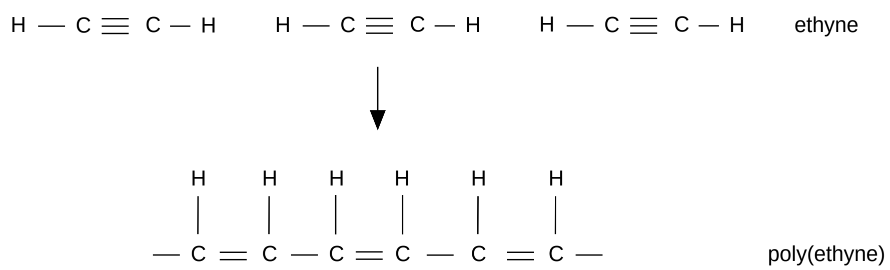
Conducting polymers information sheet

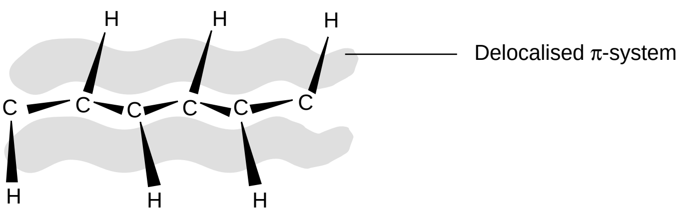
Most textbooks indicate that one of the most important properties of polymers is that they are electrical insulators – they are used for covering electrical cables, the bodies of electrical plugs and sockets, and so on. This is no longer completely true. Over the past few years several polymeric materials have been produced that conduct electricity and a range of applications is being developed. These conducting polymers are of two basic types:

- **intrinsically conducting** polymers where the polymeric material itself conducts; and
- **extrinsically conducting** polymers which are composites where a conductive material such as carbon black is embedded in a non-conducting polymer such as poly(ethene).

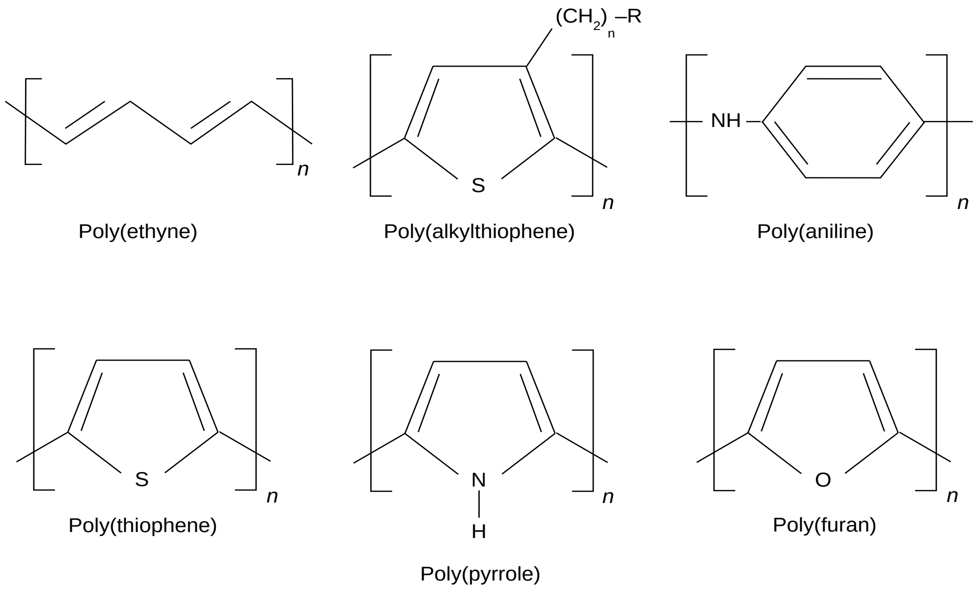
Intrinsically conducting polymers

The simplest intrinsically conducting polymer is poly(ethyne), sometimes called poly(acetylene), (see below) which, despite its name, is an alkene not an alkyne. It consists of a hydrocarbon chain with alternating single and double bonds; called a **conjugated** system. The p-orbitals which form the double bonds can overlap to form a delocalised π–system (similar to the one in benzene). Electrons flow through the delocalised system and so the polymer can conduct. In fact, additives such as iodine have to be incorporated to maximise the conductivity by ensuring that the polymer does exist in the delocalised form rather than as localised single and double bonds. Suitably doped poly(ethyne) can have a conductivity comparable with that of copper provided the material has been stretched to align the chains so that they all run in the same direction. Poly(ethyne) has problems for everyday applications as it is attacked by oxygen from the air but other more stable polymers with conjugated systems also have conducting properties. There are some examples on the next page.



