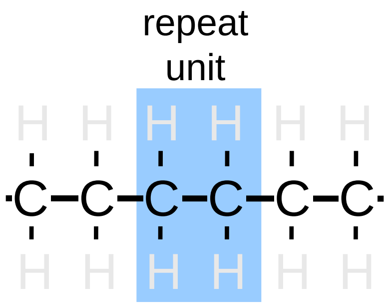
THE CHEMISTRY OF POLYMERS

POLYMERS

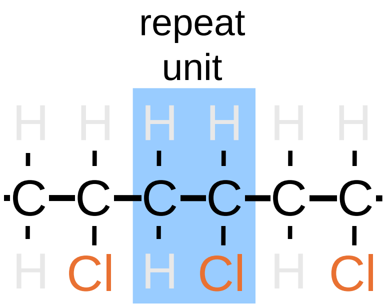
CONTENTS

What is a Polymer?

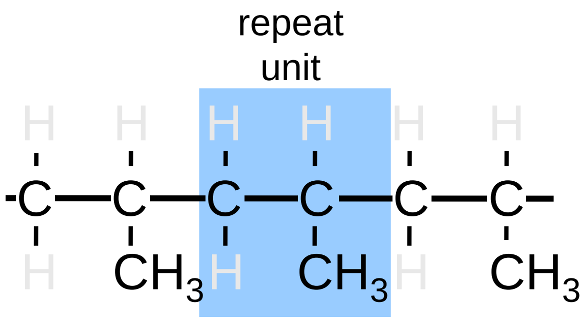
Poly	mer
many	repeat unit



Polyethylene (PE)



Poly(vinyl chloride) (PVC)



Polypropylene (PP)

Adapted from Fig. 14.2, *Callister & Rethwisch 8e.*

Ancient Polymers

Originally natural polymers were used

-Wood
-Cotton
-Leather
– Rubber
– Wool
– Silk

Oldest known uses

- Rubber balls used by Incas
- Noah used pitch (a natural polymer) for the ark

Polymer Composition

Most polymers are hydrocarbons
  – i.e., made up of H and C

- Saturated hydrocarbons
  - Each carbon singly bonded to four other atoms
  - Example:
    - Ethane, C_2H_6

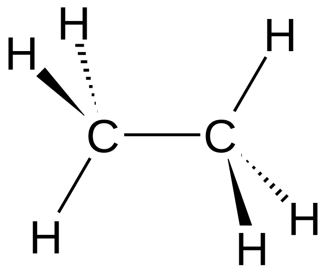
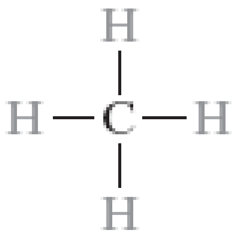
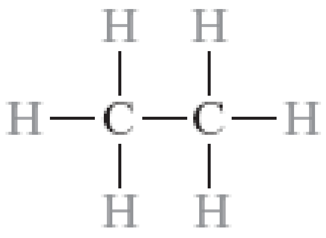
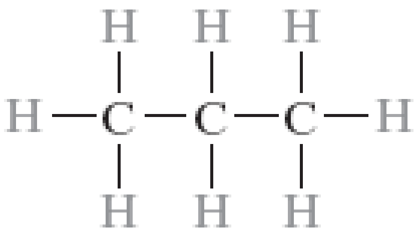
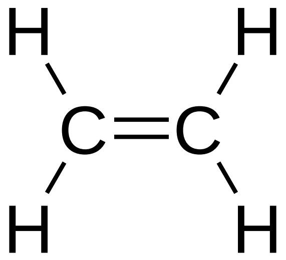


Table 14.1 Compositions and Molecular Structures for Some of the Paraffin Compounds: C_nH_{2n+2}

Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4	 $H-\underset{\overset{\vert}{H}}{\overset{\underset{\vert}{H}}{C}}-H$	−164
Ethane	C_2H_6	 $H-\underset{\overset{\vert}{H}}{\overset{\underset{\vert}{H}}{C}}-\underset{\overset{\vert}{H}}{\overset{\underset{\vert}{H}}{C}}-H$	−88.6
Propane	C_3H_8	 $H-\underset{\overset{\vert}{H}}{\overset{\underset{\vert}{H}}{C}}-\underset{\overset{\vert}{H}}{\overset{\underset{\vert}{H}}{C}}-\underset{\overset{\vert}{H}}{\overset{\underset{\vert}{H}}{C}}-H$	−42.1
Butane	C_4H_{10}		−0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

Unsaturated Hydrocarbons

- Double & triple bonds somewhat unstable – can form new bonds
  - Double bond found in ethylene or ethene - C_2H_4



  - Triple bond found in acetylene or ethyne - C_2H_2

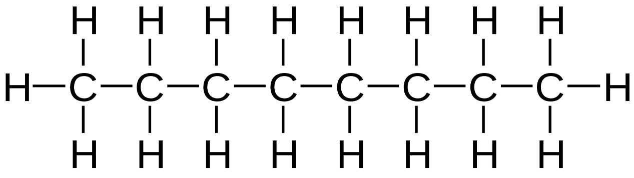
$$H-C\equiv C-H$$

Isomerism

- Isomerism
  - two compounds with same chemical formula can have quite different structures

    for example: C_8H_{18}

    - normal-octane



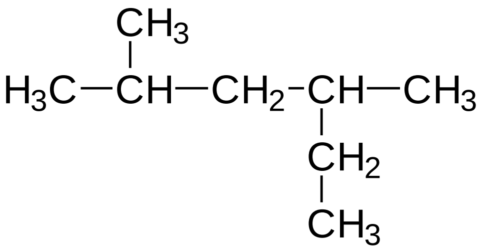
$$\begin{array}{ccccccccccccccccc} & & H & & H & & H & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & H & & H & & H & & \end{array}$$

$= H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

$$\Downarrow$$

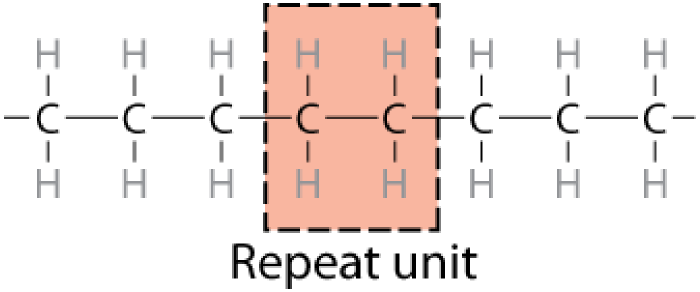
$H_3C\left(CH_2\right)_6CH_3$

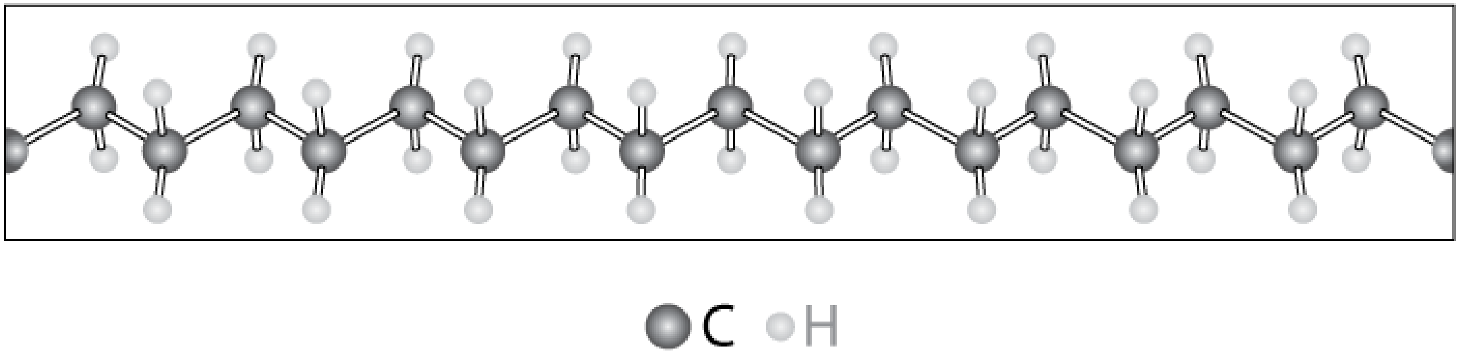
    - 2,4-dimethylhexane



$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-\underset{\underset{\underset{\underset{\displaystyle CH_3}{|}}{\displaystyle CH_2}}{|}}{CH}-CH_3$$

Chemistry and Structure of Polyethylene





Note: polyethylene is a long-chain hydrocarbon

- paraffin wax for candles is short polyethylene

Bulk or Commodity Polymers

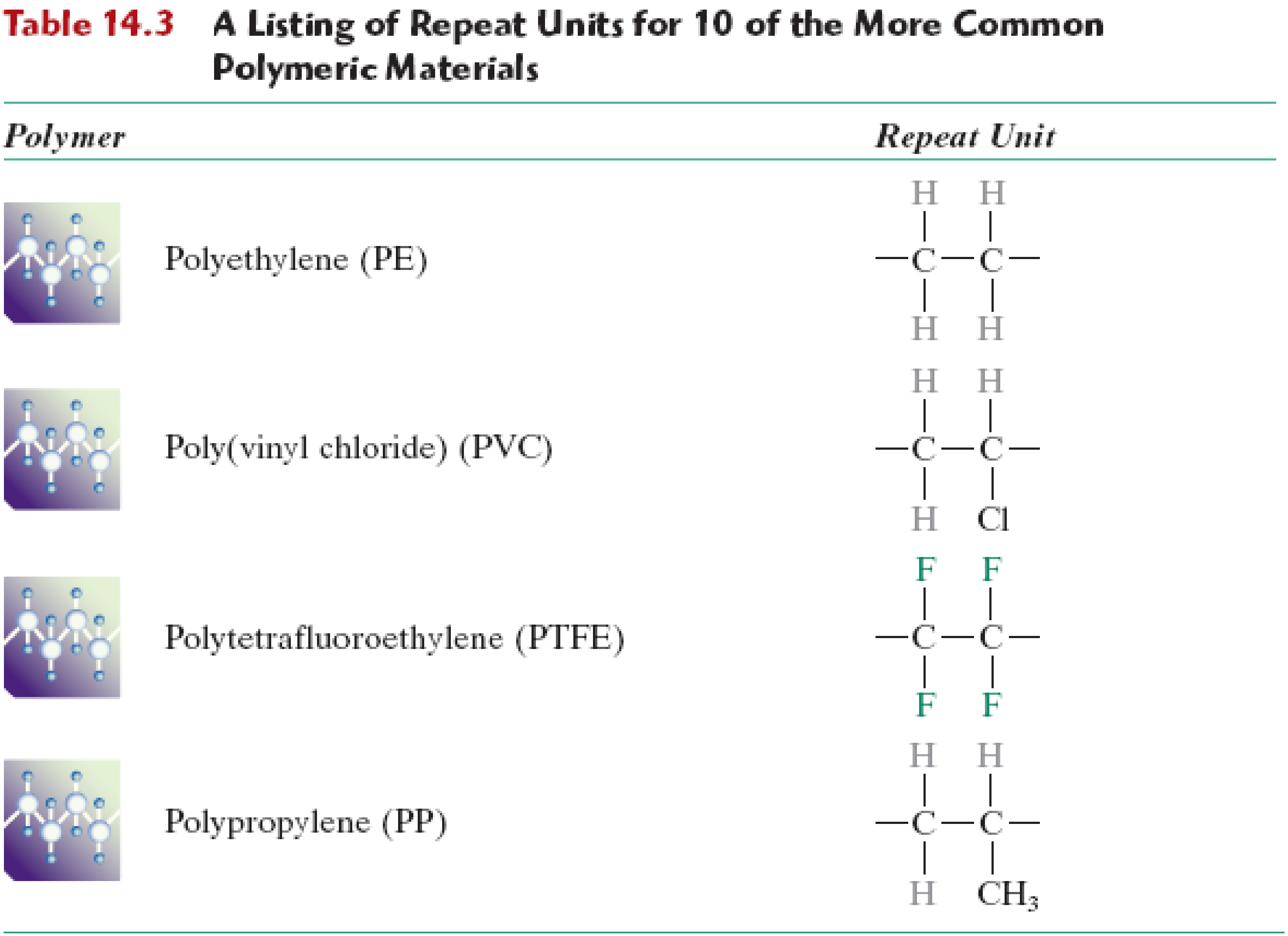
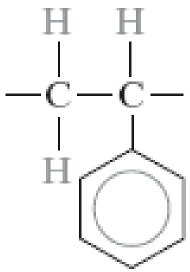
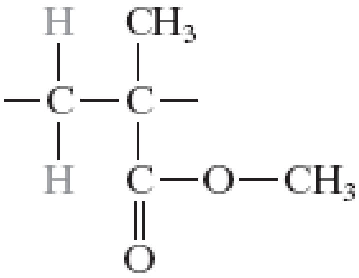
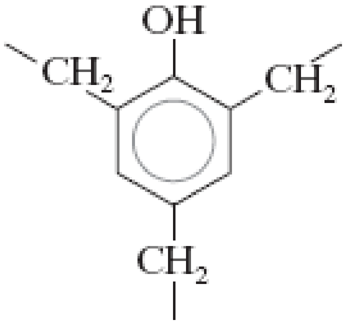


