POLYMERISATION

General A process in which small molecules called monomers join together into large molecules consisting of repeating units.

There are two basic types **ADDITION** & **CONDENSATION**

ADDITION POLYMERS

- all the atoms in the monomer are used to form the polymer
- occurs with alkenes
- mechanism can be **free radical** or **ionic**

Examples

	Formula of monomer		*Formula of polymer*	*Use(s)*
poly(ethene)	**n $CH_2{=}CH_2$**	**—>**	**— $(CH_2 — CH_2)_n$ —**	
poly(phenylethene)				
poly(chloroethene)				
poly(tetrafluoroethene)				
poly(ethenyl ethanoate) ‘PVA’				

Preparation Many are prepared by a free radical process involving high pressure, high temperature and a catalyst. The catalyst is usually a substance (organic peroxide) which readily breaks up to form radicals which, in turn, initiate a chain reaction.

Another famous type of catalyst is a Ziegler-Natta catalyst (named after the scientists who developed it). Such catalysts are based on the compound $TiCl_4$.

Properties

Physical Can be varied by changing the reaction conditions (pressure, temperature etc).

Chemical Are based on the functional groups within their structure.

eg *poly(ethene) is typical; it is fairly inert as it is basically a very large alkane. This means it is resistant to chemical attack and non-biodegradable.*

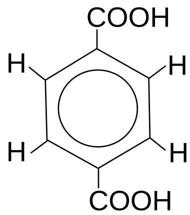
CONDENSATION POLYMERS

- monomers join up the with expulsion of small molecules
- not all the original atoms are present in the polymer
- examples include **polyamides** *nylon*
  polyesters *terylene*
  peptides
  starch

- reactions between **diprotic carboxylic acids** and **diols**
  diprotic carboxylic acids and **diamines**
  amino acids

POLYESTERS

Terylene *Reagents* *terephthalic acid* **$HOOC-C_6H_4-COOH$**
ethane-1,2-diol **$HOCH_2CH_2OH$**



Reaction *Esterification*

Eliminated *water*

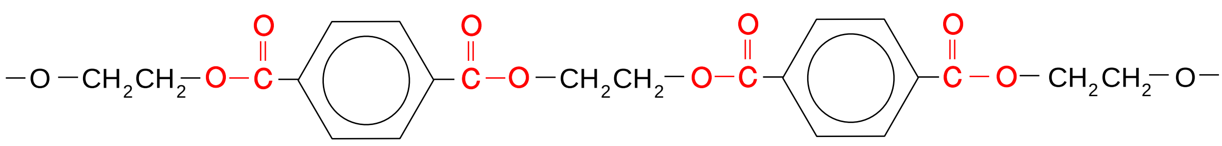
Product *poly(ethylene terephthalate)* *'Terylene', 'Dacron'*

Equation $n\ HOCH_2CH_2OH\ +\ n\ HOOC\text{-}C_6H_4\text{-}COOH \longrightarrow$

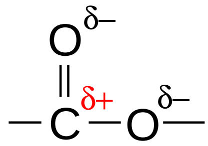
$-[\text{-}OCH_2CH_2OOC(C_6H_4)CO\text{-}]_n-\ +\ n\ H_2O$

Repeat unit $—[\text{-}OCH_2CH_2OOC(C_6H_4)CO\text{-}]_n—$

Structure



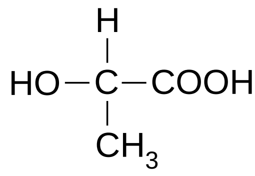
Properties
- contain an **ester link**
- can be broken down by hydrolysis
- the C-O bond breaks
- behaves as an ester
- biodegradable



Uses
-
-

Poly(lactic acid)

Reagent — *2-hydroxypropanoic acid (lactic acid)*



Reaction — *Esterification*

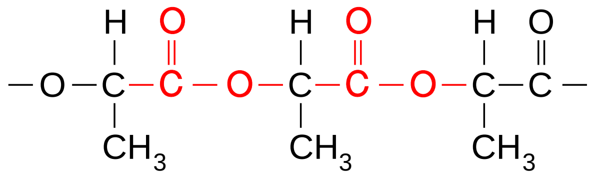
Eliminated — *water*

Equation — **n $CH_3CH(OH)COOH$ —> −[-$OCH(CH_3)CO$-]$_n$ − + n H_2O**

Product — *poly(lactic acid)*

Repeat unit — — [-$OCH(CH_3)CO$-] —

Structure



Properties
- contain an **ester link**
- can be broken down by hydrolysis
- the C-O bond breaks
- behaves as an ester (hydrolysed at the ester link)
- biodegradable
- **photobiodegradable (C=O absorbs radiation)**

Uses
- waste sacks and packaging
- disposable eating utensils
- internal stitches

Q.1 *Draw structures for the organic product(s) formed when poly(lactic acid) is treated with the following reagents. [Hint: see page 5 of these notes]*

- *HCl(aq)*

- *NaOH(aq)*

What name is given to this type of reaction?