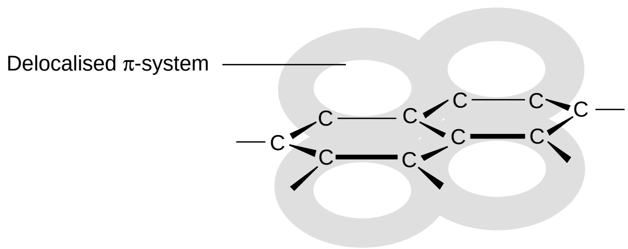


Poly(ethyne)



Examples of intrinsically conducting polymers

The well-known conductivity of graphite (see below) can be explained in the same way. Here there is a two-dimensional delocalised system covering a layer of carbon atoms so that graphite conducts well along the planes of carbon atoms but poorly at right angles to them.



Graphite

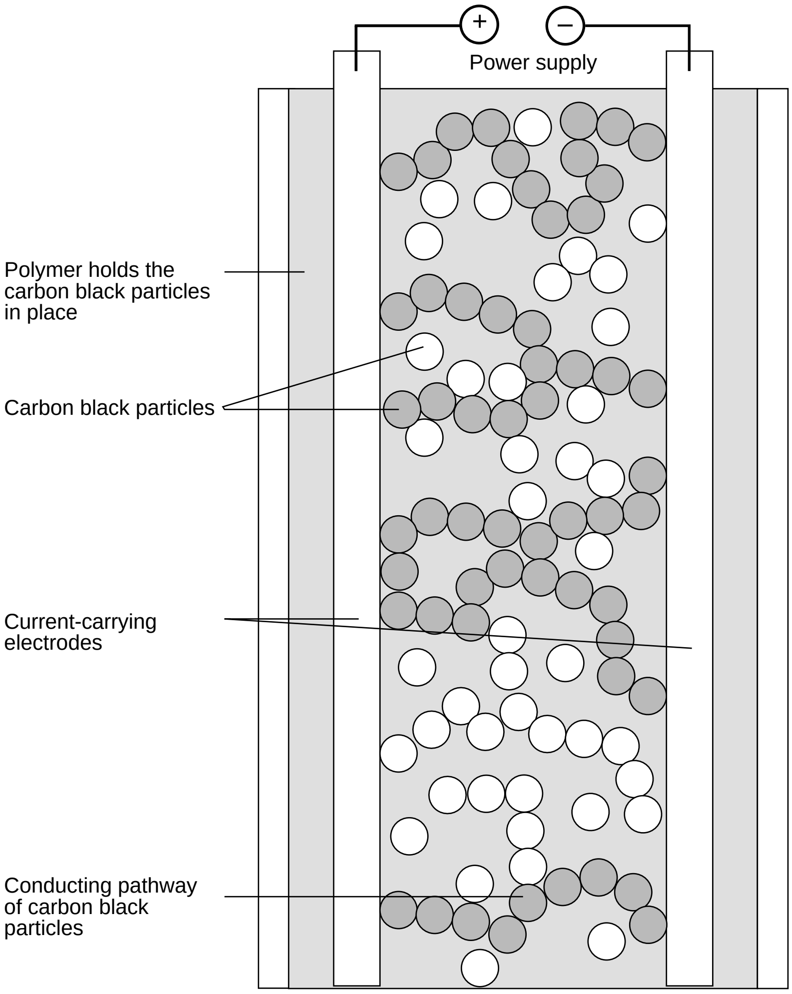
Extrinsically conducting polymers

One type of extrinsically conducting polymer consists of a matrix of poly(ethene) with a percentage of conducting carbon black (a form of powdered graphite) incorporated in it. If the carbon black particles are close enough to be in contact with one another, the material conducts. If the particles are not in contact, it is an insulator. This means that the degree of electrical conduction depends on temperature. At high temperature, the poly(ethene) matrix expands and pulls the particles of carbon black away from each other, decreasing the conductivity. At lower temperatures the poly(ethene) contracts, the carbon black particles are closer and the material conducts well. This temperature dependence of conductivity leads to the use of this material in self-regulating heater cable and PolySwitch* re-settable circuit protection devices.