Table 14.3 **A Listing of Repeat Units for 10 of the More Common Polymeric Materials**

Polymer	*Repeat Unit*
Polyethylene (PE)	$-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-$
Poly(vinyl chloride) (PVC)	$-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}-$
Polytetrafluoroethylene (PTFE)	$-\underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{C}}}-\underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{C}}}-$
Polypropylene (PP)	$-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{CH_3}}{\overset{\mathrm{H}}{\mathrm{C}}}-$

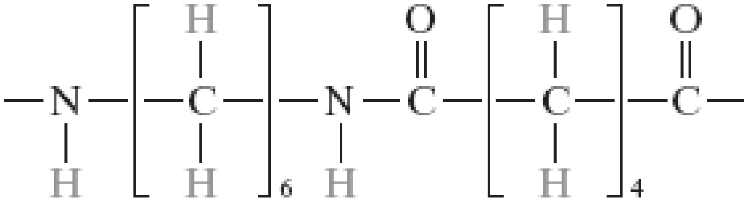
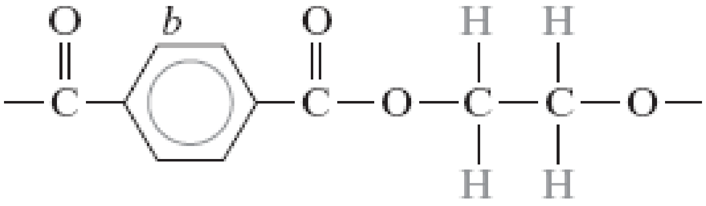
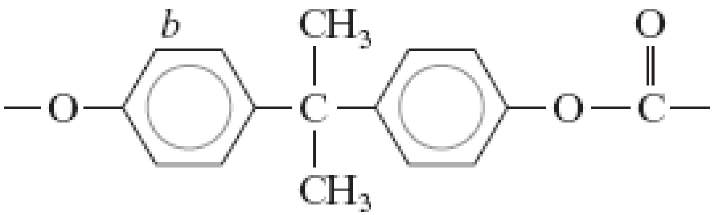
Bulk or Commodity Polymers (cont)

Table 14.3 **A Listing of Repeat Units for 10 of the More Common Polymeric Materials**

Polymer	*Repeat Unit*
Polystyrene (PS)	
Poly(methyl methacrylate) (PMMA)	
Phenol-formaldehyde (Bakelite)	

Bulk or Commodity Polymers (cont)

Table 14.3 **A Listing of Repeat Units for 10 of the More Common Polymeric Materials**

Polymer	*Repeat Unit*
Poly(hexamethylene adipamide) (nylon 6,6)	 $-\underset{\mathrm{H}}{\mathrm{N}}-\left[\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\right]_6-\underset{\mathrm{H}}{\mathrm{N}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\left[\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\right]_4-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-$
Poly(ethylene terephthalate) (PET, a polyester)	
Polycarbonate (PC)	

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	all the atoms in the monomer are used to form the polymer
CONDENSATION	monomers join up the with expulsion of small molecules not all the original atoms are present in the polymer

ADDITION POLYMERISATION

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

POLYMERISATION OF ALKENES

ADDITION POLYMERISATION

Preparation

Often by a free radical process involving high pressure, high temperature and a catalyst. The catalyst is usually a substance (e.g. an organic peroxide) which readily breaks up to form radicals which initiate a chain reaction.

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

Properties

Physical vary with reaction conditions (pressure, temperature etc).

Chemical based on the functional groups in their structure

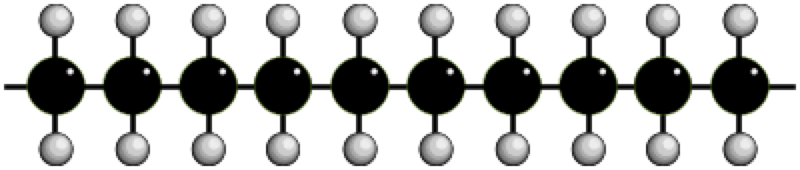
poly(ethene) is typical; it is fairly inert as it is basically a very large alkane. This means it is resistant to chemical attack and non-biodegradable.

POLYMERISATION OF ALKENES

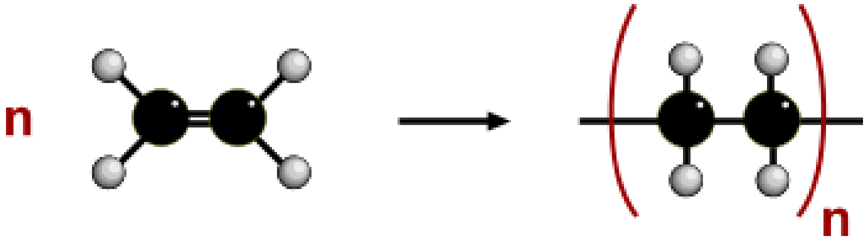
ADDITION POLYMERISATION

Process

- during polymerisation, an alkene undergoes an addition reaction with itself
- all the atoms in the original alkenes are used to form the polymer
- long hydrocarbon chains are formed



The equation shows the original monomer and the repeating unit in the polymer



ethene

MONOMER

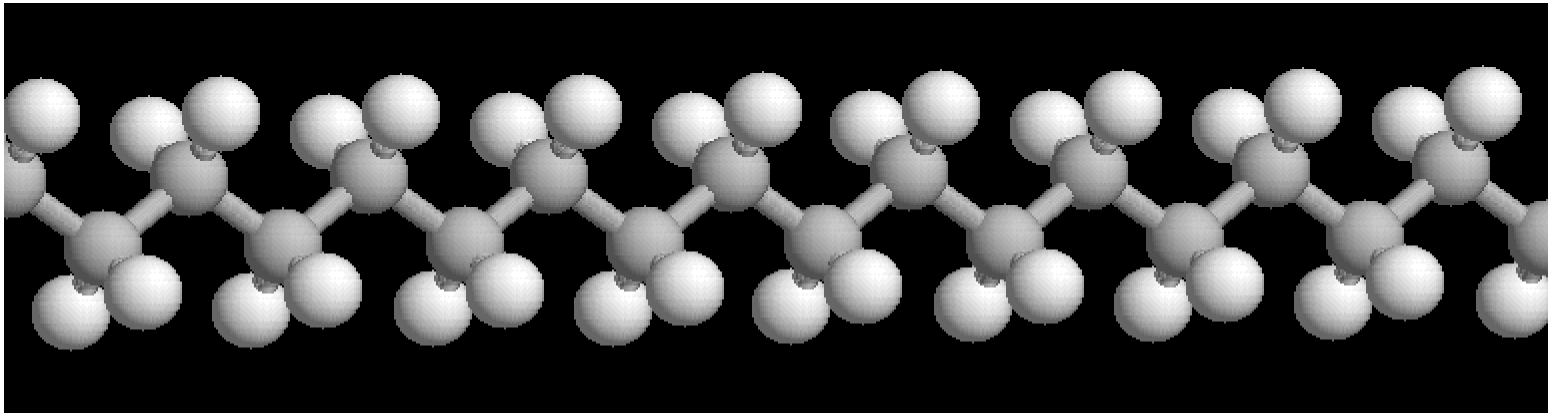
poly(ethene)

POLYMER

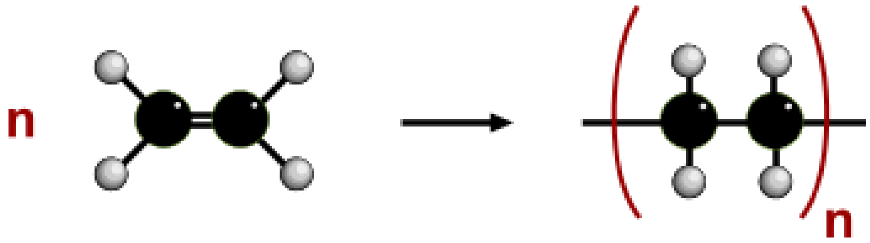
n represents a large number

POLYMERISATION OF ALKENES

ADDITION POLYMERISATION



The equation shows the original monomer and the repeating unit in the polymer



ethene

MONOMER

poly(ethene)

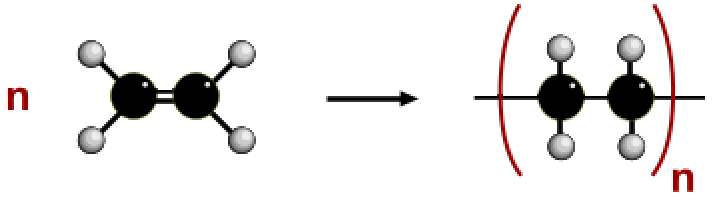
POLYMER

n represents a large number

POLYMERISATION OF ALKENES

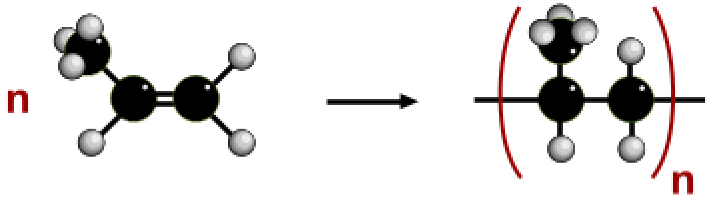
EXAMPLES OF ADDITION POLYMERISATION

ETHENE



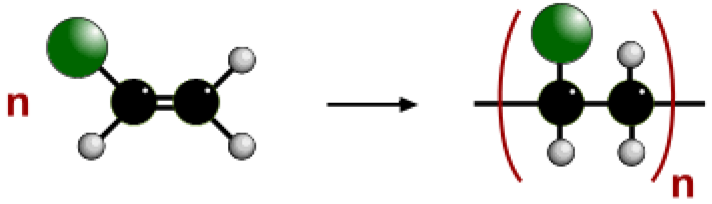
POLY(ETHENE)

