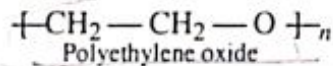
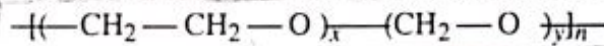


and reptation motions. This movement will allow an ion to transfer from a coordination site on one polymer to a similar site on another. Hence, a cation, for example, will be passed towards the cathode from one polymer molecule to another in a hand-to-hand fashion. Free-volume effects must also be important in ion transport to provide a pathway through which ions can diffuse.

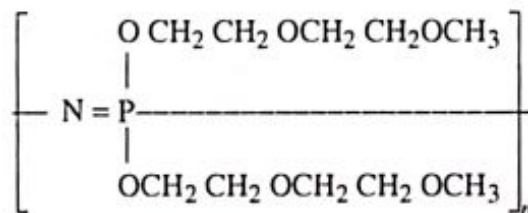
Host polymers for solid Electrolytes : Poly (ethylene oxide) was the first polymer studied for this purpose. Oxygen atoms in the polymer molecules are the donor sites that coordinate to alkali metal cations. Thus coordination of the polymer to one of the ions brings about ion separation, and the solid becomes an ionic conductor.



A defect of poly (ethylene oxide) as a solid electrolyte host is its partial crystallinity. Ion transport occurs in the amorphous regions only, and systems based on this polymer must be heated to 70 to 100°C before melting occurs and the maximum conductivity can be obtained. A non-crystalline copolymer that contains both ethylene oxy and methylene oxy chain units can also be used.



Poly [bis (methoxy ethoxy ethoxy) phosphazene], 'MEEP' has been synthesized to function as solvating polymer



It has a low glass transition (-84°C), is completely amorphous, dissolves in organic solvents such as tetrahydrofuran that are also solvents for salts such as lithium triflate, LiOS(O)OCF₃ and it bears a high concentration of alkyl ether units in the side chains.

Salts : The salts used in solid polymeric electrolytes must have a low crystal lattice energy. Otherwise, ion pairing and crystal forces will predominate over solvation by the polymer and ion-pair separation. This is the reason why bulky anions, such as triflate are often used. The concentration of salt in the polymer has a great effect on the conductivity behaviour. At low salt concentrations the conductivity is low because, although the ion pairs are well separated, they are few in number. As the salt concentration is raised, the conductivity rises.

Application : Ion-polymer solid electrolyte systems may be used in light weight, high-energy batteries. Rechargeable lithium cells based on polymeric systems should be able to store two to five times as much energy per unit weight and volume as a conventional lead-acid car battery.

Other proposed applications include electrochromic displays, electrochromic windows, solid-state photo electrochromic cells, sensors etc.

5.10.1.2. Electronic conducting materials in non-conducting polymers ; The conversion of electrically insulating polymers to conducting materials by pyrolysis to graphite or by the incorporation of graphite powder or metal particles into a polymer structure has been an aspect of polymer technology for many years. Materials such as pyrolyzed polyacrylonitrile or pyrolyzed polyesters have electrical conductivities in the semiconductor range. The incorporation of particles or metals into a polymer matrix also provides a reasonable high electrical conductivity. The electronic conductivity depends on contact between the conducting particles. Hence high loadings of the conducting material are usually needed.

Electrically conducting composite materials are used as antistatic coating and packaging materials; electrodes and in a variety of devices used in the electrical engineering industry.

5.10.1.3. Electronically conducting polymers : Some examples of this type of polymers are : Poly (sulphur nitride), polyacetylene, poly phenylene, poly (phenylene sulphide), polypyrrole, polythiophene, polyaniline and transition metal-bound polymers.

These polymers in solid state provide pathways for electronic conduction. Electrons migrate along the polymer chain and jump from chain to chain. The process, in polymers is generally due to the presence of arrays of conjugated delocalized double bonds.

Such polymers can be used as light weight and easily fabricated replacements for semiconductor chips and integrated circuits, light weight wiring, electrode materials in fuel cells and batteries and components in a wide variety of optoelectronic devices.

Theory : Let us consider a simple diatomic molecule derived from two identical atoms that have only one electron available for bonding. Due to bond formation, two new energy levels are generated—bonding orbitals, occupied by two electrons, and an unoccupied antibonding orbital.

Bond formation in more complex molecules follows the same principle. As each bond is formed an additional bonding and anti-bonding level is added to the overall electronic structure. Thus, the larger the number of atoms that are linked together in a molecule, the greater will be the number of bonding and antibonding orbitals. In a polymer molecule, thousands or millions of atoms are involved and the number of molecular orbitals becomes correspondingly large and form a set of closely spaced energy levels. This set is known as a bonding band or 'valence band'. The term 'band' is used because the energy levels are so closely spaced that for all practical purposes they form an energy continuum within which electrons can exchange places and are free to wander throughout the material. A similar band formation occurs with the antibonding orbitals which are termed as conduction band. The two bands are usually separated by an energy gap known as the "band-gap".