* PolySwitch is a registered trademark of Raychem Corporation.

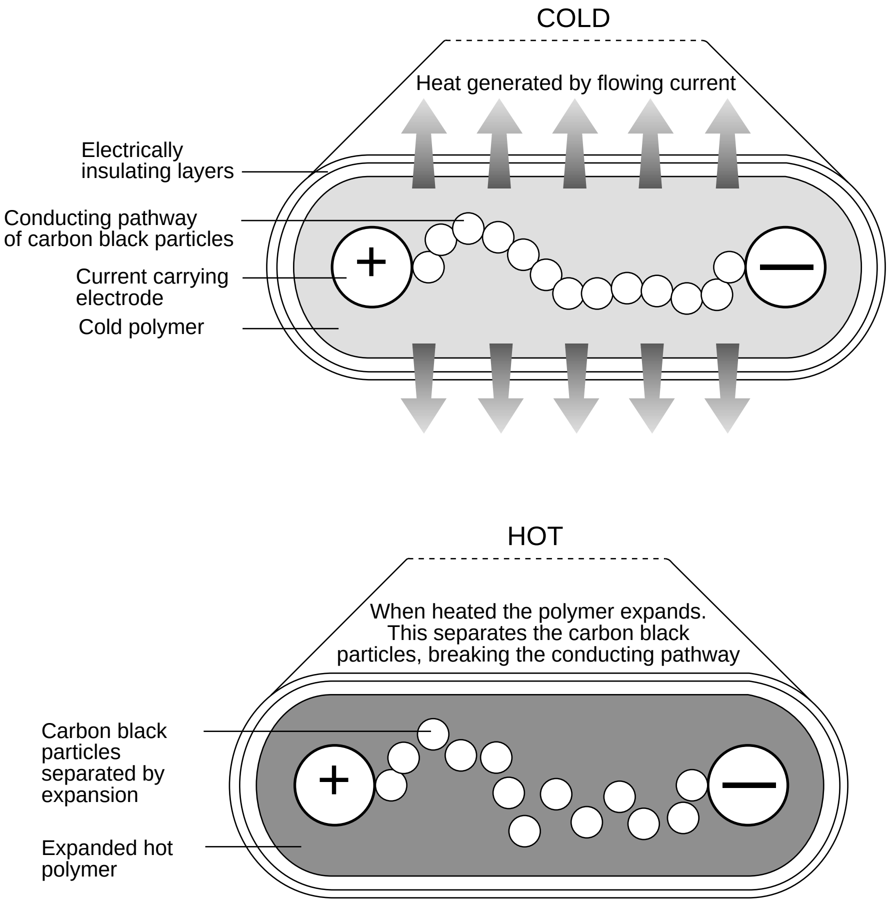
Beat the freeze – the IceStop ‡ system

Ice can cause a lot of damage – burst pipes, slippery walkways, collapsing roofs - all of which can be prevented by low level heating. Conventional heating circuits have some disadvantages here as they have a constant current which can result in 'hot spots' and energy wastage. The IceStop system consists of parallel copper wires embedded in a conducting polymer. Carbon granules form conducting pathways between the wires resulting in a large number of miniature parallel circuits. The polymer conducts electricity well and thus acts as a heater, only when it is cold. As the material warms up the poly(ethene) expands, interrupting some of the conducting pathways and switching off the miniature circuits (see below).



Heat is generated only where electric current flows through the carbon black pathways

‡IceStop is a registered trademark of Raychem Corporation.