PROPENE



POLY(PROPENE)

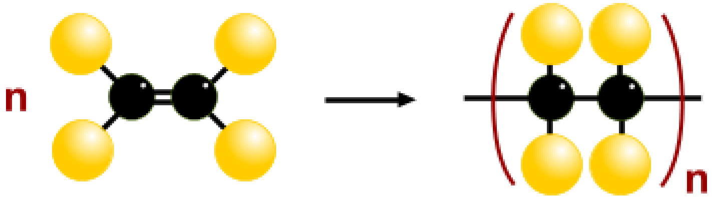
CHLOROETHENE



POLY(CHLOROETHENE)

POLYVINYLCHLORIDE PVC

TETRAFLUOROETHENE

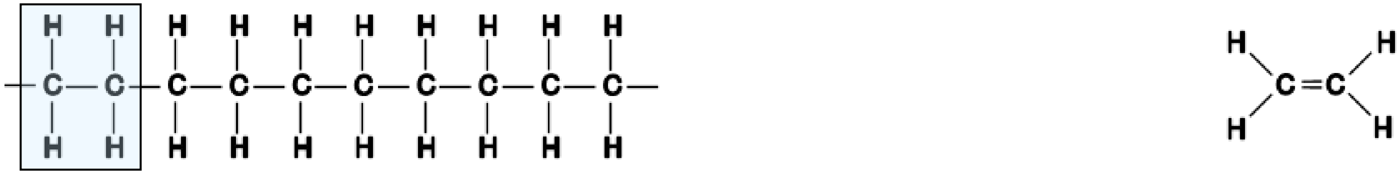


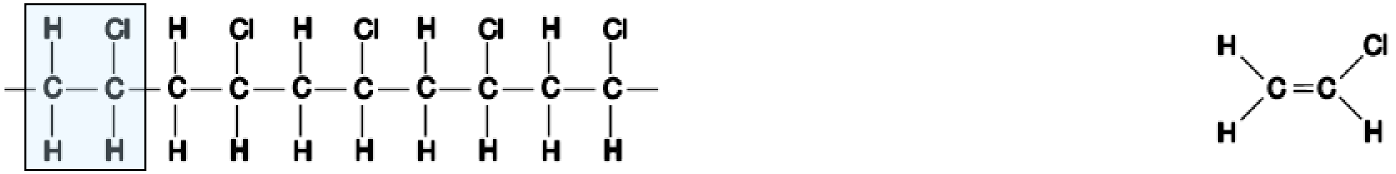
POLY(TETRAFLUOROETHENE)

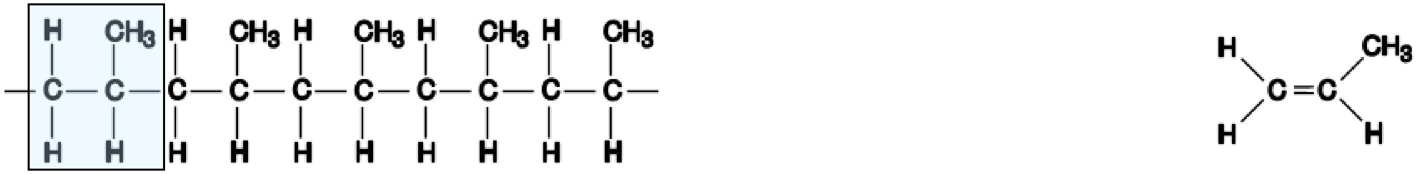
PTFE “Teflon”

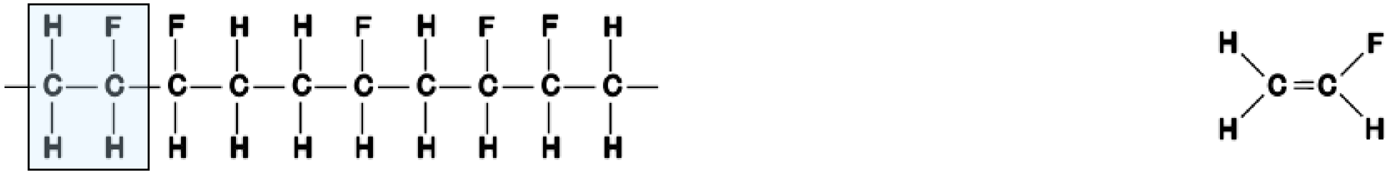
POLYMERISATION OF ALKENES

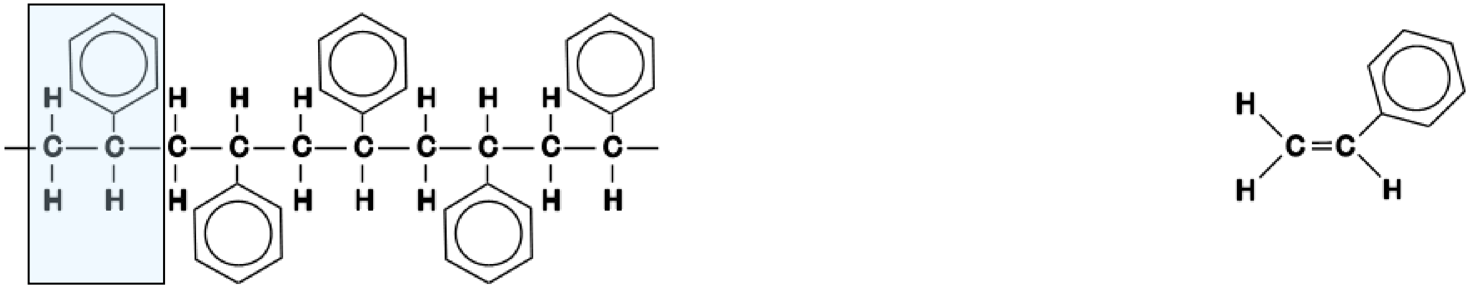
SPOTTING THE MONOMER



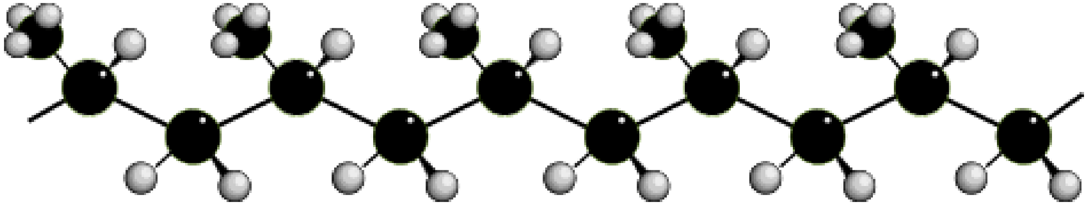








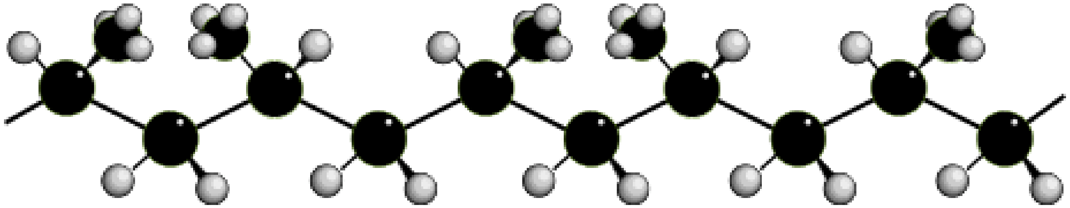
POLY(PROPENE)



ISOTACTIC

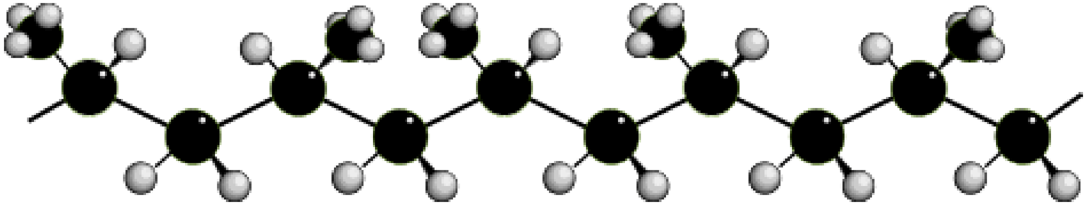
CH_3 groups on same side

- most desirable properties
- highest melting point



SYNDIOTACTIC

CH_3 groups alternate sided



ATACTIC

random

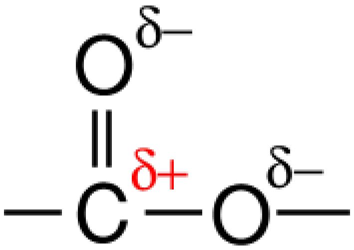
most likely outcome

CONDENSATION POLYMERS

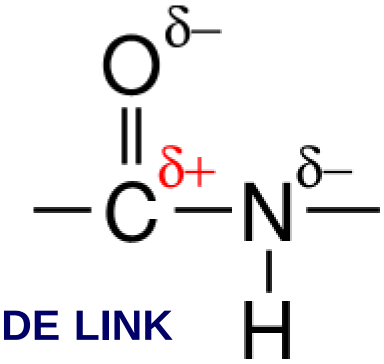
- monomers join up the with expulsion of small molecules
- not all the original atoms are present in the polymer

Examples polyamides (nylon) (kevlar)
polyesters (terylene) (polylactic acid)
peptides
starch

Synthesis reactions between diprotic carboxylic acids and diols
diprotic carboxylic acids and diamines
amino acids



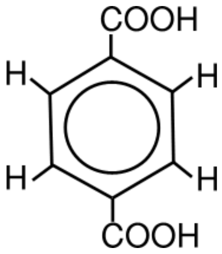
ESTER LINK

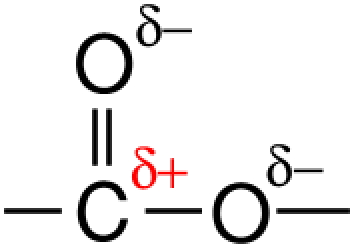


AMIDE LINK

POLYESTERS - TERYLENE

Reagents	terephthalic acid	$HOOC\text{-}C_6H_4\text{-}COOH$
	ethane-1,2-diol	$HOCH_2CH_2OH$
Reaction	esterification	
Eliminated	water	
Equation	$n\ HOCH_2CH_2OH\ +\ n\ HOOC\text{-}C_6H_4\text{-}COOH \longrightarrow \text{-}[OCH_2CH_2OOC(C_6H_4)CO]_n\text{-}\ +\ n\ H_2O$	
Repeat unit	$\text{—}\ [\text{-}OCH_2CH_2OOC(C_6H_4)CO\text{-}]_n\ \text{—}$	
Product	poly(ethylene terephthalate)	‘Terylene’, ‘Dacron’
Properties	contains an ester link can be broken down by hydrolysis the C-O bond breaks behaves as an ester biodegradable	
Uses	fabrics	