POLYAMIDES

Nylon-6,6

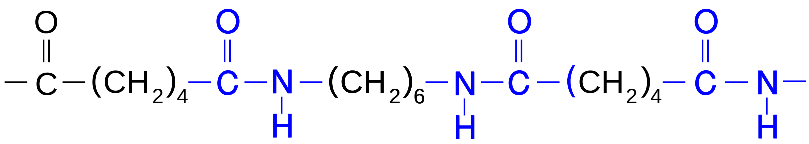
Reagents	*hexanedioic acid*	**$HOOC(CH_2)_4COOH$**
	hexane-1,6-diamine	**$H_2N(CH_2)_6NH_2$**
Mechanism	*Addition-elimination*	
Eliminated	*water*	
Product	*Nylon-6,6*	*two repeating units, each with 6 carbon atoms*

Equation

$$n\ HOOC(CH_2)_4COOH + n\ H_2N(CH_2)_6NH_2 \longrightarrow -[-NH(CH_2)_6NHOC(CH_2)_4CO-]_n- + n\ H_2O$$

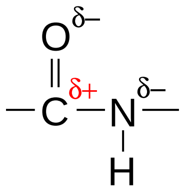
Repeat unit $-[-NH(CH_2)_6NHOC(CH_2)_4CO-]_n-$

Structure



Properties

- contain a **peptide (or amide) link**
- can be broken down by hydrolysis
- the C-N bond breaks
- behave as amides
- biodegradable
- can be spun into fibres for strength



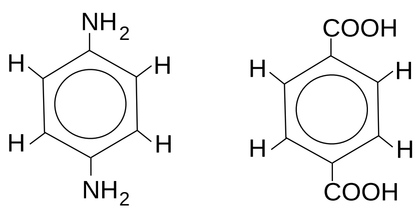
Uses

-
-

Kevlar

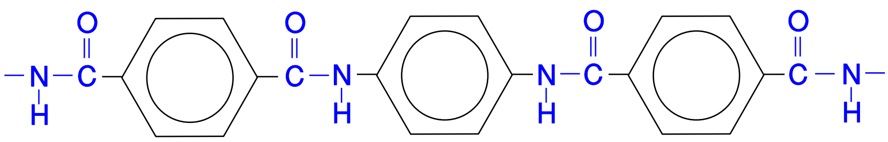
Reagents *benzene-1,4-diamine*

benzene-1,4-dicarboxylic acid



Product *Kevlar*

Structure



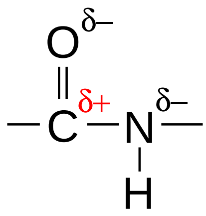
Use *body armour*

Peptides

- formed by joining amino acids together
- are examples of **polyamides**
- amino acids have two main functional groups

-COOH	carboxylic acid
$-NH_2$	amine

- amino acids can join together using a **peptide link**

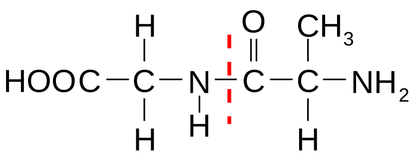


- **dipeptide** two amino acids joined together
  tripeptide three amino acids joined
  polypeptide many amino acids joined together

- a **protein** is a polypeptide with a **large relative molecular mass** (>10000)

- peptides/proteins **are broken down** into the original amino acids **by hydrolysis**

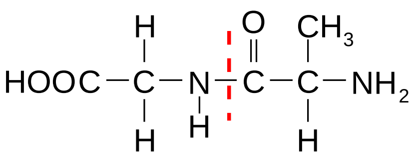
Hydrolysis



$$+ \ H_2O \longrightarrow HOOCCH_2NH_2 + HOOCCH(CH_3)NH_2$$

The acid and amine groups remain as they are

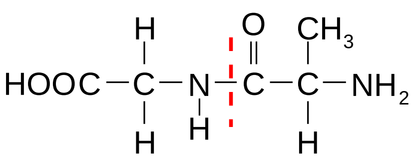
Acid Hydrolysis



$$+ \ 2HCl \longrightarrow HOOCCH_2NH_3^+Cl^- + HOOCCH(CH_3)NH_3^+Cl^-$$

The amine groups are protonated and the acid groups remain as they are

Base (alkaline) Hydrolysis

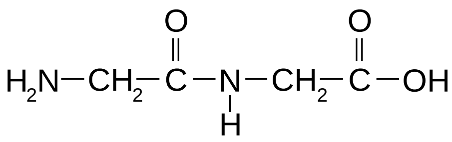


$$+ \ 2NaOH \longrightarrow Na^+ \ ^-OOCCH_2NH_2 + Na^+ \ ^-OOCCH(CH_3)NH_2$$

The acid groups become sodium salts and the amine groups remain as they are

Q.2 *Look up the structures of alanine and glycine. Draw the structure of the* ***dipeptide*** *formed when they react together.*

Q.3 *Look at the structure of the following dipeptide.*



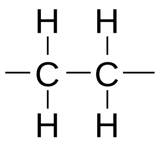
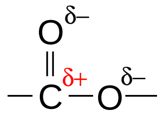
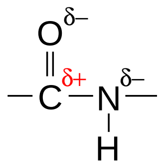
How many different amino acids formed the dipeptide? Draw their structure(s).

Give the ***formulae*** *of the organic products formed when the dipeptide is hydrolysed using...*

a) NaOH(aq)

b) HCl(aq)

POLYMER FORMATION - A SUMMARY

	ADDITION	CONDENSATION
Monomers	**ALKENES** C=C bond	**ALCOHOLS** + **ACIDS** **AMINES** + **ACIDS** **AMINO ACIDS** **AMINES** + **ACYL CHLORIDES**
Process	All the atoms in the original monomers end up in the polymer	Monomers join up with the expulsion of a small molecule (e.g. water)
Bonding	ALKANE LINK 	ESTER LINK  AMIDE (PEPTIDE) LINK 
Reactivity	**UNREACTIVE** - NON-POLAR Resistant to hydrolysis	**REACTIVE** - POLAR BONDS Hydrolysed by acids and alkalis with acid $RCOOH$ + ROH $RCOOH$ + $RNH_3^+Cl^-$ with alkali $RCOO^-Na^+$ + ROH $RCOO^-Na^+$ + RNH_2
Uses	Packaging Insulation	Clothing Ropes
Examples	poly(ethene) poly(propene) poly(phenylethene) poly(chloroethene)	nylon 6,6 Terylene peptides