2. The temperature-dependent variation in the colour of cholesteric liquid crystals had led to the use of these substances in the measurement of temperature and temperature gradients.

3. Cholesteric liquid-crystal substances, when applied to the surface of the skin, have been used to locate the veins, arteries, infections, tumours, and the fetal placenta, which are warmer than the surrounding tissues.

4. Nematic liquid crystals are useful research tools in the application of magnetic resonance. Molecules that are dissolved in nematic liquid crystal solvents give a highly resolved nmr spectrum.

5. Some liquid crystals have been used in chromatographic separations, as solvents to direct the course of chemical reactions and to study molecular rearrangement and kinetics.

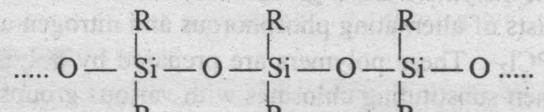
6. Oscillographic and TV displays using liquid crystals screens are also being developed. Other applications include radiation and pressure sensors, optical switches and shutters, etc. Polymers that form the intermediate phase are important in the fabrication of light weight, ultra-high-strength and temperature resistant fibres.

16.2 INORGANIC POLYMERS

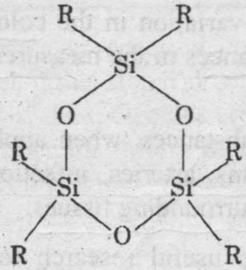
Polymers are the substances formed by combining together a large number of small molecules. The small molecules which are used to form polymer are called *monomers*. Polystyrene, polyproplyene, polyvinyl chloride etc. are typical examples of polymers. All these polymers have backbone of carbon atoms and are organic in nature. Most of the organic polymers tend to become brittle when cold and deteriorate on heating. Moreover they tend to be flammable and swell in organic solvents. These problems are minimized with the development and synthesis of inorganic polymers whose backbone consist of atoms other than carbon. Following are the important types of inorganic polymers along with their properties and uses.

1. Silicones

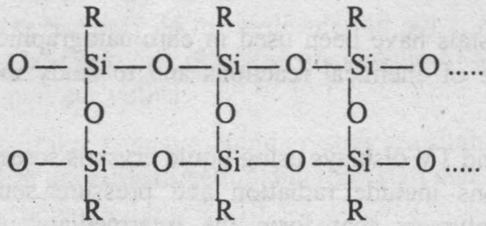
Silicones are synthetic polymerized organo-silicon polymers containing –Si–O–Si–O–Si– linkages along with –C–C–C– linkages present as the side chains. The silicones may be linear, cyclic or cross-linked as shown below.



Linear silicon



Cyclic silicone



Cross-lined silicone

Here R stands for CH_3, C_2H_5 or C_6H_5 groups

Silicones are obtained by the hydrolysis and subsequent condensation of dialkyl or diaryl substituted silicon chloride, R_2SiCl_2. The Si–OH bonds subsequently expel water and form Si–O–Si linkages. The lower silicones are oily liquids, but the higher members containing long chains or ring structures are waxy and rubbery solids. They are remarkably stable towards heat and chemical reagents. They are not wetted by water and are non-toxic and chemically inert.

Silicones are present in the form of oils, greases or rubbers. They are highly stable and non-volatile even on heating. They are, therefore, used in high temperature oil baths, high vacuum pumps, paints, vaseline greases, polishes, water proofing treatments for fabrics and leather. They are also used as insulating materials for electric motors and other electric appliances, since they can withstand high temperature without charring.

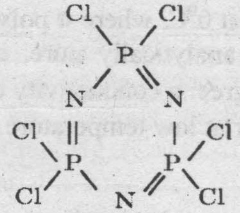
2. Phosphazenes

The phosphazene polymers are a group of cyclic or linear compounds in which the polymer backbone consists of alternating phosphorous and nitrogen atoms. The repeat unit in these polymers is $-N{=}PCl_2-$. These polymers are prepared by polymerizing the ring shaped trimmer $(PNCl_2)_3$ and then substituting chlorines with various groups. The trimer $(PNCl_2)_3$ is obtained by treating PCl_5 with NH_4Cl at 146°C.

