# polymerisation

## addition polymerisation

Addition polymerisation involves adding together many alkene monomers to form a long polymer chain.

There is no loss of small molecules when monomers join, and the resulting polymer contains repeating units joined by carbon-carbon single bonds, e.g. poly(ethene).

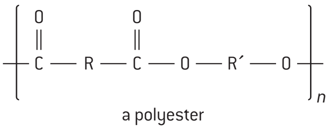
## condensation polymerisation

Condensation polymers are formed when monomers link together to form a long chain in which each link is accompanied by the loss, or condensation, of a small molecule such as $H_2O$ or HCl.

The two main types of condensation polymer are polyesters and polyamides.

## polyesters

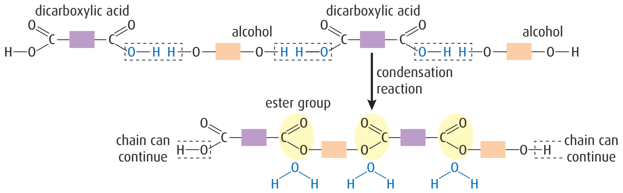
Polyesters contain ester linkages formed between the alcohol and carboxylic acid/or acyl chloride functional groups.



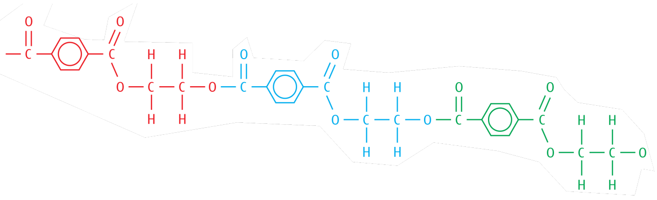
$$\left[ -\overset{O}{\overset{\|}{C}} - R - \overset{O}{\overset{\|}{C}} - O - R' - O - \right]_n$$

a polyester

## polyesters



## polyesters: terylene (PET)



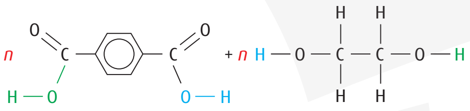
## terylene (PET)

Terylene® (or PET, polyethylene terephthalate) is a common polyester used in synthetic fibres and in containers for food and beverages.

It is one of the most important raw materials of synthetic fibres.

## terylene (PET)

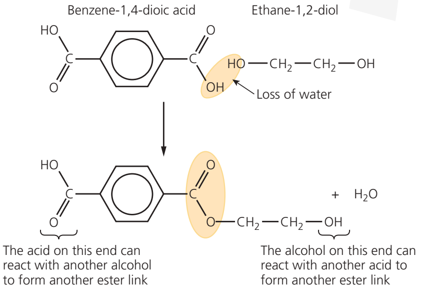
It is made by reacting the monomers benzene-1,4-dicarboxylic acid and ethane-1,2-diol:



benzene-1,4-dicarboxylic acid

ethane-1,2-diol

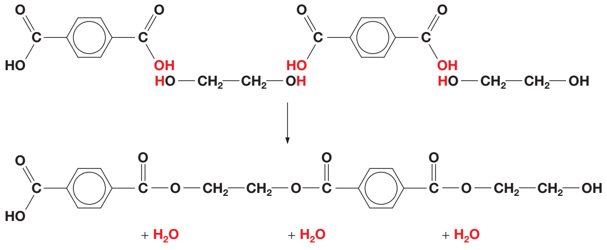
## terylene (PET)



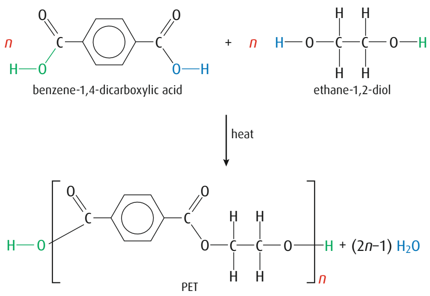
The acid on this end can react with another alcohol to form another ester link

The alcohol on this end can react with another acid to form another ester link

## terylene (PET)



## terylene (PET)



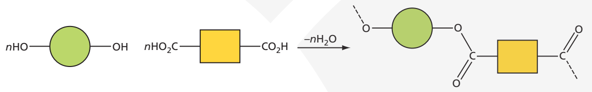
## type 2 polymers

Starts with two different monomers,

one containing two carboxylic acid groups or two acyl chloride groups,

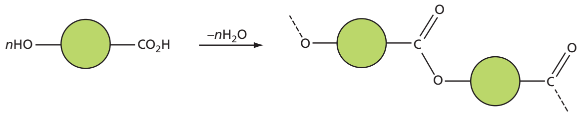
and the other containing two alcohol groups.