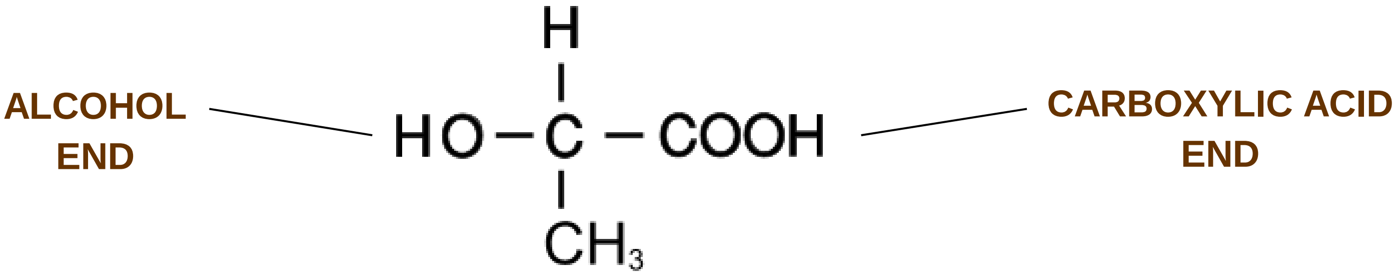




an ester link

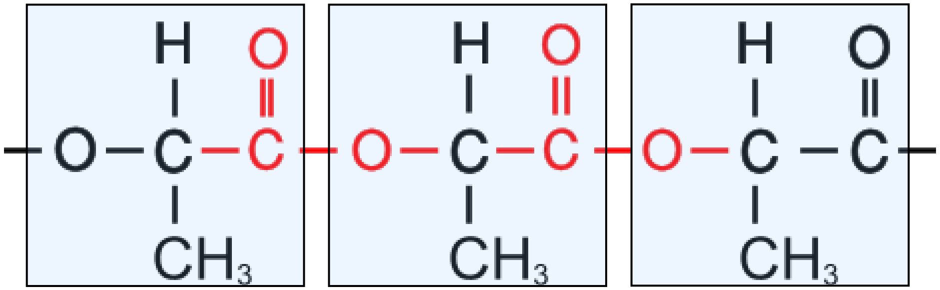
POLYESTERS – POLY(LACTIC ACID)

Reagent	2-hydroxypropanoic acid (*lactic acid*)	$CH_3CH(OH)COOH$



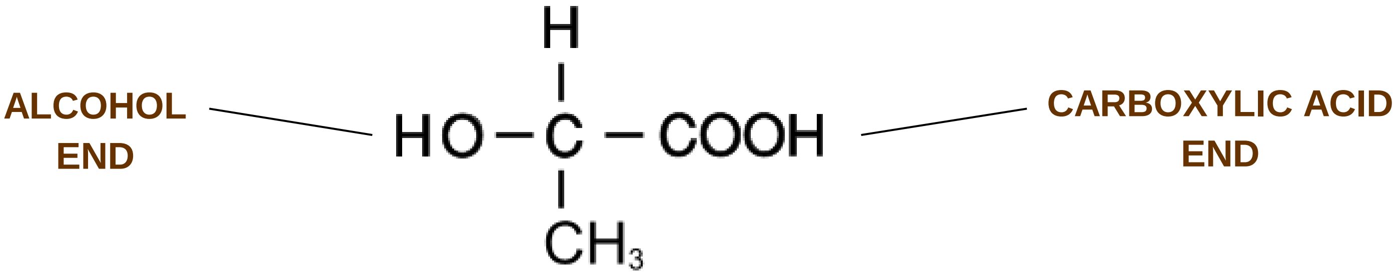
$$\mathrm{HO-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-COOH}$$

Reaction	esterification
Eliminated	water
Equation	$n\ CH_3CH(OH)COOH \longrightarrow -[\text{-}OCH(CH_3)CO\text{-}]_n- \quad + \quad n\ H_2O$
Product	poly(lactic acid)
Repeat unit	$—\ [\text{-}OCH(CH_3)CO\text{-}]\ —$



POLYESTERS – POLY(LACTIC ACID)

Reagent	2-hydroxypropanoic acid (*lactic acid*)	$CH_3CH(OH)COOH$

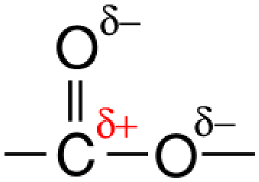


$$HO-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-COOH$$

ALCOHOL END

CARBOXYLIC ACID END

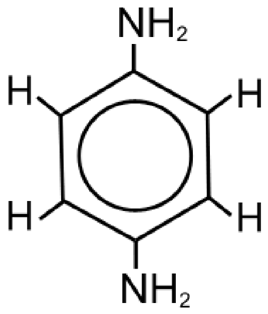
Product	poly(lactic acid)
Properties	contains an ester link can be broken down by hydrolysis the C-O bond breaks behaves as an ester (hydrolysed at the ester link) biodegradable photobiodegradable (C=O absorbs radiation)
Uses	waste sacks and packaging disposable eating utensils internal stitches



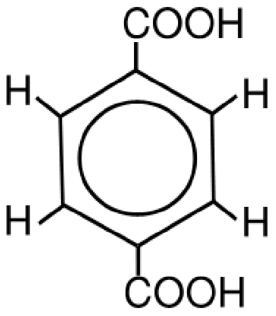
POLYAMIDES – KEVLAR

Reagents

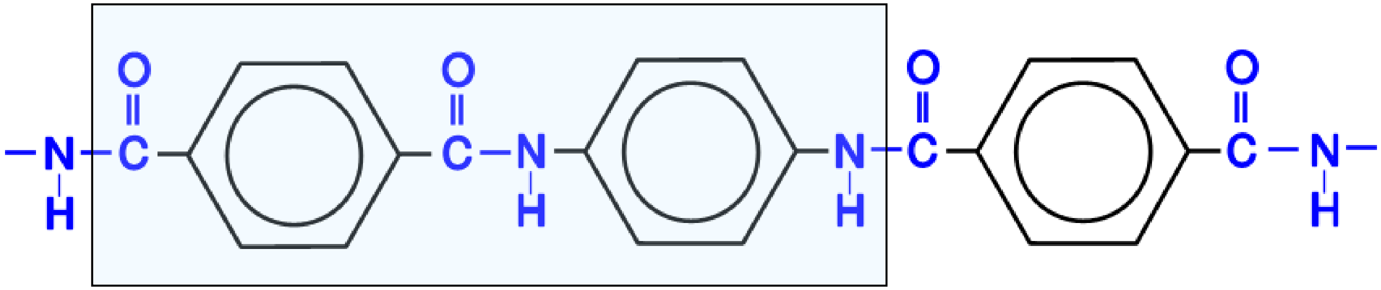
benzene-1,4-diamine



benzene-1,4-dicarboxylic acid



Repeat unit



Properties

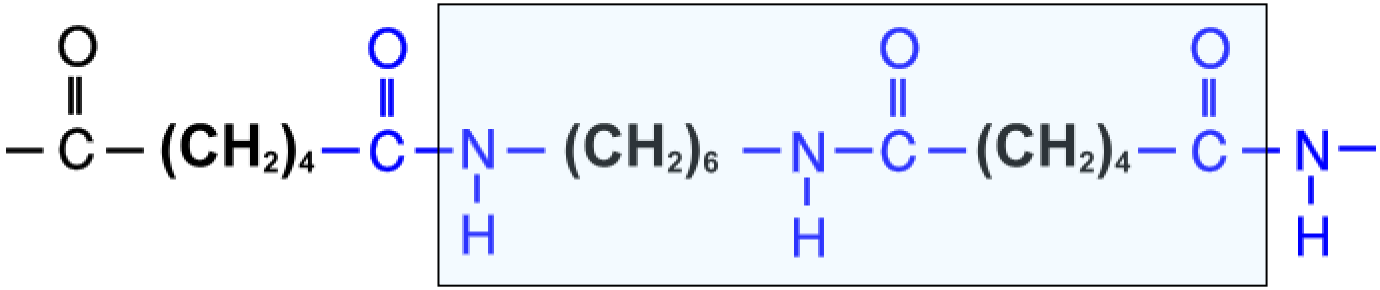
contains an amide link

Uses

body armour

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	
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	$—[-NH(CH_2)_6NHOC(CH_2)_4CO-]_n—$	

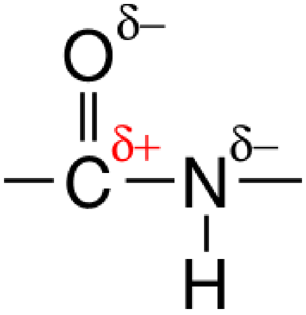


$$-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-(CH_2)_6-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-$$

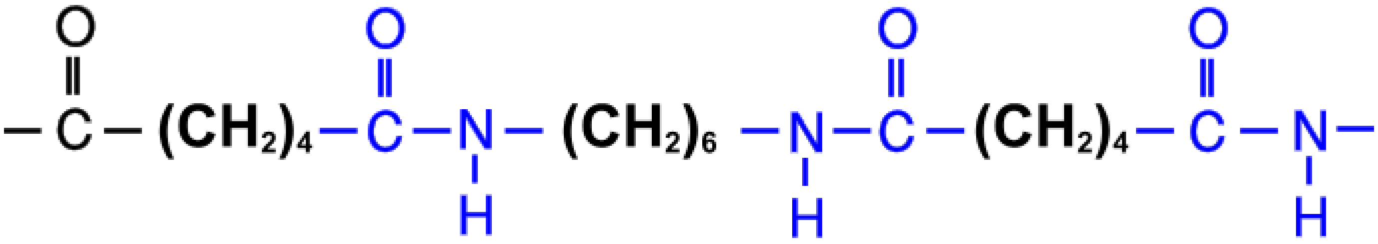
Product	Nylon-6,6 two repeating units, each with 6 carbon atoms

Polyamides - NYLON-6,6

Properties	contains 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	fibres and ropes



$$-\overset{\overset{\delta-}{O}}{\overset{\|}{\underset{\delta+}{C}}}-\underset{\underset{H}{|}}{\overset{\delta-}{N}}-$$

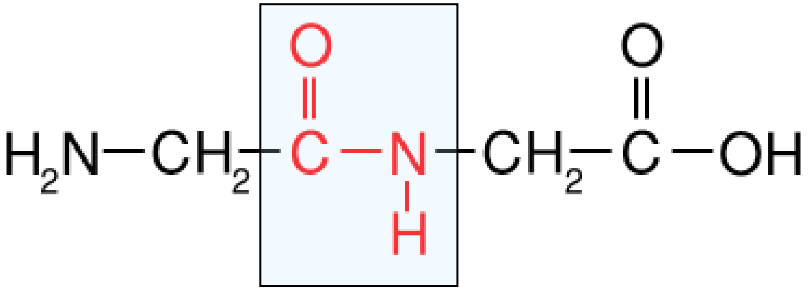


$$-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-(CH_2)_6-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-$$

Peptides

Reagents	amino acids
Equation	$H_2NCCH_2COOH + H_2NC(CH_3)COOH \longrightarrow H_2NCCH_2CONHHC(CH_3)COOH + H_2O$
Product	peptide (the above shows the formation of a dipeptide)
Eliminated	water
Mechanism	addition-elimination

Amino acids join together via an amide or peptide link



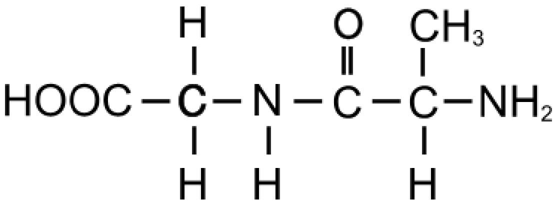
$$H_2N-CH_2-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

a dipeptide

2 amino acids joined	dipeptide
3 amino acids joined	tripeptide
many amino acids joined	polypeptide

Hydrolysis of peptides

Hydrolysis



$$HOOC-\underset{H}{\overset{H}{C}}-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{CH_3}{C}}-NH_2 + H_2O \longrightarrow HOOCCH_2NH_2 + HOOCCH(CH_3)NH_2$$

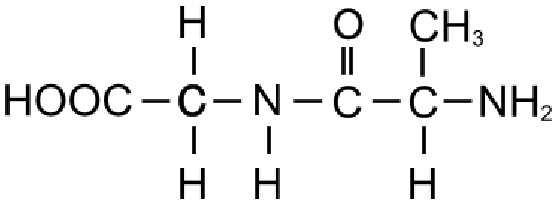
The acid and amine groups remain as they are

Hydrolysis is much quicker if acidic or alkaline conditions are used.