Heater cable

IceStop cable can be laid along water pipes, under pathways and along guttering to provide low-level, self-regulating heating which keeps the environment frost-free. It is flexible and easy to install, can be cut to any length required and can be overlapped or wound round a pipe.

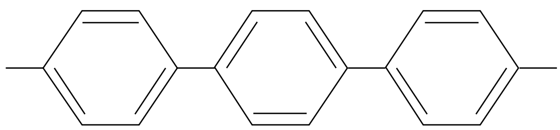
Protecting batteries – the PolySwitch device

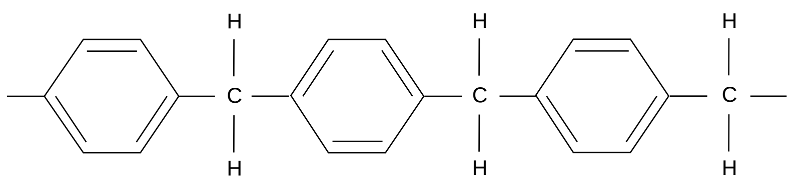
Lithium batteries are used in many small hand-held electrical appliances such as cameras but a current overload can lead to overheating resulting in, at best, damage to the appliance, and, at worst, the battery exploding. Lithium batteries are also used in telecom systems, audio speakers, fire and burglar alarms and personal computers. A conventional fuse could provide the required protection but needs to be replaced if it blows. A PolySwitch device does the same job but can be reset, rather than having to be replaced, once the fault has been rectified. As in IceStop cable, carbon granules form conducting pathways through the polymer and these pathways are broken if the material becomes too warm. This protects the appliance from current overload.

Why doesn't the fuse keep resetting itself?
When the PolySwitch device gets hot, it does not switch off the current completely as does a melted wire in a fuse. A very small current still flows through the device. This is enough to keep it hot. Once the fault has been rectified, the PolySwitch device can be reset by first turning off the power to allow it to cool.

Questions

1. Explain the term conjugated.
2. The groups attached to the double bonds in poly(ethyne) can be either *cis* or *trans.* Poly(ethyne) exists in two extreme forms – all *cis*– and all *trans*–. Draw the structure of each. You should draw at least five repeating units.
3. What is the functional group in poly(ethyne)?
4. Why would you expect oxygen to attack poly(ethyne)? Suggest a possible product of the reaction.
5. Suggest some advantages which a conducting polymer might have over a conducting metal. Assume that the typical polymer properties are essentially unchanged (except for electrical conductivity).
6. Draw a displayed formula for poly(pyrrole) showing at least three repeating units.
7. What is a composite material? What affects its properties?
8. Does the electrical conduction of metals rise or fall as the temperature increases? (Hint: think about superconductivity.)
9. Look at the formulae of the two polymers below. Predict which one you might expect to be an intrinsic conductor and explain your choice.

a) 

b) 

