— 1

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) $n CH_2=CH_2 \longrightarrow (CH_2-CH_2)_n$

poly(phenylethene)

poly(chloroethene)

poly(tetrafluoroethene)

poly(ethenyl ethanoate)

Preparation Many are prepared by a free radical process involving high pressure, high temperature and a catalyst. The catalyst is usually a substance (eg an 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 TiCl₄.

Properties

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

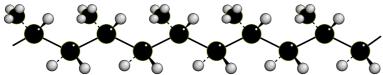
Chemical Are based on the functional groups within their structure.

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

Structures

Polymers based on substituted alkenes (propene and phenylethene) can exist in a variety of forms.

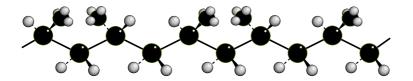
POLY(PROPENE)



ISOTACTIC

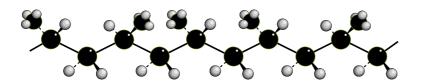
substituents on same side most desirable properties

Has the highest melting point because chains can get closer together giving greater intermolecular attraction



SYNDIOTACTIC

substituents on alternate sides



ATACTIC

random arrangement most likely outcome

COOH

COOH

CONDENSATION POLYMERS

• monomers join up the with expulsion of small molecules

2814

• not all the original atoms are present in the polymer

• examples include polyamides (nylon)

polyesters (terylene)

peptides starch

• reactions occur between diprotic carboxylic acids and diols

diprotic carboxylic acids and diamines

amino acids

POLYESTERS

Terylene Reagents terephthalic acid **HOOC-C**₆**H**₄**-COOH**

ethane-1,2-diol HOCH₂CH₂OH

Reaction Esterification

Eliminated water

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

Repeat unit — [-OCH₂CH₂OOC(C₆H₄)CO-] _n—

Structure

Equation HOCH₂CH₂OH + HOOC-C₆H₄-COOH —> -[-OCH₂CH₂OOC(C₆H₄)CO-]_n-

+ n H₂O

Properties • contain an ester link

• can be broken down by hydrolysis

the C-O bond breaks

• behaves as an ester

• biodegradable

Uses •

•

POLYAMIDES

Nylon-6,6 Rea

Reagents hexanedioic acid

HOOC(CH₂)₄COOH

hexane-1,6-diamine H₂N(CH₂)₆NH₂

Mechanism Addition-elimination

Eliminated water

Product Nylon-6,6 two repeating units, each with 6 carbon atoms

Repeat unit —[-NH(CH₂)₆NHOC(CH₂)₄CO-]_n—

Structure

Equation HOOC(CH₂)₄COOH + H₂N(CH₂)₆NH₂ \longrightarrow -[-NH(CH₂)₆NHOC(CH₂)₄CO-]_n- + n H₂O

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

 $-\operatorname{C}^{\overset{\delta_{+}}{\circ}}\operatorname{N}^{\overset{\delta_{-}}{\circ}}$

Uses

Q.1 Find out details of the synthesis of Nylon-6.

Peptides

· formed by joining amino acids together

• are examples of polyamides

amino acids have two main functional groups -COOH carboxylic acid
 -NH₂ 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 can be broken down into the original amino acids by hydrolysis
- **Q.2** Look up the structures of alanine and glycine. Draw the structure of the **dipeptide** formed when they react together.

How many different amino acids formed the dipeptide? Draw any structures.

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 H H -C-C- H H	ESTER LINK $O^{\delta-}$ $-C^{\delta+}O^{\delta-}$
		AMIDE (PEPTIDE) LINK $ \begin{array}{c} O^{\delta-} \\ -C \stackrel{\delta+}{-} N \stackrel{\delta-}{-} \\ H \end{array} $
Reactivity	UNREACTIVE - NON-POLAR Resistant to hydrolysis	REACTIVE - POLAR BONDS Hydrolysed by acids and alkalis reflux with acid RCOOH + ROH reflux with alkali RCOOTNa+ + ROH
Uses	Packaging Insulation	Clothing Ropes
Examples	poly(ethene) poly(propene) poly(phenylethene) poly(chloroethene)	nylon 6,6 Terylene peptides