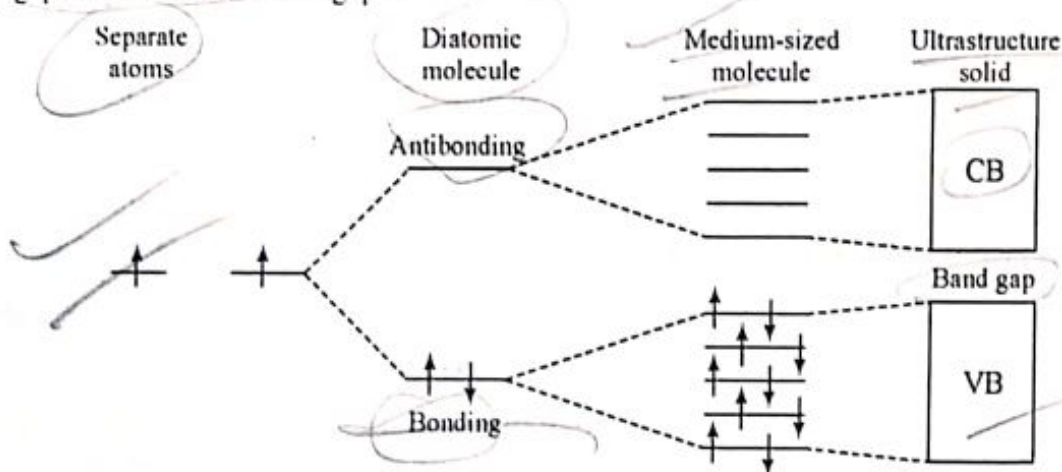


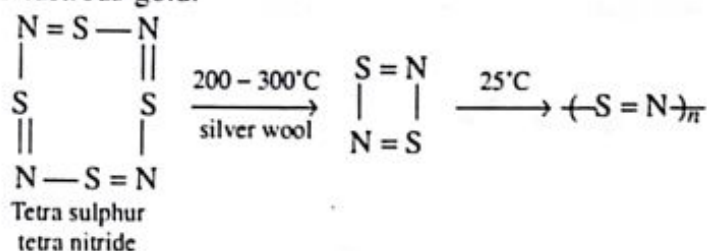
Fig. 2. Progression from atomic orbitals in two isolated atoms, through the formation of a bonding orbital in a simple diatomic molecule, and the generation of several bonding orbitals in a medium-sized molecule

1. Examples of Electronically Conducting Polymers :

1. Poly (sulphur nitride) (Polythiazyl), $(SN)_x$: It is prepared by a sequence of reactions that start from cyclic tetra sulphur tetra nitride, which itself is prepared from elemental sulphur and liquid NH_3 or from SF_4 and NH_3 or more commonly by the reaction of S_2Cl_2 with NH_3 . The cyclic tetramer is an orange-yellow, crystalline solid m.p. $178^\circ C$. It can explode if stored as a solid.

When heated to the sublimation temperature ($85^\circ C$) in vacuum and when the vapour is passed through heated silver wool at $200-300^\circ C$, the cyclic tetramer is converted to the potentially explosive cyclic dimer which is condensed as a white solid. The cyclic dimer is then purified by vacuum sublimation to form colourless crystals.

A solid-state polymerisation of the cyclic dimer then occurs at 25°C during 3 days, followed by heating in vacuum at 75°C for 2 hours. During polymerisation the crystals changes from colourless to blue-black and then to lustrous gold.



Crystals of (SN)_n have a parallel fibrous structure. The crystals are soft and malleable. Its gold colour constitutes a metallic-type reflectance.

Great interest has been shown in this polymer because of its metal-level electrical conductivity at room temperature. This conductivity (3 × 10³ Ω⁻¹ cm⁻¹) is only slightly lower than that of mercury, nichrome or bismuth (1 × 10⁴ Ω⁻¹ cm⁻¹). When cooled to 0.3K, the material undergoes a change to a superconductor, at which point there is no resistance to electrical flow.

The electrical conductivity of the polymer can be explained in terms of its structure. The packing of the chains is shown in the figure 3.