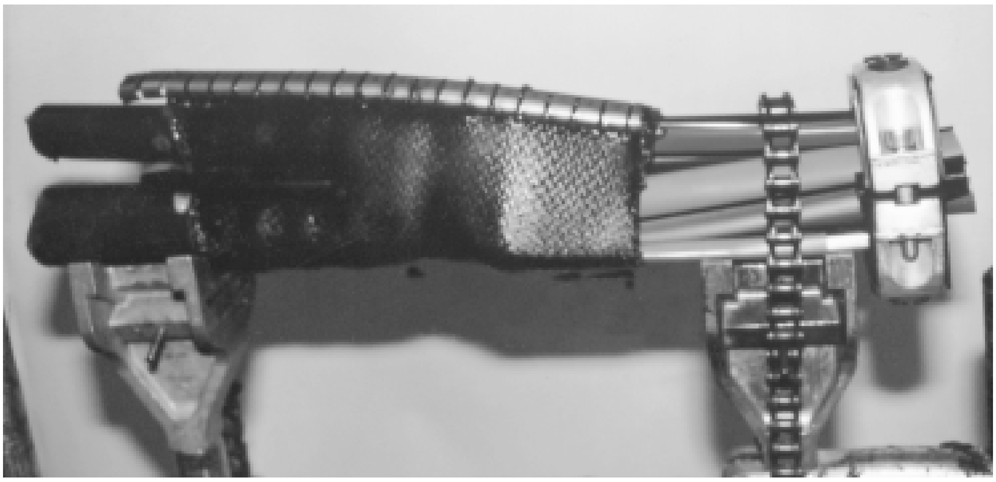
Conducting polymers

10. Use a data book to find the bond lengths you would expect for C–C and for C=C. What is the carbon–carbon distance in benzene? What technique might you use to find out if poly(ethyne) were in the delocalised or non-delocalised form?
11. Describe the way in which electrons move in metals and allow them to conduct electricity. Compare this with the situation in poly(ethyne) and graphite. Write down any similarities and differences.

Shape memory polymers information sheet

These polymers 'remember' the shape into which they have been moulded and will return to it on gentle heating.

They are based on thermoplastic polymers. During manufacture the polymer is moulded into a particular shape and irradiated with β-radiation. It is then heated, re-shaped and cooled. It does, however, remember the shape which it had when irradiated and returns to it when re-heated. One application of this effect is heat-shrinkable sleeves which are used to hold together bundles of wires in car wiring harnesses (see below).



Applying a shrinkable sleeve

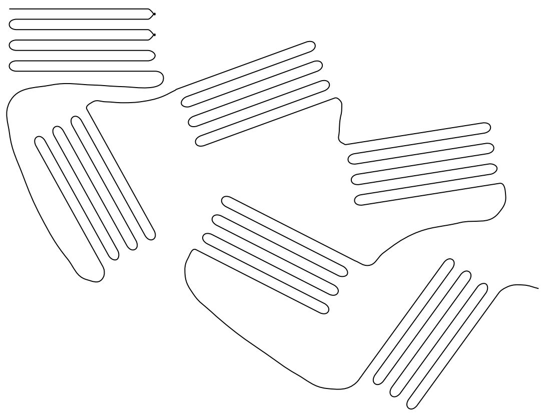
Here a cylindrical length of poly(ethene) sleeve is moulded into shape so that it has a narrow internal diameter which firmly holds together a bunch of wires. The sleeve is now irradiated, which causes covalent crosslinks between the poly(ethene) chains.

The tube is next heated to above its crystalline melting point to soften it. Then it is stretched into a larger diameter. This stretches the crosslinks. The tube is cooled and this locks the chains in their stretched position.

Now the large diameter tube can easily be slipped over a bunch of wires. If it is heated (by a hot air gun or blowlamp) above its crystalline melting point, the stretched crosslinks pull the material back into the shape it had on irradiation and it holds the bunch of wires firmly together.

Bonding within polymers

Polymers can be classified as thermoplastic (thermosoftening) or thermosetting. Thermoplastics soften on heating and can be moulded into a shape which they retain on cooling. They can be reheated and moulded indefinitely. They consist of long chain molecules, each chain being essentially independent of the others. There are no covalent bonds between the chains. The plastics retain their shape when cool because of intermolecular forces between the chains. In particular there are areas where the the chains line up in an ordered way – so-called areas of crystallinity. If crystalline areas on two adjacent chains line up, the intermolecular interactions are particularly strong. This is responsible for much of the strength of thermoplastics in the solid state. On heating above the crystalline melting point, increased thermal motion makes the crystalline areas disappear. The polymer softens, the chains become free to move past one another and the plastic can be moulded. On cooling, new crystalline areas re-form, which help retain the new shape (see below).