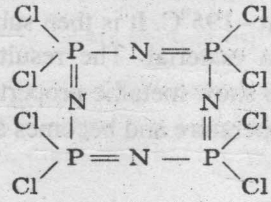
$$NH_4Cl + PCl_5 \xrightarrow[\text{refluxing } Cl_2HCCHCl_2]{146^0C} (NPCl_2)_n$$

The major product and the easiest to separate is the trimer, n=3. Smaller amounts of tetramer and other oligomers up to n=8 have been characterized and higher polymers exist.

$$[PNCl_2]_3 \xrightarrow{\Delta} [PNCl_2]_x$$

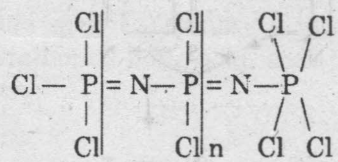


Trimer



Tetramer

Higher cyclic polymers have been characterized but none studied so extensively as the trimer and tetramer. Linear polymers are also known. If excess PCl_5 is used in the preparation, it is possible to isolate the linear polymers of the type:



Analogous bromo compounds may be prepared in the same manner except that bromine should be added to suppress the decomposition of PBr_5.

$$PBr_5 \longrightarrow PBr_3 + Br_2$$

$$PBr_5 + NH_4Br \xrightarrow[Br_2]{excess} [NPBr_2]_n$$

The phosphazene polymers are generally non-flammable. Some of them are glasses and others are elastomers. Their elasticity is more than natural rubber. They retain their elasticity even at low temperatures. They are used to replace blood vessels because they do not react with living tissues. They are also used as crystals, in silicone manufacture and in flame-proofing fabrics.

3. Polymeric Sulphur Nitride

Polymeric sulphur nitride (also called polythiazyl) is an important inorganic polymer which is composed of atoms of two non-metals, i.e., sulphur and nitrogen. This polymer is prepared from tetrasulphur tetranitride.

$$S_4N_4 \xrightarrow{Ag} S_2N_2 \longrightarrow (SN)n$$

Tetrasulphur tetranitride (S_4N_4) is bright orange solid insoluble in water but soluble in organic solvents. Although the crystals are reasonably stable to attack by air, they are explosively sensitive to shock or friction. The ammonolysis of sulphur monochloride (S_2Cl_2) either in solution in an inert solvent or heated over solid ammonium chloride, yields tetrasulphur tetranitride:

$$6S_2Cl_2 \xrightarrow[CCl_4]{NH_3} S_4N_4 + S_8 + 12NH_4Cl$$

The S_4N_4 is pumped in a vacuum line over silver wool at 220°C, and S_2N_2 is collected on a cold finger at −195°C. It is then sublimed to a trap at 0°C, where it polymerizes slowly to a lustrous golden material. The resulting product is analytically pure, and this purity is necessary for it to show metallic properties to a high degree: a conductivity of 2.5×10^3 ohm^{-1} cm^{-1} at room temperature and becomes a superconductor at low temperature.

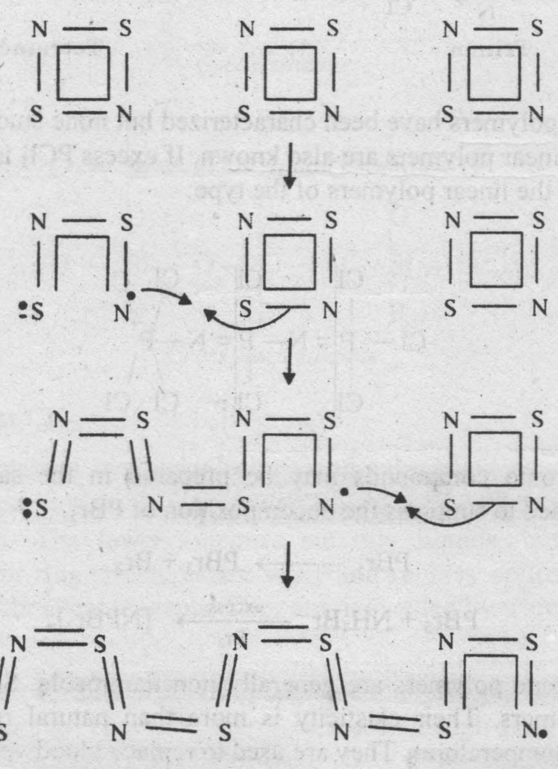


Fig. 16.2. Polymerization of S_2N_2 to form (SN)n chains

16.3 ENGINEERING CERAMICS

Ceramics comprises all engineering materials or products that are inorganic except metals and alloys and are usually rendered serviceable through high temperature processing. Ceramics has also been defined as the field of high temperature technology, because usually either in the manufacture or in the application and use of ceramic materials high temperatures are involved. The important products of ceramic industries are building bricks and tiles, sewer pipes, drain tiles, refractory bricks of all kinds, electrical and chemical porcelain and stoneware, whiteware, china, floor and wall tiles, enamels and abrasives and insulators in spark plugs.

The ceramic materials which might be used in place of other engineering materials such as metals, wools or plastics, are termed as *engineering ceramics*. These materials withstand high temperatures, resist greater pressures, have superior mechanical properties and can protect against corrosive chemicals.