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.*

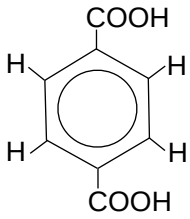
CONDENSATION POLYMERS

- 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* **$HOOC\text{-}C_6H_4\text{-}COOH$**
ethane-1,2-diol **$HOCH_2CH_2OH$**



Reaction *Esterification*

Eliminated *water*

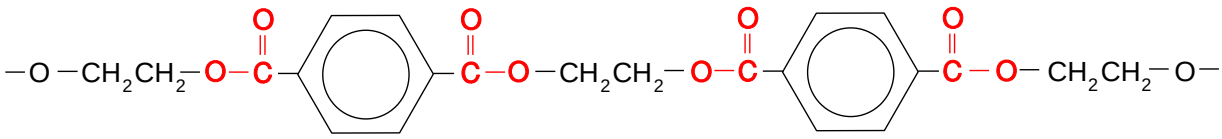
Product *poly(ethylene terephthalate)* *'Terylene', 'Dacron'*

Equation ***n*** **$HOCH_2CH_2OH$ + *n* $HOOC\text{-}C_6H_4\text{-}COOH$ —>**

$H\text{–}[OCH_2CH_2OOC(C_6H_4)CO]_n\text{–}OH$ + *n* H_2O

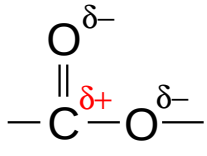
Repeat unit — $[\text{-}OCH_2CH_2OOC(C_6H_4)CO\text{-}]_n$ —

Structure



Properties

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



Uses

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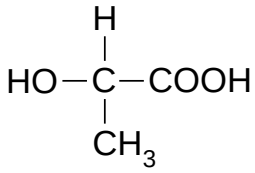
Poly(lactic acid)

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



Reaction — *Esterification*

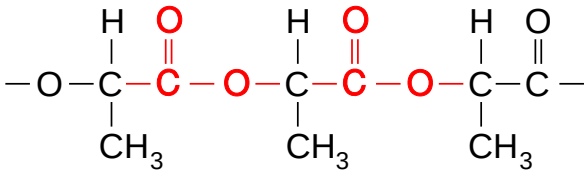
Eliminated — *water*

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

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*

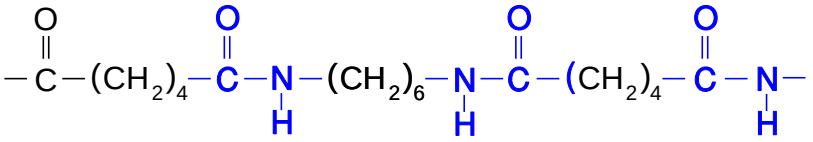
Equation

$$n\ HOOC(CH_2)_4COOH + n\ H_2N(CH_2)_6NH_2 \longrightarrow H\text{–}\ [\text{-}NH(CH_2)_6NHOC(CH_2)_4CO\text{-}]_n\ \text{–}OH + n\ H_2O$$

Repeat unit

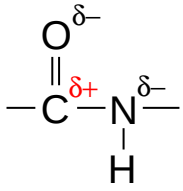
$$-\ [\text{-}NH(CH_2)_6NHOC(CH_2)_4CO\text{-}]_n\ —$$

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

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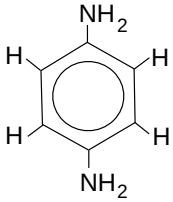
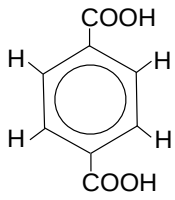
Kevlar

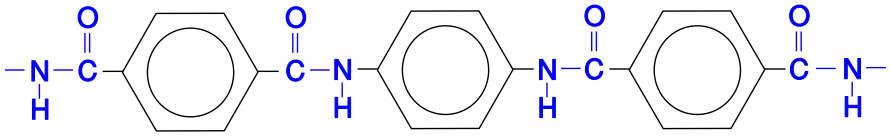
Reagents — *benzene-1,4-diamine*; *benzene-1,4-dicarboxylic acid*





Product — *Kevlar*

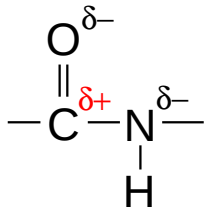
Structure



Use — *body armour*

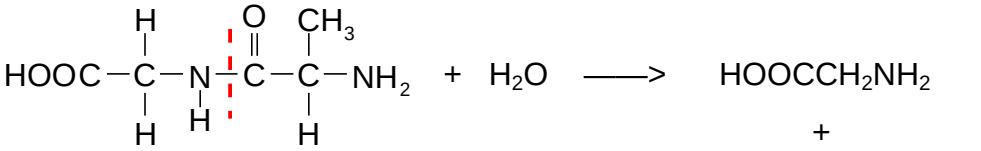
Peptides

- 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**



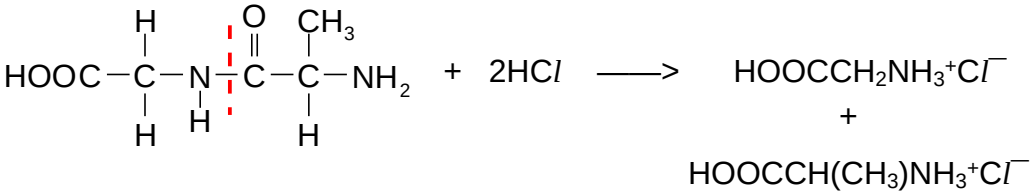
- **dipeptide** two amino acids joined together
  tripeptide three amino acids joined
  polypeptide many amino acids joined together
- a **protein** is a polypeptide with a **large relative molecular mass** (>10000)
- peptides/proteins **are broken down** into the original amino acids **by hydrolysis**

Hydrolysis



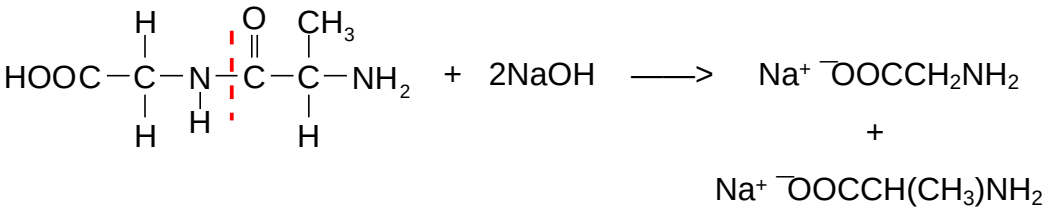
The acid and amine groups remain as they are

Acid Hydrolysis



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

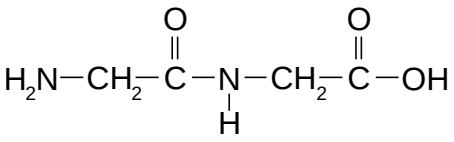
Base (alkaline) Hydrolysis



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.*



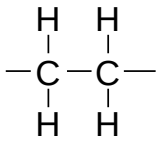
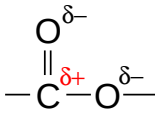
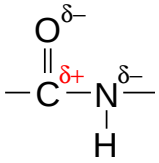
How many different amino acids formed the dipeptide? Draw their structure(s).

*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