## type 2 polymers



## type 1 polymers

starts with a monomer containing two different functional groups that can condense together to form either ester or amide groups.



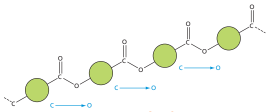
## type 1 polymers

## type 1 vs type 2

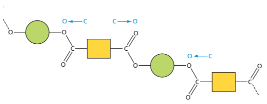
The two types of polymer differ in the direction of successive functional groups along the chain.

In type I polymers, the direction of each ester or amide linkage is the same, whereas in type II polymers, the direction of the ester or amide linkages alternates.

## type 1 vs type 2



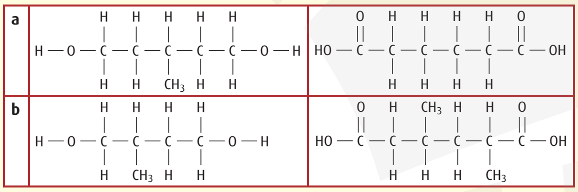
*type I polymer*



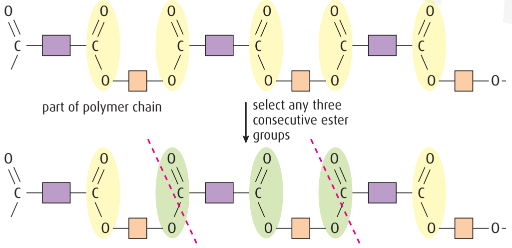
*type II polymer*

## polyesters skillcheck

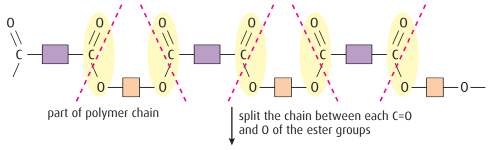
Draw two repeat units of the polymer formed when the following molecules react:



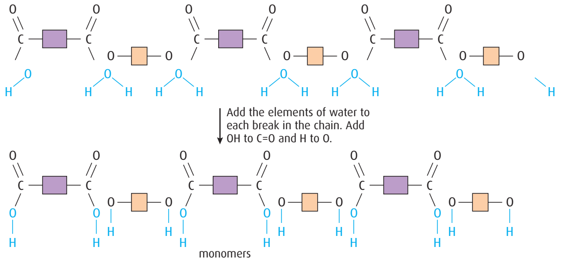
## generating repeat units from polyesters



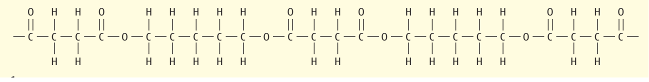
## generating monomers from polyesters



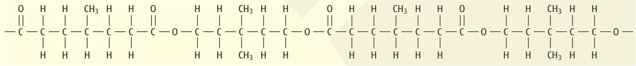
## 21 generating monomers from polyesters



## 22 generating repeat units from polyesters


$$-\mathrm{CO{-}CH_2{-}CH_2{-}CO{-}O{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}O{-}CO{-}CH_2{-}CH_2{-}CO{-}O{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}O{-}CO{-}CH_2{-}CH_2{-}CO}-$$

## 23 generating repeat units from polyesters


$$-\mathrm{CO{-}CH_2{-}CH_2{-}CH(CH_3){-}CH_2{-}CH_2{-}CO{-}O{-}CH_2{-}CH_2{-}C(CH_3)_2{-}CH_2{-}CH_2{-}O{-}CO{-}CH_2{-}CH_2{-}CH(CH_3){-}CH_2{-}CH_2{-}CO{-}O{-}CH_2{-}CH_2{-}C(CH_3)_2{-}CH_2{-}CH_2{-}O}-$$

## 24 polyamides

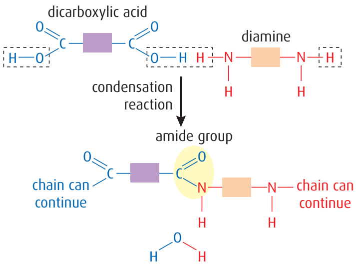
Polyamides contain amide linkages formed between the amine and carboxylic acid/or acyl chloride functional groups.