However, there is a slight variation in products.

Hydrolysis of peptides

Acid hydrolysis



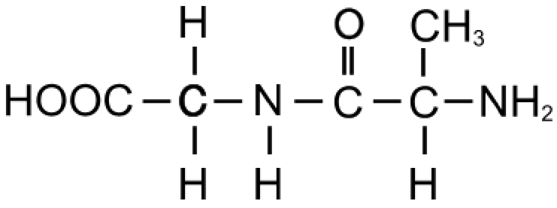
$$HOOC-CH_2-NH-\overset{O}{\overset{\|}{C}}-CH(CH_3)-NH_2$$

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

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

Hydrolysis of peptides

Base (alkaline) hydrolysis



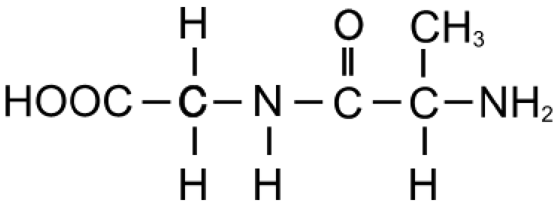
$$HOOC-CH_2-NH-CO-CH(CH_3)-NH_2$$

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

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

Hydrolysis of peptides

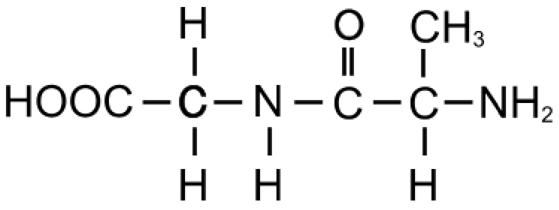
Hydrolysis



$$\mathrm{HOOC{-}\overset{H}{\underset{H}{C}}{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{CH_3}{\underset{H}{C}}{-}NH_2} \quad + \quad H_2O \quad \longrightarrow \quad \begin{array}{c} HOOCCH_2NH_2 \\ + \\ HOOCCH(CH_3)NH_2 \end{array}$$

The acid and amine groups remain as they are

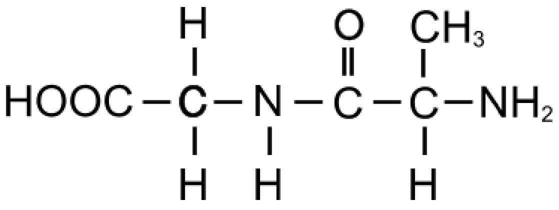
Acid hydrolysis



$$\mathrm{HOOC{-}\overset{H}{\underset{H}{C}}{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{CH_3}{\underset{H}{C}}{-}NH_2} \quad + \quad 2HCl \quad \longrightarrow \quad \begin{array}{c} HOOCCH_2NH_3^+Cl^- \\ + \\ HOOCCH(CH_3)NH_3^+Cl^- \end{array}$$

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

Base (alkaline) hydrolysis



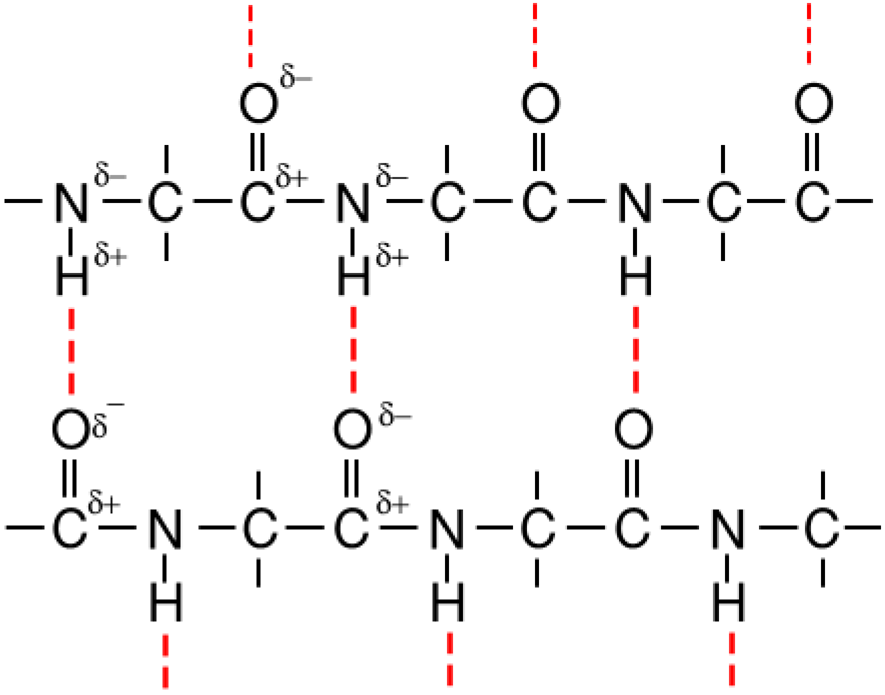
$$\mathrm{HOOC{-}\overset{H}{\underset{H}{C}}{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{CH_3}{\underset{H}{C}}{-}NH_2} \quad + \quad 2NaOH \quad \longrightarrow \quad \begin{array}{c} Na+\ {}^-OOCCH_2NH_2 \\ + \\ Na+\ {}^-OOCCH(CH_3)NH_2 \end{array}$$

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

Proteins

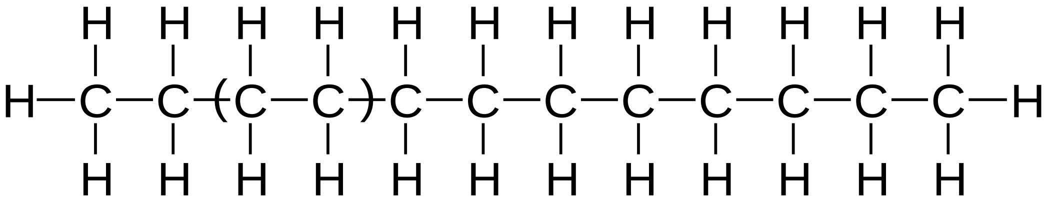
- polypeptides with large relative molecular masses (>10000)
- chains can be lined up with each other
- the C=O and N-H bonds are polar due to a difference in electronegativity
- hydrogen bonding exists between chains

dotted lines ---------- represent hydrogen bonding



Degree of Polymerization, *DP*

DP = average number of repeat units per chain



$$H-CH_2-CH_2-(CH_2-CH_2)-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-H$$

DP = 6

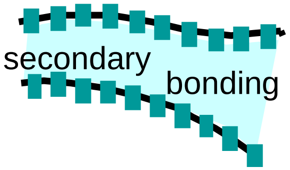
$$DP = \frac{\overline{M}_n}{\overline{m}}$$

where $\overline{m}$ = average molecular weight of repeat unit

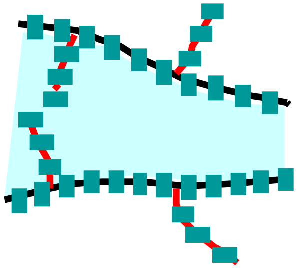
for copolymers this is calculated as follows:

$$\overline{m} = \Sigma \underbrace{f_i}_{\text{Chain fraction}} \underbrace{m_i}_{\text{mol. wt of repeat unit } i}$$