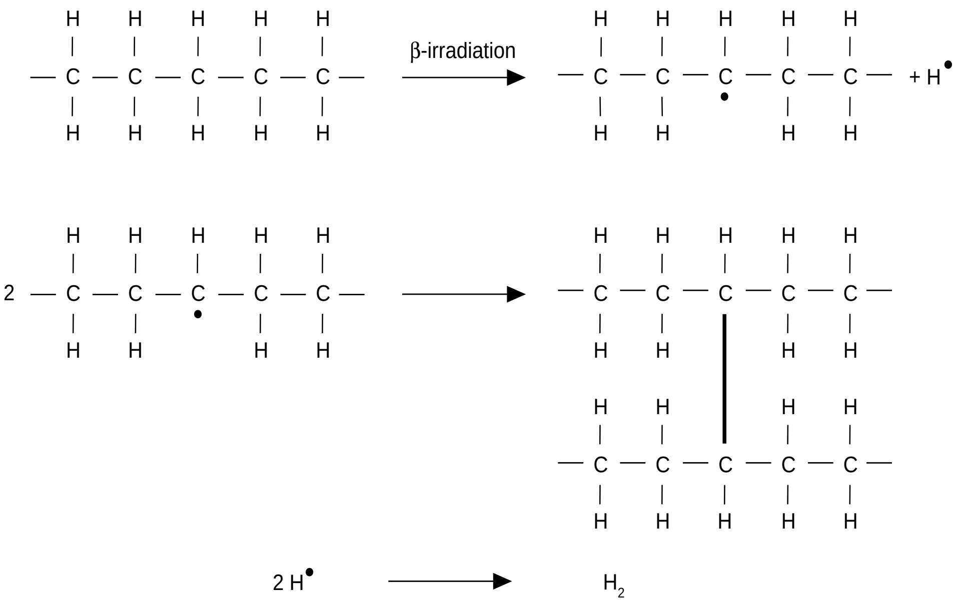
Crystalline areas in a polymer chain

Thermosetting plastics have many covalent crosslinks between the polymer chains which form as the polymer is made. Once made, the polymer is unaffected by heat (until it begins to burn or decompose).

Shape memory plastics have a degree of crosslinking (after irradiation) which is less than that of a thermoset but more than that of a thermosoftening plastic.

Irradiation

How does the irradiation process produce the cross links? β-radiation is a stream of electrons each with more than enough energy to break covalent bonds. β-irradiation of poly(ethene) breaks some of the C–H bonds in the poly(ethene) chains. As carbon and hydrogen atoms have similar electronegativity, the bonds tend to break homolytically leaving a free hydrogen atom and a carbon free radical, a carbon atom with a single –*ie* unpaired – electron. Such carbon atoms are extremely reactive and two close together may form a covalent bond thus pairing up their electrons. This forms a crosslink between the chains (see below).



The effect of β-irradiation on poly(ethene)

The hydrogen atoms, which also have an unpaired electron each, tend to come together to form hydrogen molecules which escape from the polymer.

Questions

1. What other bonds will the β-radiation break? Suggest what effects this might have on the polymer.

2. What might happen if too many crosslinks are formed in the polymer? What effect might this have on its properties?

3. What are the intermolecular forces which operate within the crystalline regions of a thermosoftening plastic called? Compare the strength of a single intermolecular interaction with that of a typical covalent bond. Explain why, when cool, these intermolecular forces have comparable effects to covalent bonds – *ie* thermosets and thermoplastics have comparable strengths.

4. Another free radical reaction is that of bromine with methane in ultraviolet light. The steps are:

   1. $Br{-}Br \longrightarrow 2Br^{\bullet}$

   2. $CH_4 + Br^{\bullet} \rightarrow HBr + CH_3^{\bullet}$

      and

      $Br_2 + CH_3^{\bullet} \rightarrow Br^{\bullet} + CH_3Br$

      UV

   3. $Br^{\bullet} + Br^{\bullet} \rightarrow Br_2$

      $CH_3^{\bullet} + CH_3^{\bullet} \rightarrow C_2H_6$

      $Br^{\bullet} + CH_3^{\bullet} \rightarrow CH_3Br$

   a) The first step is called initiation. Name the other two.

   b) In this case, there are no hydrogen free radicals formed by the reaction

      $CH_4 \rightarrow H^{\bullet} + CH_3^{\bullet}$

      Suggest a reason for this.

      What does this tell you about the energy of ultraviolet light compared with that of β-radiation?

   c) Which of the three possibilities for step 3 above is most similar to the reaction which occurs in the polymer crosslinking reaction? Explain your choice.

5. Explain the terms *homolytically* and *electronegativity* as used in the passage.