## 25 polyamides

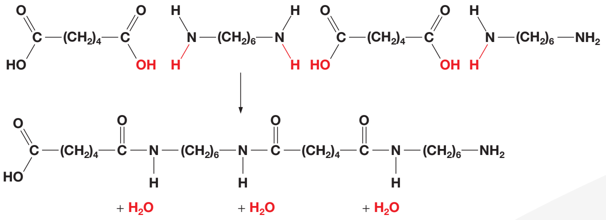
Polyamides are polymers in which the monomers are linked by an amide bond. This is exactly the same as the amide bond in proteins, in which it is usually called the peptide bond.

The first synthetic and commercially important polyamides were various forms of nylon.

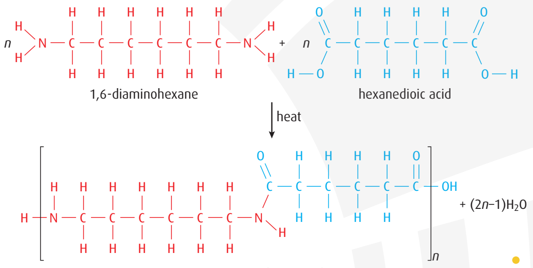
## 26 polyamides



## 27 type 2 polyamides



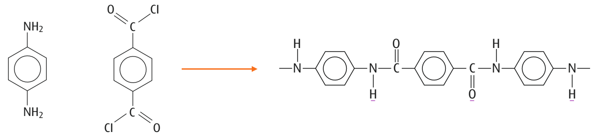
## 28 nylon



repeat unit of polymer (nylon 6,6)

## 29 kevlar

Kevlar is created by the reaction between 1,4-diaminobenzene and the diacyl chloride of benzene-1,4-dioic acid.



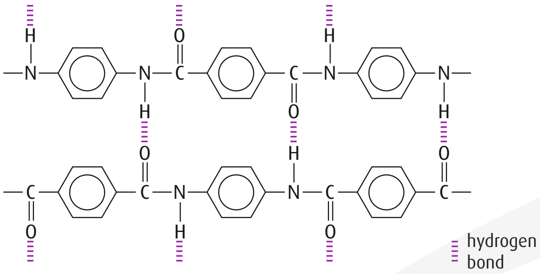
## 30 kevlar

The exceptional properties of Kevlar® have led to its use in making bullet-proof vests, ropes, re-protective clothing (as used by Formula 1 racing drivers) and modern ‘leathers’ worn by motorcycle riders. It is also used to reinforce other materials, such as the rubber in tyres.

## 31 kevlar

The polymer chains align themselves in such a way that allows for the formation of comparatively strong intermolecular hydrogen bonds between amide groups (C=O to H-N) along the whole chain.

## 32 kevlar

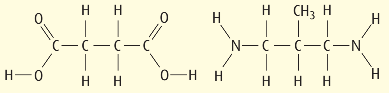


## 33 kevlar

Additional intermolecular interactions arise in the form of extensive van der Waals' forces. These hold the polymer chains together very tightly and contribute to Kevlar's high tensile strength.

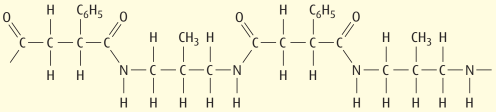
## 34 polyamides skillcheck

Write an equation for the formation of a polymer from the monomers shown.



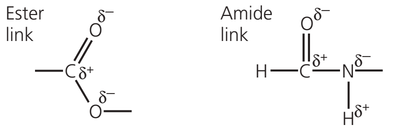
## 35 polyamides skillcheck

Give the structures of the monomers that could be used to produce the polymer shown:



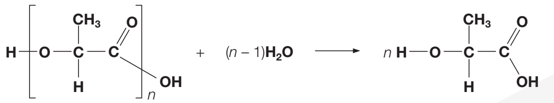
## 36 Hydrolysis

The ester link in a polyester and the amide link in a polyamide are both polar and are subject to acid-catalysed and base-catalysed hydrolysis.