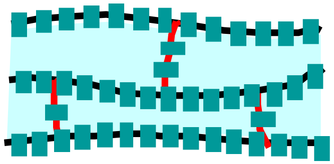
Molecular Structures for Polymers



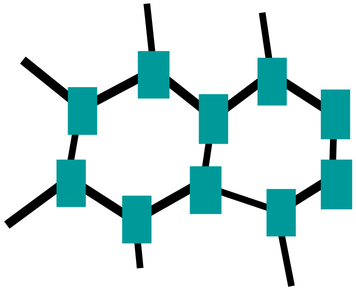
Linear



Branched



Cross-Linked

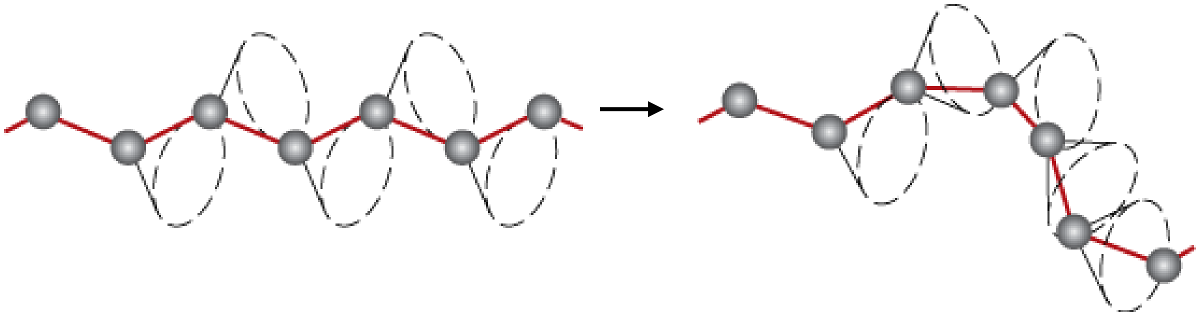


Network

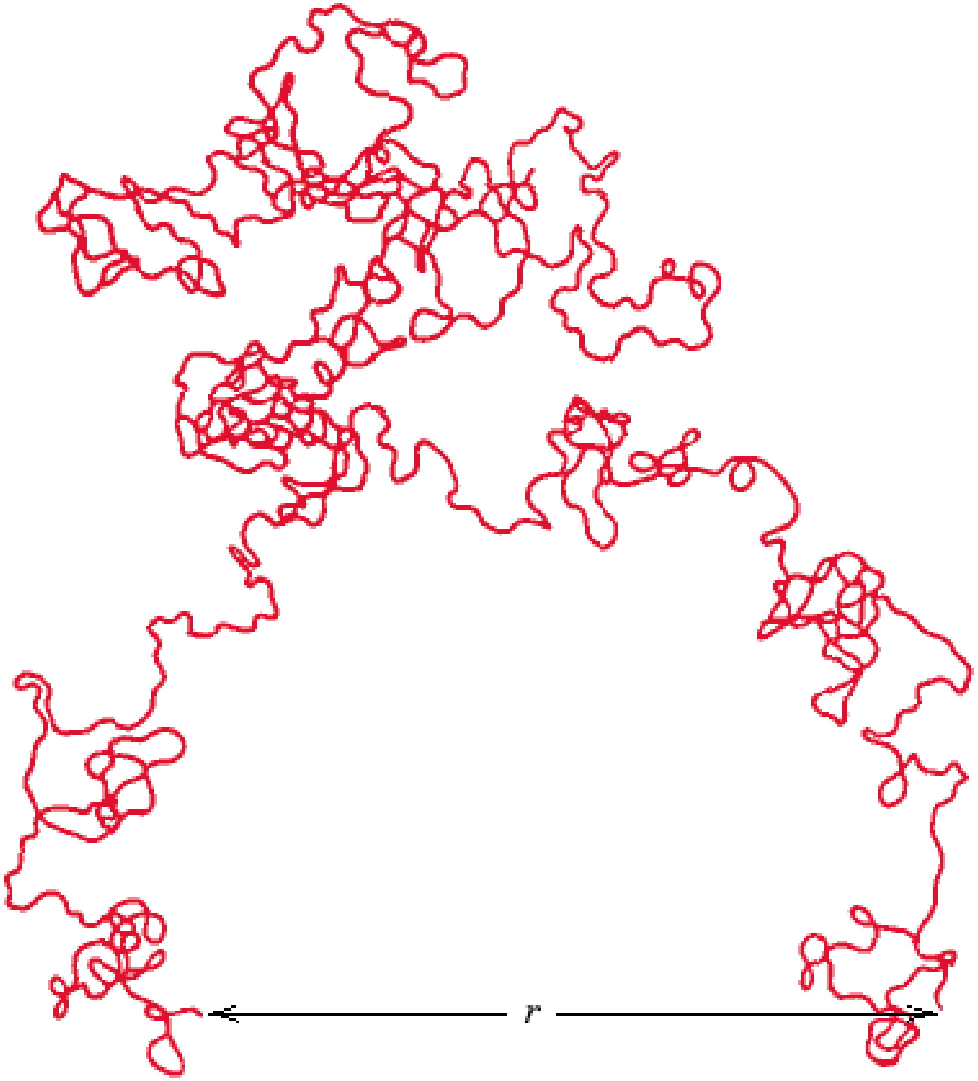
Polymers – Molecular Shape

Molecular Shape (or Conformation) – chain bending and twisting are possible by rotation of carbon atoms around their chain bonds

- note: not necessary to break chain bonds to alter molecular shape



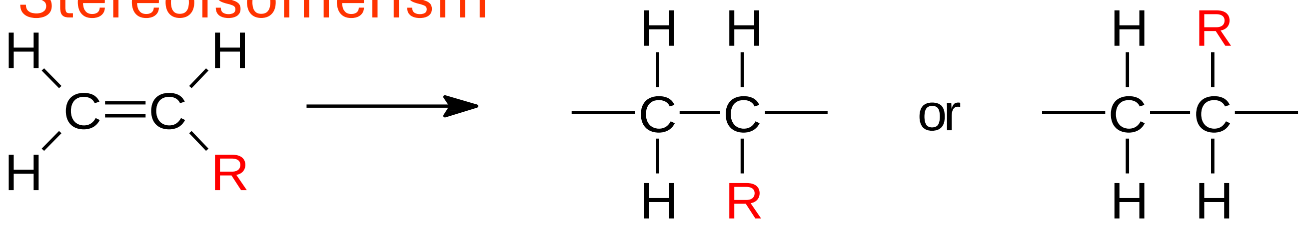
Chain End-to-End Distance, *r*



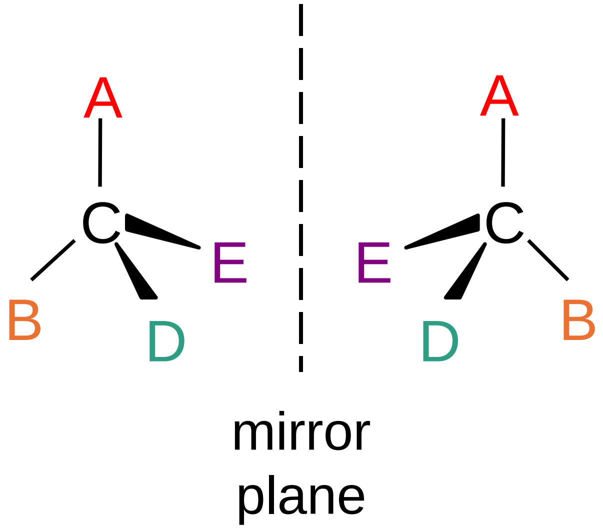
Molecular Configurations for Polymers

Configurations – to change must break bonds

- Stereoisomerism



Stereoisomers are mirror images – can't superimpose without breaking a bond

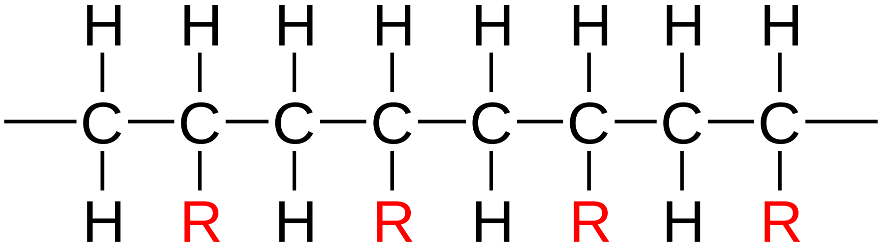


Tacticity

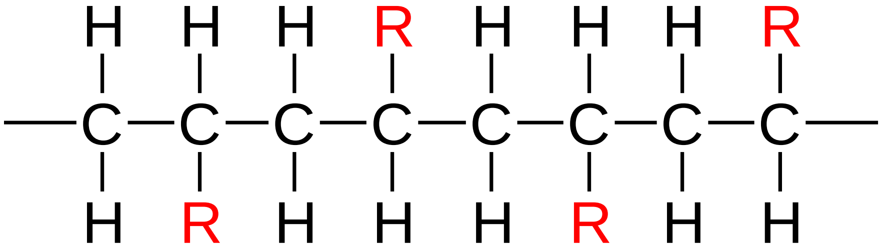
Tacticity – stereoregularity or spatial arrangement of R units along chain

isotactic – all R groups on same side of chain

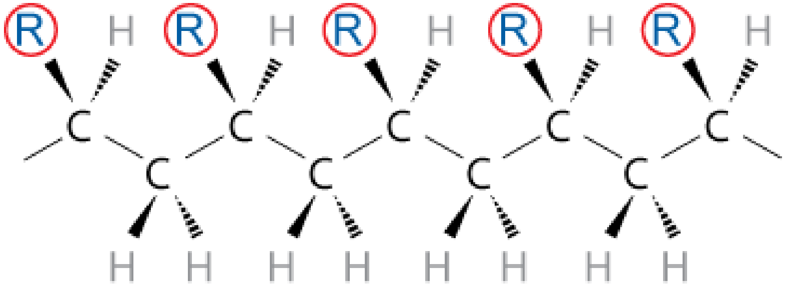
syndiotactic – R groups alternate sides

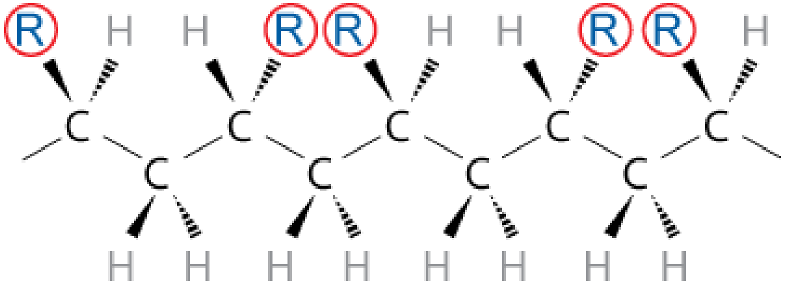


$$\begin{array}{ccccccccccccccccc}
 & H & & H & & H & & H & & H & & H & & H & & H & \\
 & | & & | & & | & & | & & | & & | & & | & & | & \\
— & C & — & C & — & C & — & C & — & C & — & C & — & C & — & C & — \\
 & | & & | & & | & & | & & | & & | & & | & & | & \\
 & H & & R & & H & & R & & H & & R & & H & & R &
\end{array}$$



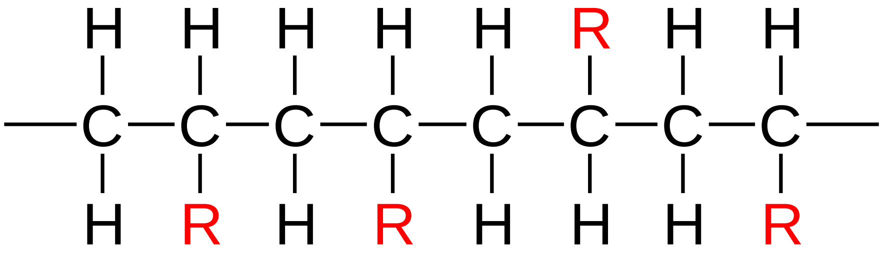
$$\begin{array}{ccccccccccccccccc}
 & H & & H & & H & & R & & H & & H & & H & & R & \\
 & | & & | & & | & & | & & | & & | & & | & & | & \\
— & C & — & C & — & C & — & C & — & C & — & C & — & C & — & C & — \\
 & | & & | & & | & & | & & | & & | & & | & & | & \\
 & H & & R & & H & & H & & H & & R & & H & & H &
\end{array}$$



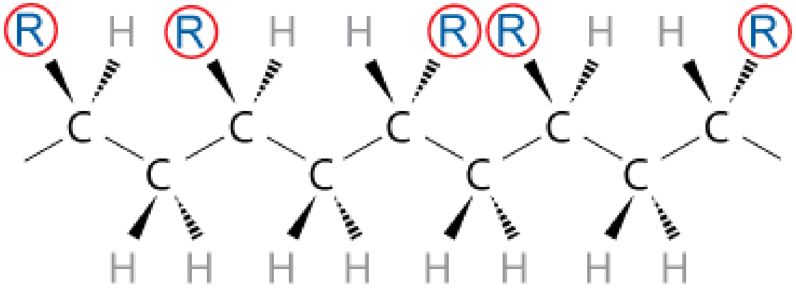


Tacticity (cont.)

