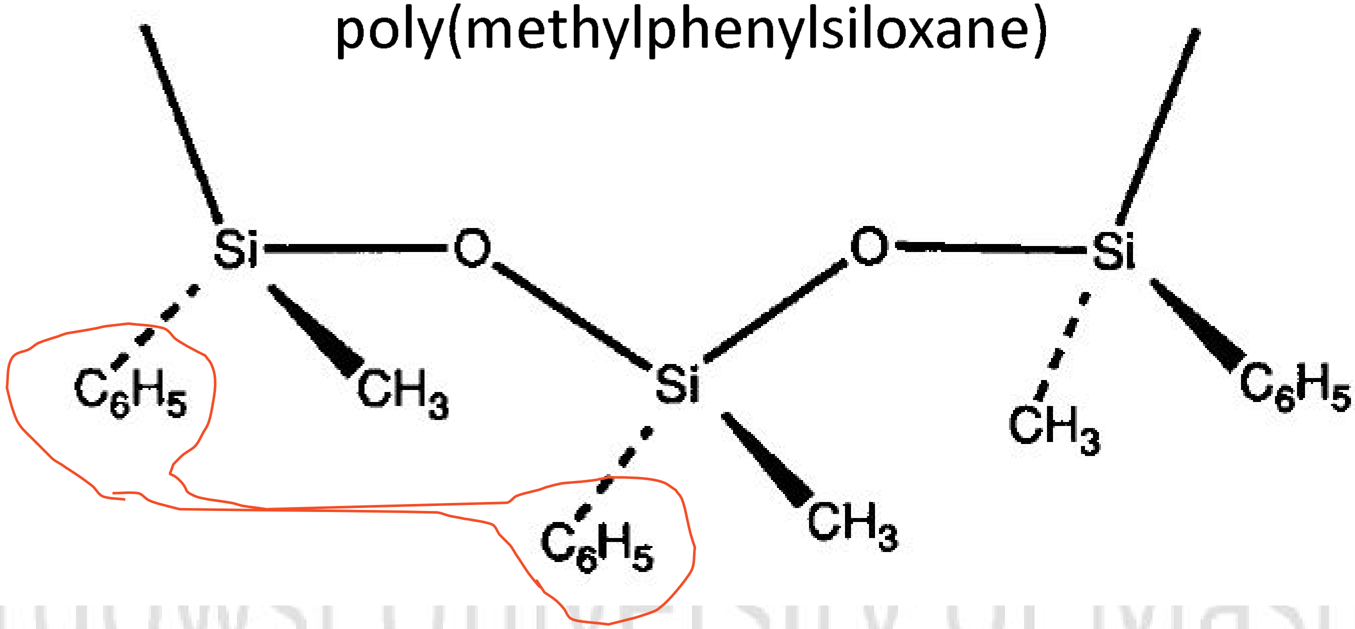
Conformations and Spatial Configurations

all-*trans*

dynamic flexibility



poly(methylphenylsiloxane)



Flexibility of the Polymer Chains

Equilibrium Flexibility → effect on the T_m

High flexibility

↓

high conformational randomness in the amorphous state

↓

high entropy of fusion

↓

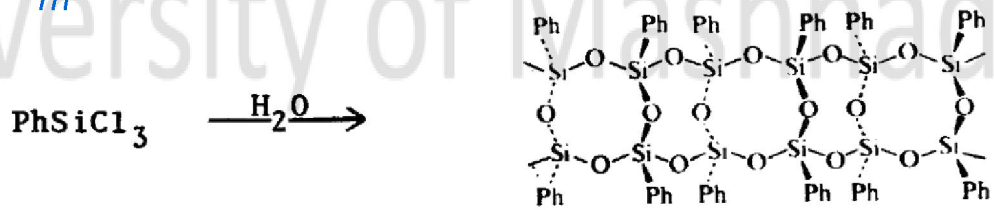
low melting point

polysiloxane elastomers → too low melting points

Increase T_m → increase rigidity (less flexible)

The basic point is to decrease the entropy of fusion and thus increase the melting point T_m

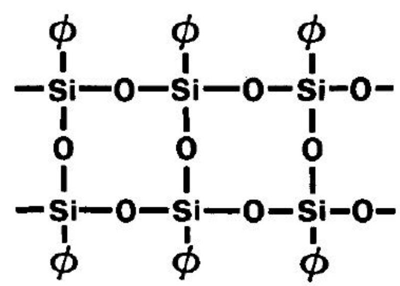
ladder structure



increased glass-transition temperature T_g

Cross-linking

Bulky side group (phenylene)



Flexibility of the Polymer Chains

Dynamic Flexibility → *change spatial arrangements by rotations around its skeletal bonds*