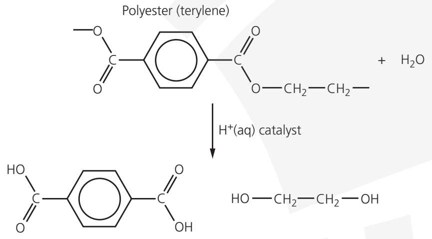
## 37 Hydrolysis of polyesters

Polyesters can be hydrolysed in a similar way to simple esters forming products with carboxylic acid and alcohol groups.



lactic acid
(2-hydroxypropanoic acid)

## 38 Hydrolysis of terylene



Benzene-1,4-dioic acid

Ethane-1,2-diol

## 39 Hydrolysis of polyamides

Polyamides are hydrolysed in the same way. The products are compounds containing carboxylic acid groups, $-CO_2H$, and amine groups, $-NH_2$.

If the hydrolysis is catalysed by acid, the $-NH_2$ groups are converted to $-NH_3^+$; and if the reaction is catalysed by base, the $-CO_2H$ groups are converted to $-COO^-$

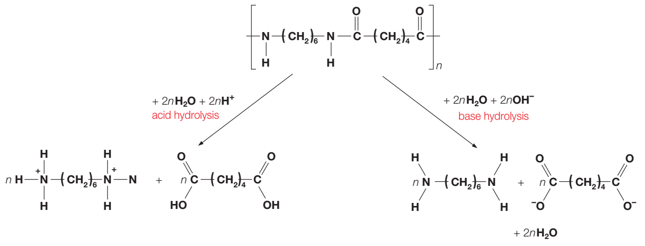
## 40 Hydrolysis of polyamides

Simple amides are easily hydrolysed by reacting with dilute acids and alkalis.

Hydrolysis is faster at high temperatures.

Kevlar is far more resistant to hydrolysis than nylon.

## 41 Hydrolysis of polyamides



## 42 addition polymers: skill check

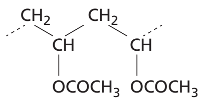
Draw two repeat units of the polymer formed from each of the following monomers or pair of monomers.

- **a** $CH_2{=}CH{-}OCOCH_3$
- **b** $CH_2{=}CCl{-}CH{=}CH_2$
- **c** $CH_2{=}CHCl$ and $CH_2{=}CH{-}CH_3$

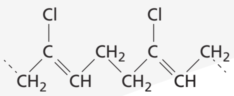
## 43 addition polymers: skill check

draw the structures of the monomers of the following polymers.

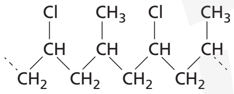
**a**



**b**

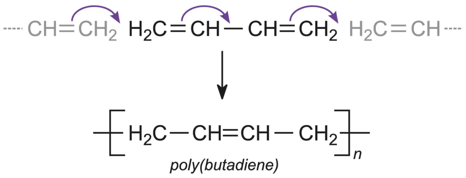


**c**



## 44 dienes

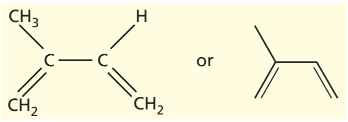
When a diene undergoes addition polymerisation, a double bond is still present in the product.



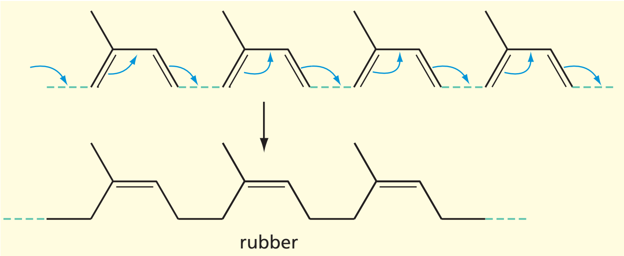
poly(butadiene)

## 45 rubber

Rubber is an addition polymer of 2-methylbutadiene.



## 46 rubber



## 47 addition polymers: skill check

The following are sections of addition polymers.
Draw the monomer(s) from which they are formed.