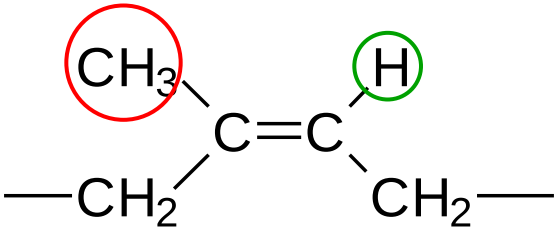
atactic – R groups randomly positioned



$$\begin{array}{ccccccccccccccccc} & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{R} & & \mathrm{H} & & \mathrm{H} & \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ & \mathrm{H} & & \mathrm{R} & & \mathrm{H} & & \mathrm{R} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{R} & \end{array}$$



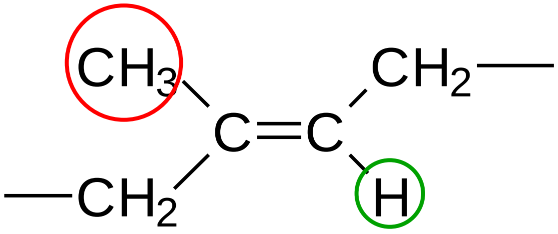
cis/trans Isomerism



cis

cis-isoprene
(natural rubber)

H atom and CH_3 group on
same side of chain

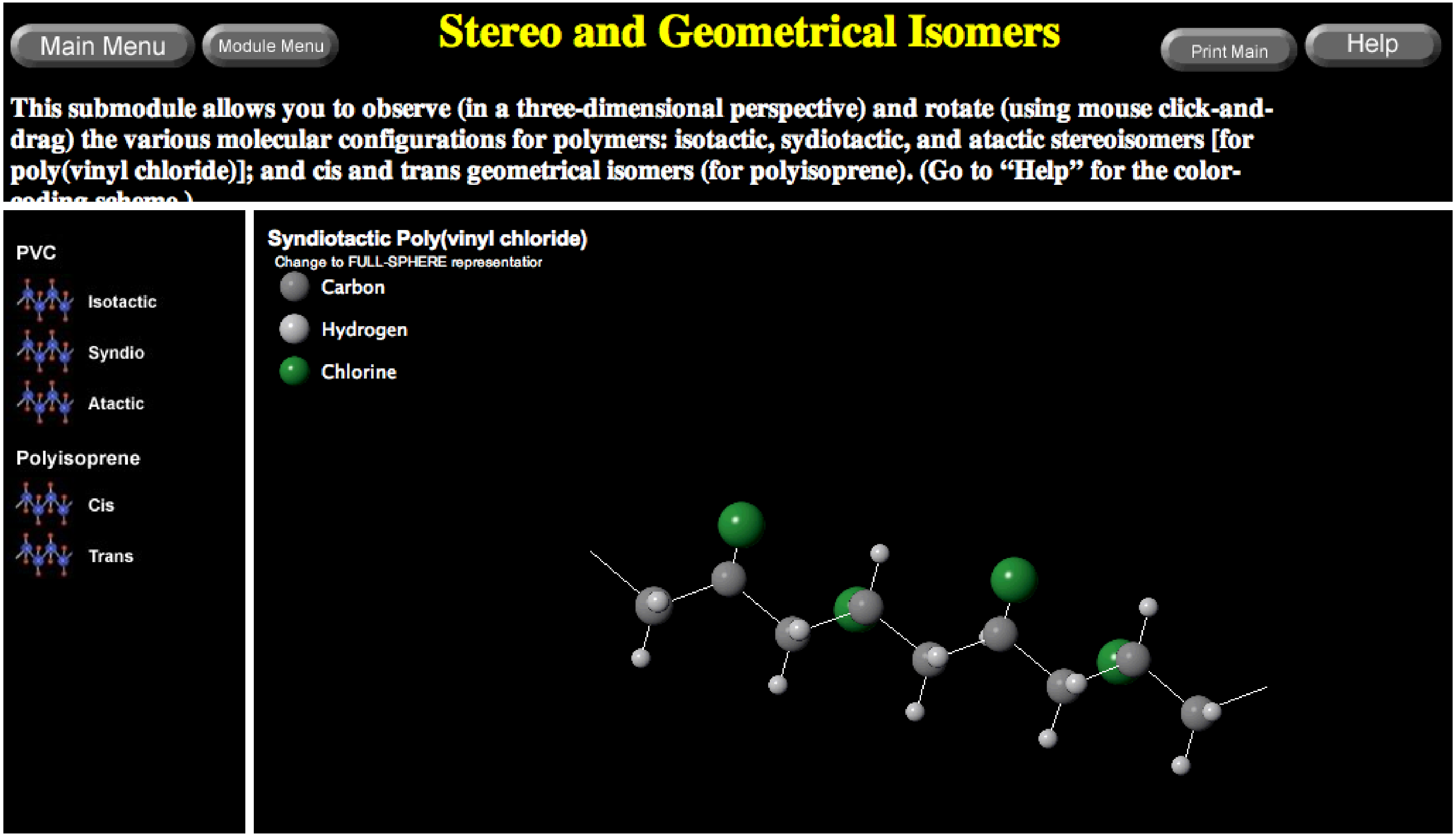


trans

trans-isoprene
(gutta percha)

H atom and CH_3 group on
opposite sides of chain

VMSE: Stereo and Geometrical Isomers



This submodule allows you to observe (in a three-dimensional perspective) and rotate (using mouse click-and-drag) the various molecular configurations for polymers: isotactic, sydiotactic, and atactic stereoisomers [for poly(vinyl chloride)]; and cis and trans geometrical isomers (for polyisoprene). (Go to "Help" for the color-coding scheme.)

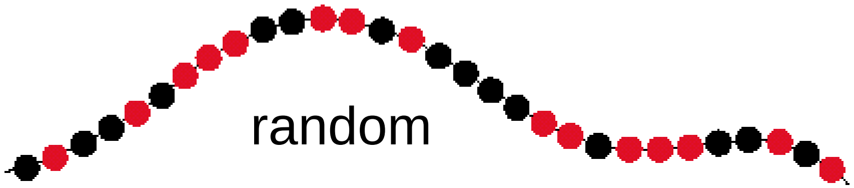
Manipulate and rotate polymer structures in 3-dimensions

Copolymers

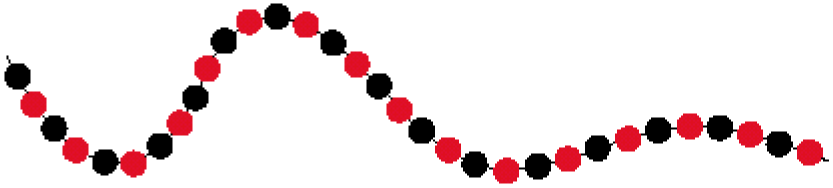
two or more monomers polymerized together

- random – A and B randomly positioned along chain
- alternating – A and B alternate in polymer chain
- block – large blocks of A units alternate with large blocks of B units
- graft – chains of B units grafted onto A backbone

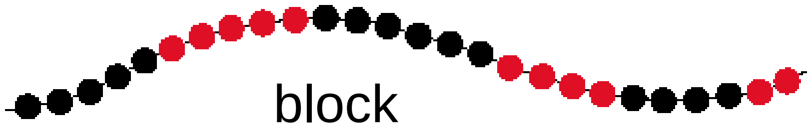
A – 🔴 B – ⚫



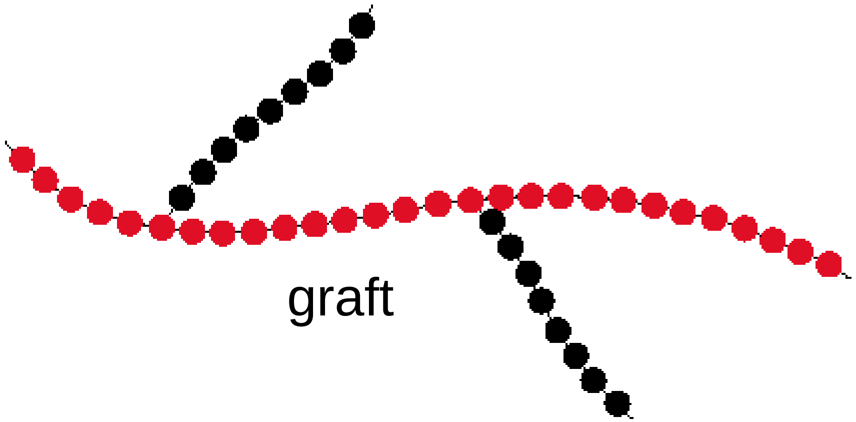
random



alternating



block

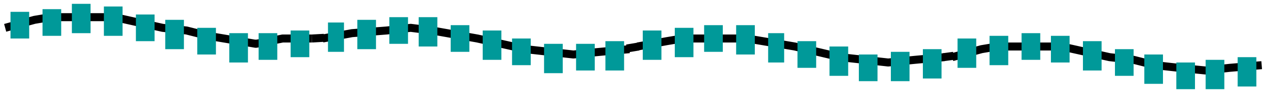


graft

MOLECULAR WEIGHT

- Molecular weight, *M*: Mass of a mole of chains.

Low *M*



high *M*

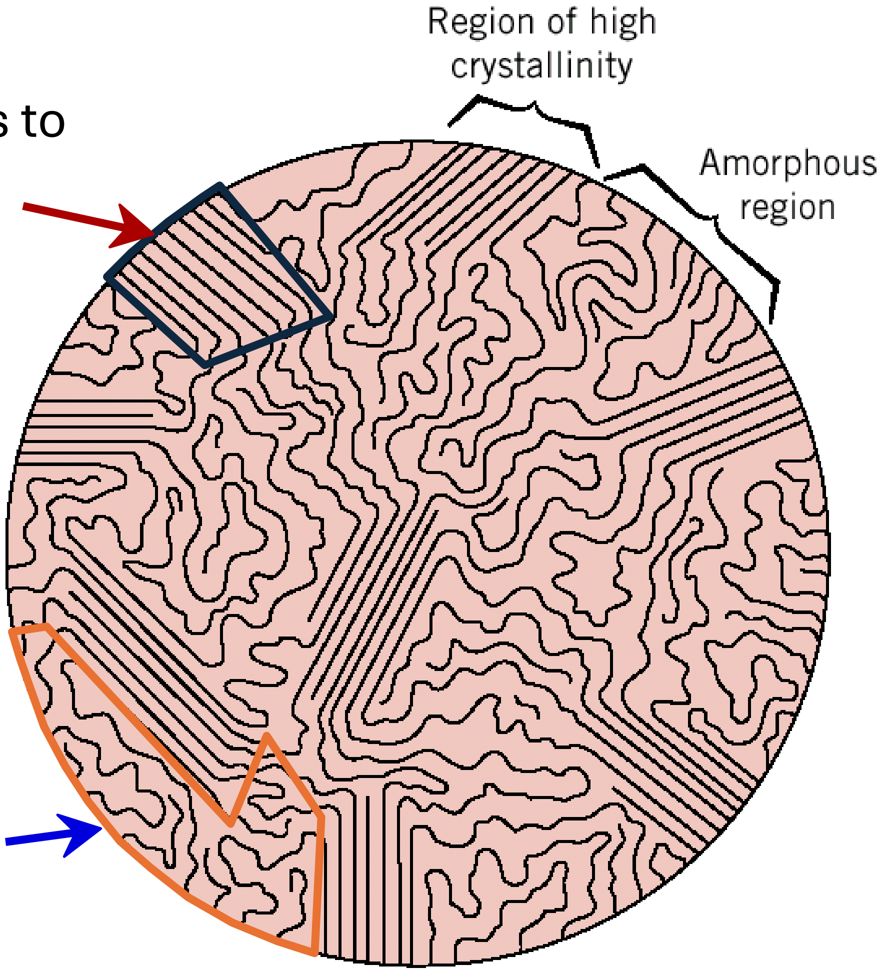
Not all chains in a polymer are of the same length
— i.e., there is a distribution of molecular weights

Polymer Crystallinity (cont.)