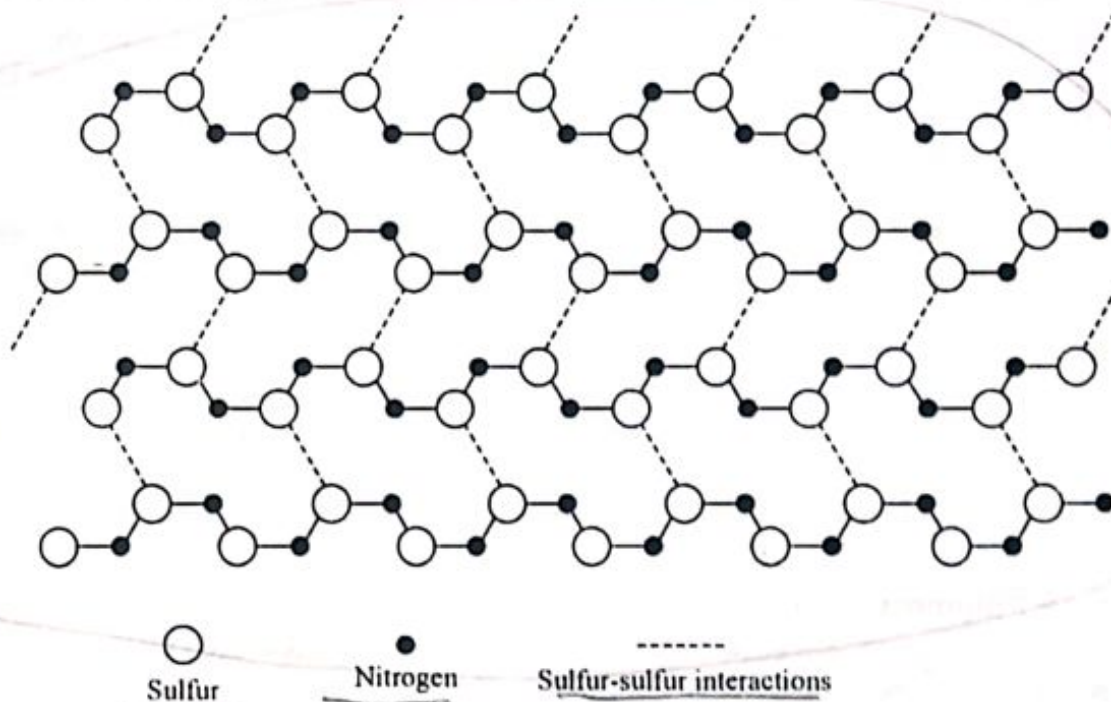


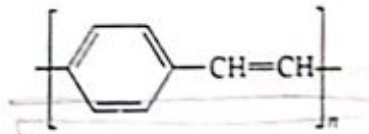
Fig. 3. Packing of the (SN)_n chains in a crystalline matrix

Individual chains occupy a cis-trans-planar conformation, with S—N bond lengths intermediate between those of single and double bonds. This suggests that a delocalised bonding arrangement exists along the chain via delocalised, half-filled π-orbitals, and this would permit the existence of a metallic conduction band. The interchain packing is such that electronic transmission could occur via orbital overlaps between S—S, N—N or S—N pairs on adjacent chains. This would produce a system of pockets of electrons.

Brominated derivatives of (SN)_x are formed when the polymer is exposed to bromine vapour. A black polymer of composition (SNBr_{0.4})_x is formed. This retains the fibrous structure of (SN)_x and also shows increased electrical conductivity.

oligophenylene is low ($10^{-14} \Omega^{-1} \text{ cm}^{-1}$), but doping with AsF_5 raises the conductivity into the range of $5 \times 10^2 \Omega^{-1} \text{ cm}^{-1}$.

Poly (para-phenylene vinylene)



This polymer is also found to be electrical conducting, showing conductivities in the range of 5×10^2 to $3 \times 10^3 \Omega^{-1} \text{ cm}^{-1}$ when doped with AsF_5 or iodine.

5.10.2. Fire Retardant

A fire retardant is a substance that helps to delay or prevent combustion. Fire retardants are commonly used in fire fighting.

How do fire retardants work ?

In general, fire retardants reduce the flammability of material by either blocking the fire physically or by initiating a chemical reaction that stops the fire.

Physical

There are several ways in which the combustion process can be retarded by physical action :

- (i) **By cooling** : Some chemical reactions actually cool the material down.
- (ii) **By forming a protective layer** : This protects the remaining material.
- (iii) **By dilution** : Some retardants release water and/or carbon dioxide while burning. This may dilute the radicals in the flame enough for it go out.

Chemical

(1) **Reaction in gas phase** : Chemical reaction in the flame (i.e., gas phases) can be interrupted by fire retardants. Generally, this class of retardants uses halogens such as bromine or chlorine.

Brominated flame retardants are major chemical flame retardant. They are applied to prevent electronics, clothes and furniture from taking fire.

Since most polymers are inherently inflammable, this is an important aspect of polymer technology. Flame involves free radical processes and so species which produce halogen atom, particularly bromine atom, are good flame retardants.