**a** $\cdots CH_2{-}CH(CN){-}CH_2{-}CH(CN){-}CH_2\cdots$

**b** $\cdots CH_2{-}C(CN){=}CH{-}CH(CN){-}CH_2{-}C(CN){=}CH{-}CH(CN){-}CH_2\cdots$

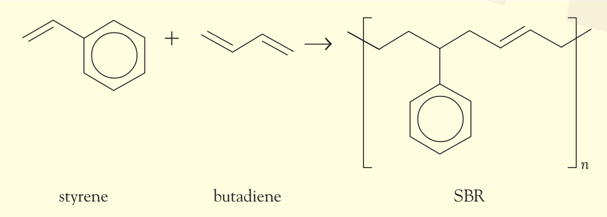
**a** $CH_2{=}CH(CN)$ **b** $CH_2{=}C(CN){-}CH{=}CH(CN)$

## 48 co-polymers

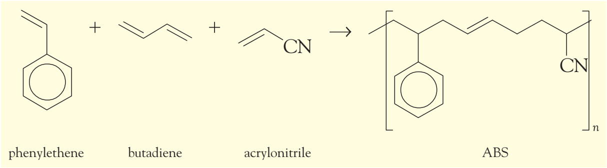
A co-polymer is formed when two or more different alkenes are polymerised together.

Even if the ratio of monomers is 50:50, there is no guarantee that the monomer fragments will alternate along the chain. The order is fairly random (in contrast to condensation co-polymerisation).

## 49 co-polymers



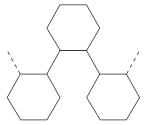
## 50 co-polymers



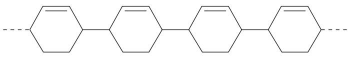
## 51 skill check

Q. Suggest the monomer(s) from which the following polymers have been made.

1



2

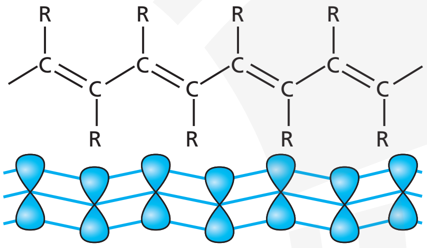


## 52 conducting polymers

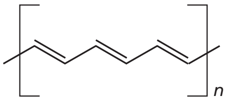
Some long-chain polymer molecules act as 'molecular wires'.

They contain conjugated double bonds, which means that the π bonds on adjacent alkene units overlap, and the π electrons become delocalised throughout the whole length of the polymer chain.

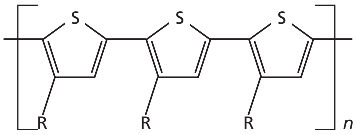
## 53 conducting polymers



## 54 conducting polymers

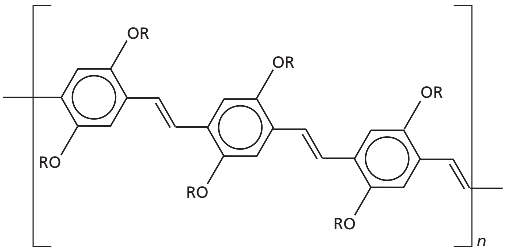


polyacetylene (polyethyne)



a substituted polythiophene (PT)

## 55 conducting polymers



a disubstituted polyphenylene vinylene (PPV)

## 56 conducting polymers

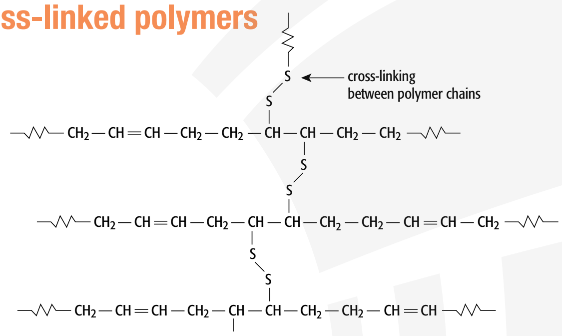
Just as with the three-dimensional delocalised electrons in metals, or the two- dimensional delocalised electrons in the sheets of graphite or graphene, these one- dimensional delocalised electrons can conduct a current when a potential difference is applied to the ends of the polymer.

## 57 Cross-linked polymers

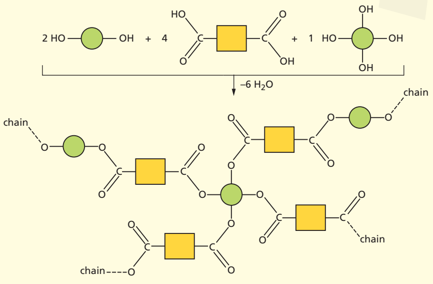
A cross-link is a bond that links one polymer chain to another. They can be covalent bonds or ionic bonds.