Polymers rarely 100% crystalline

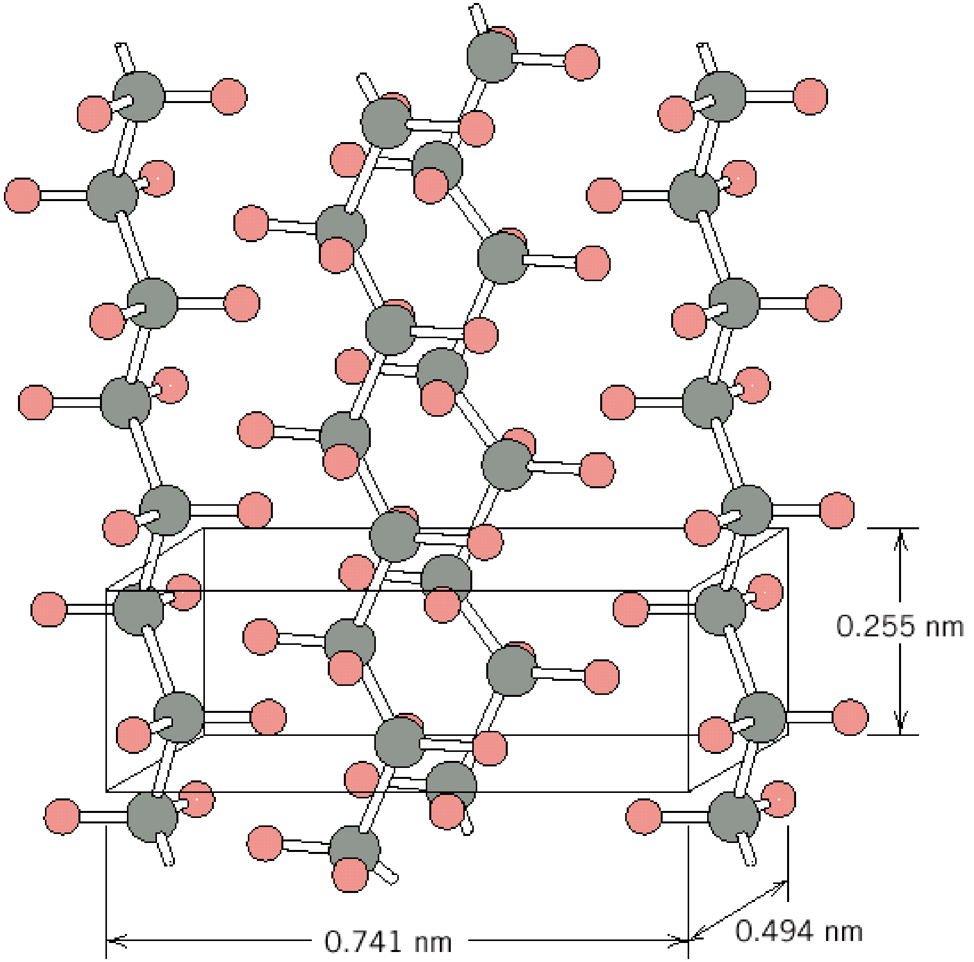
- Difficult for all regions of all chains to become aligned

- Degree of crystallinity expressed as % crystallinity.
  - -- Some physical properties depend on % crystallinity.
  - -- Heat treating causes crystalline regions to grow and % crystallinity to increase.



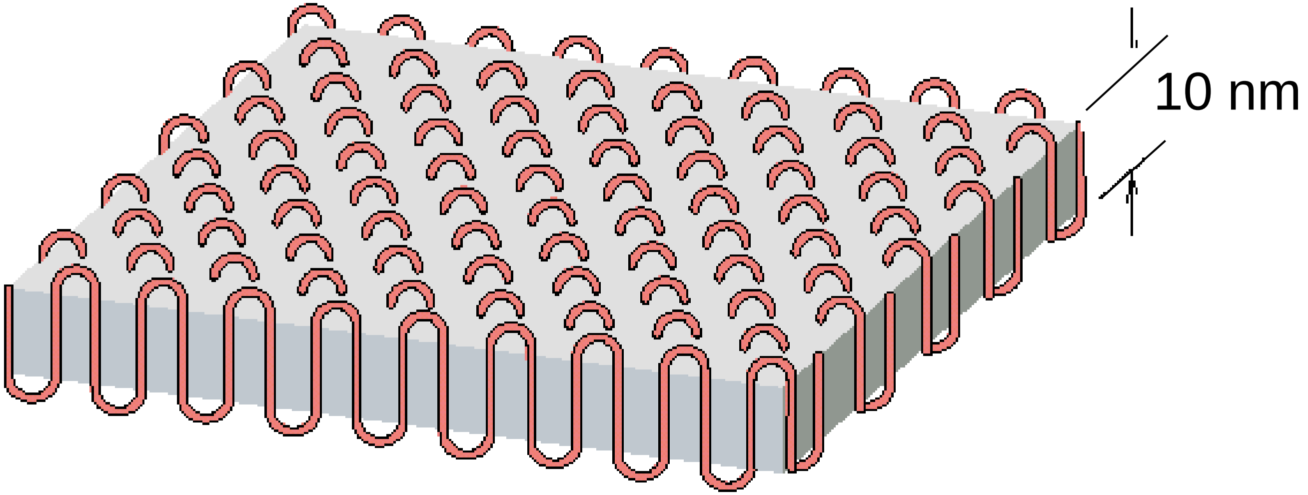
Crystallinity in Polymers

- Ordered atomic arrangements involving molecular chains
- Crystal structures in terms of unit cells
- Example shown
  - polyethylene unit cell



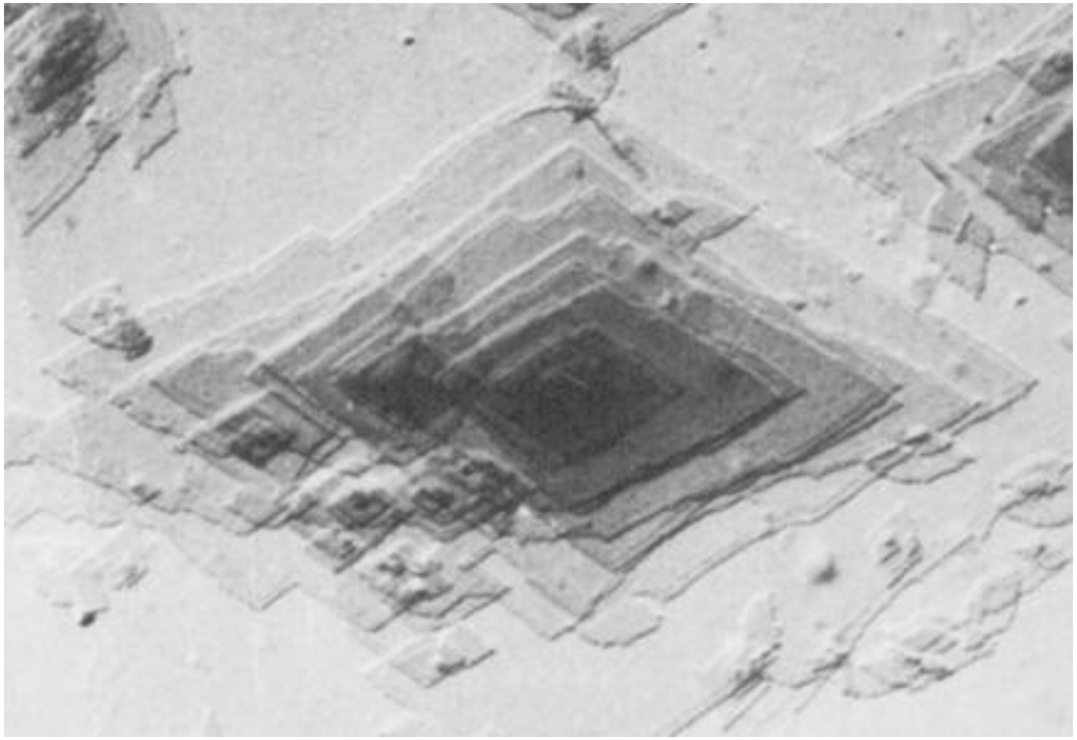
Polymer Crystallinity

- Crystalline regions
  - thin platelets with chain folds at faces
  - Chain folded structure

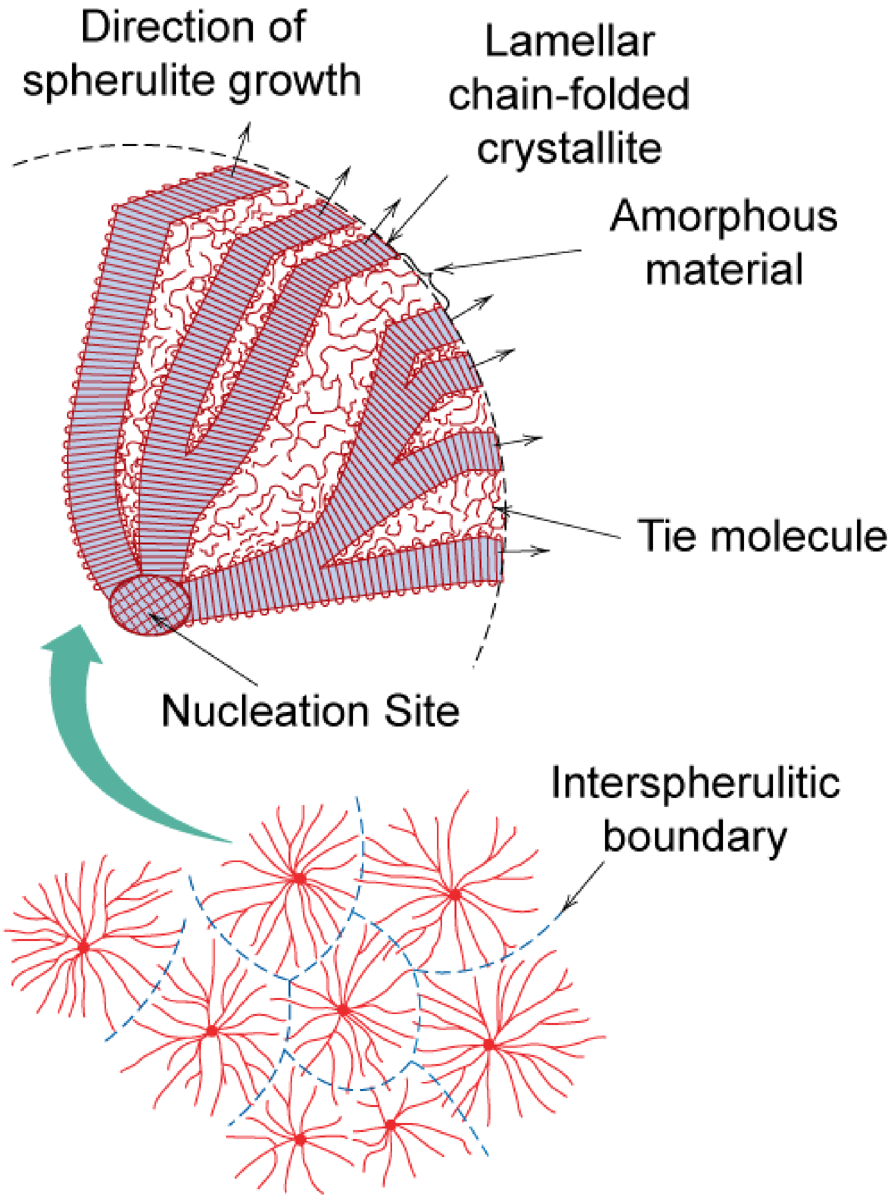


Polymer Single Crystals

- Electron micrograph – multilayered single crystals (chain-folded layers) of polyethylene
- Single crystals – only for slow and carefully controlled growth rates



Semicrystalline Polymers



- Some semicrystalline polymers form spherulite structures
- Alternating chain-folded crystallites and amorphous regions
- Spherulite structure for relatively rapid growth rates

Photomicrograph – Spherulites in Polyethylene

Cross-polarized light used
-- a maltese cross appears in each spherulite