High flexibility

↓

the more it can be cooled before the chains lose their flexibility

↓

bulk material becomes glassy

↓

low T_g

low values of T_g *can be advantageous, particularly* in the case of fluids and elastomers

Permeability

Siloxane polymers have much higher permeability to gases than most other elastomeric materials → gas separation membranes

Stability, Safety Aspects, and Environmental Impact

Stability : the chain is already in a high oxidation state

Environmental : degradation can occur in water, in air, and particularly in the soil.

atomic oxygen→ UV light →hydroxyl radicals

Applications

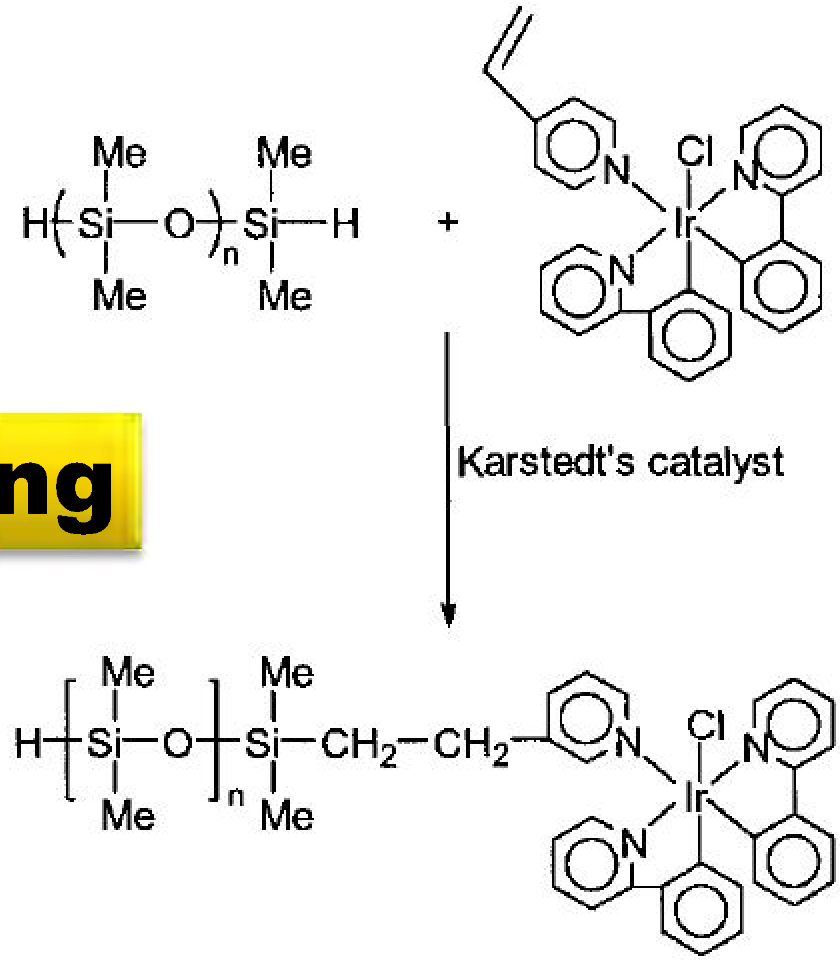
Medical:

Lenses, drug-delivery, tubing, catheters

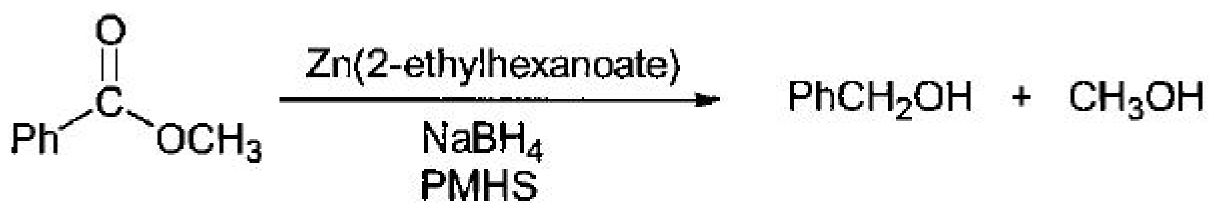
Non-Medical:

high-performance elastomers, membranes, electrical insulators, water repellents, anti-foaming agents, mold-release agents, adhesives, protective coatings,368 release control agents for agricultural chemicals, encapsulation media, mold-making materials, coatings, layers in high-tech laminates, and hydraulic, heat transfer, and dielectric fluids

Anchoring



Karstedt's catalyst = Pt(0)-tetramethyldisiloxane complex


O
C
Ph
OCH3
Zn(2-ethylhexanoate)
NaBH4
PMHS
PhCH2OH + CH3OH