The cross-linking of the chains of the rubber molecules makes the rubber harder, stronger, less flexible and less 'sticky'.

## 58 Cross-linked polymers



## 59 Cross-linked polymers



## 60 properties of polymers

| Structural property | Physical property | Example |
|---|---|---|
| **Chain length** | The longer the chain, the stronger the polymer. | Longer polymer chains have higher melting point, increased strength, and increased impact resistance due to increased van der Waals' forces. |
| **Branching and packing structures** | Straight unbranched chains can pack more closely. A higher degree of branching keeps strands apart and weakens intermolecular forces. | HDPE with no branching is more rigid than the more branched LDPE. Use of plasticizers in PVC to soften the polymer. |
| **Side groups on monomers** | Hydrogen bonding can increase strength, eg Kevlar. Atactic and isotactic placement can influence strength, eg polystyrene. | Polystyrene |
| **Cross-linking** | Extensive covalently bonded cross-linkage increases polymer strength. | Vulcanized rubber, Bakelite |

## 61 addition vs condensation

| Differences | Addition polymers | Condensation polymers |
|---|---|---|
| The type of reaction | Addition reaction only | Addition reaction followed by elimination reaction, resulting in the condensation of a small molecule such as $H_2O$ or HCl |
| Type of links along the central chain | C-C single bonds only, which are non-polar | Short aliphatic or aryl sections linked by either ester groups or amide groups, which are polar |
| The type of monomer involved | All monomers have C=C double bond | The monomers have molecules with at least two functional groups, which may be the same or different |
| Hydrolysis | Resistant to hydrolysis | Undergo hydrolysis |
| Conditions for preparation | Require an initiator, together with high temperature and high pressure, unless a catalyst is involved | Do not require initiators and usually occur at much lower temperatures and atmospheric pressure |
| Polymer properties | Non-polar and resistant to attack | Polar and subject to hydrolysis |

## 62 enviromengtal concerns

As it becomes more and more expensive to dump waste in landfill sites, plastics are seen as an increasing problem. The major problem with most plastic waste is that it is non-biodegradable. This means that the only choices for dealing with plastic waste are recycling and energy recovery.

## 63 degradable polymers

Chemists are now developing degradable plastics that break down when they are discarded: biodegradable plastics and photodegradable plastics.

## 64 biodegradable polymers

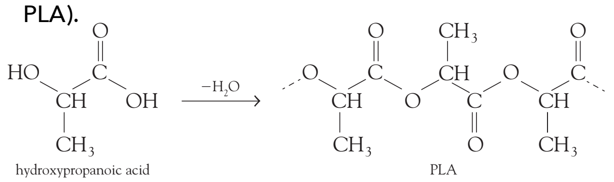
Scientists have developed plastics that contain small amounts of starch granules that the bacteria and fungi in moist soil can break down. So the plastic is broken into smaller pieces, with a larger surface area for decomposition to occur faster.

## 65 photodegradable polymers

Polymer chains also have been designed that incorporate carbonyl groups (C=O) at intervals down their length. These carbonyl groups absorb uv radiation which causes the bonds in the region of the carbonyl group to weaken and break down. As the polymer breaks into smaller fragments, the plastic will biodegrade much more quickly if it is not chemically inert.

## 66 PLA

The most commonly used degradable polymer is poly(2-hydroxypropanoic acid) (poly(lactic acid), PLA).



## 67 PLA

PLA is easily hydrolysed, either chemically or by esterase enzymes, to re-form hydroxypropanoic acid, which is readily metabolised by all living matter into $CO_2$ and water.

## 68 PLA

The uses of PLA include replacing conventional plastics in the manufacture of bottles, disposable cups and textiles, but it is also used in applications where its slow biodegradability is an advantage.

## 69 definitions

Plastics are materials made of long- chain molecules, which at some stage can be moulded into shapes which are retained.

Biodegradable materials break down due to the action of microorganisms.

## 70 definitions

Photodegradable materials break down when exposed to sunlight.

Co-polymers are polymers made from two or more monomers, each of which could produce a polymer.