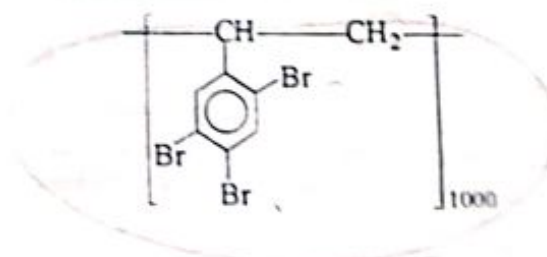
(2) **Reaction in solid phase** : This kind of flame retardant works by breaking down the plastic polymer so it melts and flow away from the flame.

(3) **Char formation** : Solid phase flame retardants are those which cause a layer of carbon char to form on the surface. This carbon char layer is much harder to burn and prevent further burning.

(4) **Intumescent** : This type of retardant materials add chemicals which cause swelling up behling the protective char layer to swell, providing much better insulation.

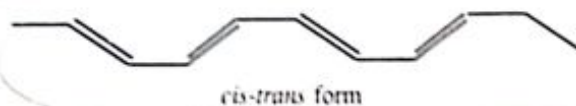
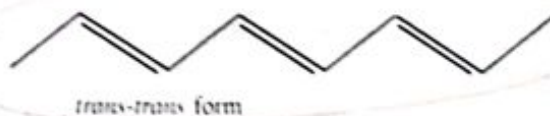
(A) Brominated fire retarding materials

Pyro Chek 68PB is brominated flame retardant (FR) in the form of a polymer. It is produced by the bromination in solution of a commercial grade of polystyrene having a weight average molecular



2. Polyacetylene

Polyacetylene has received more attention than any other electronically conducting polymer because the monomer is inexpensive and readily available and the synthesis of polyacetylene is a relatively straight forward process.



The most widely used method for the synthesis of polyacetylene involves the polymerisation of acetylene in the presence of Ziegler-Natta catalyst (a 4 : 1 mixture of triethyl aluminium and titanium tetra-*n*-butoxide).

The polymer is metallic in appearance despite the porous structure. If the polymerisation is carried out at -78°C , the polymer occupies a *cis-trans*-planar conformation. If the reaction temperature is 150°C , the polymer is generated as the *trans-trans* form.

Electrical conductivity

The electrical conductivity of the pure polymer is quite low ($10^{-9} \Omega^{-1} \text{cm}^{-1}$ for the *cis-trans* and $10^{-5} \Omega^{-1} \text{cm}^{-1}$ for the *trans-trans* form), both values being near the insulator-semiconductor boundary. It has been found that pure polyacetylene can be reduced by alkali metals or electrochemically or oxidised by electron acceptors such as AsF_5 , SbF_5 and Iodine to give materials with markedly increased conductivities. Any change in structure or morphology that lowers the planarity of the chains, the length of the delocalized sequences or the degree of crystallinity also lowers the conductivity. For example, polyacetylenes having alkyl or aryl side groups that force the chain into non-planar conformations show markedly reduced conductivities.

Applications

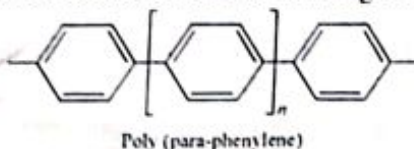
Polyacetylene is particularly suitable for use as light weight electrodes in batteries or fuel cells because of its highly porous structure. The use of fibres of polyacetylene as light weight "wires" to replace copper or other metals in electrical circuits is a long-range possibility. Devices based on *p-n* junctions formed from oxidised and reduced regions on a poly acetylene film or by pressing two films together, is an additional possibility.

3. Phenylene Polymers

Since aryl rings in a polymer chain can also serve to generate a delocalised skeletal structure, several phenylene polymers have been used as electronically conducting polymers.

Poly (para-phenylene)

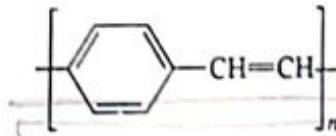
Since poly (para-phenylene) has extensively delocalised π -electron system, it has been considered to be a good electrical conducting polymer. But it is difficult to synthesise the polymer because short-chain polyphenylenes are insoluble in most solvents and have very high melting points. Thus during a synthesis process, oligomers precipitate out from the solution and chain growth is terminated.



However, some evidence exists that polyphenylene oligomer molecules are linked together to form higher polymers when treated with oxidising dopants such as AsF_5 . The conductivity of undoped

oligophenylene is low ($10^{-14} \Omega^{-1} \text{cm}^{-1}$), but doping with AsF_5 raises the conductivity into the range of $5 \times 10^2 \Omega^{-1} \text{cm}^{-1}$.

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