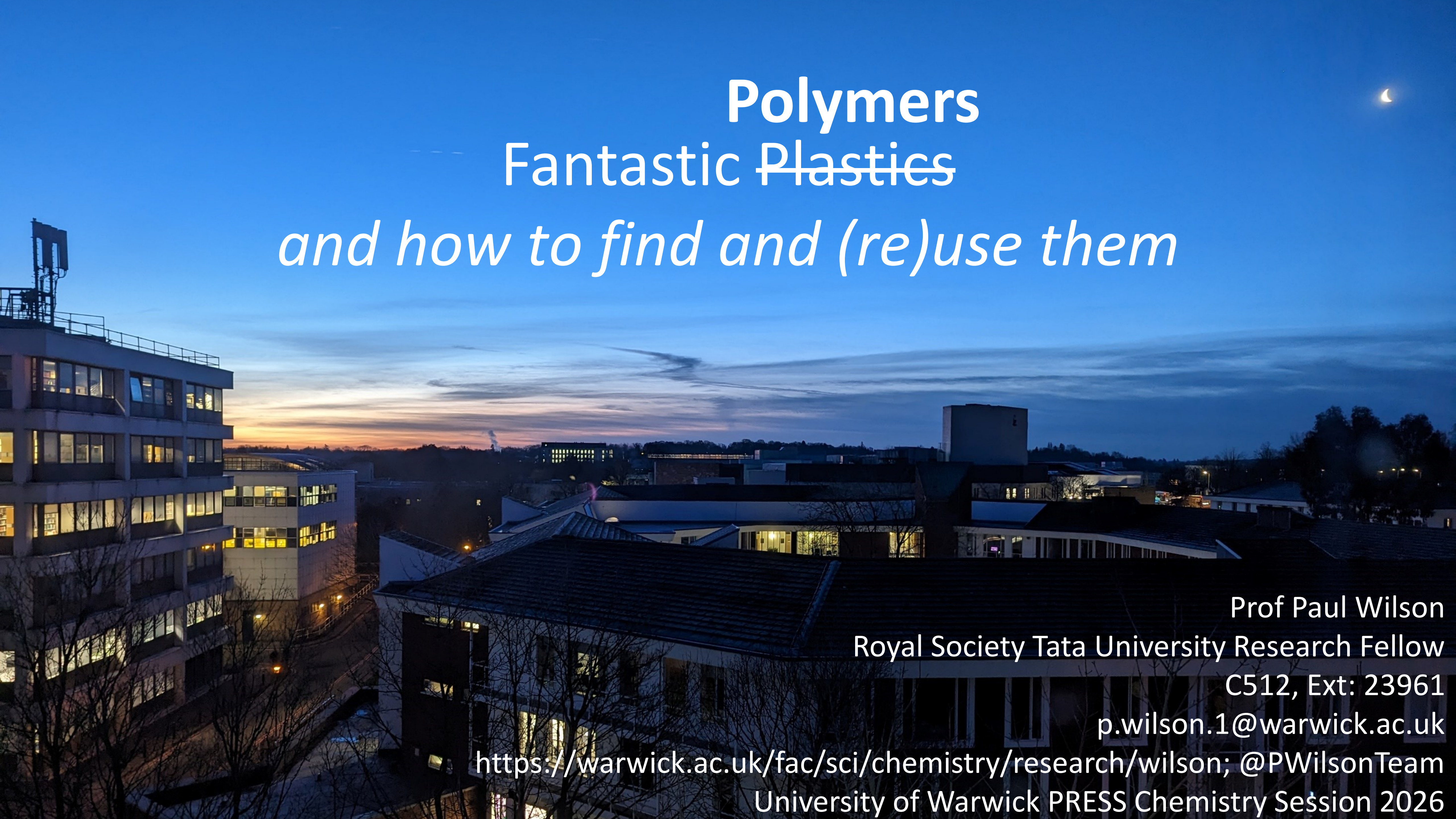

Polymers

Fantastic ~~Plastics~~

and how to find and (re)use them

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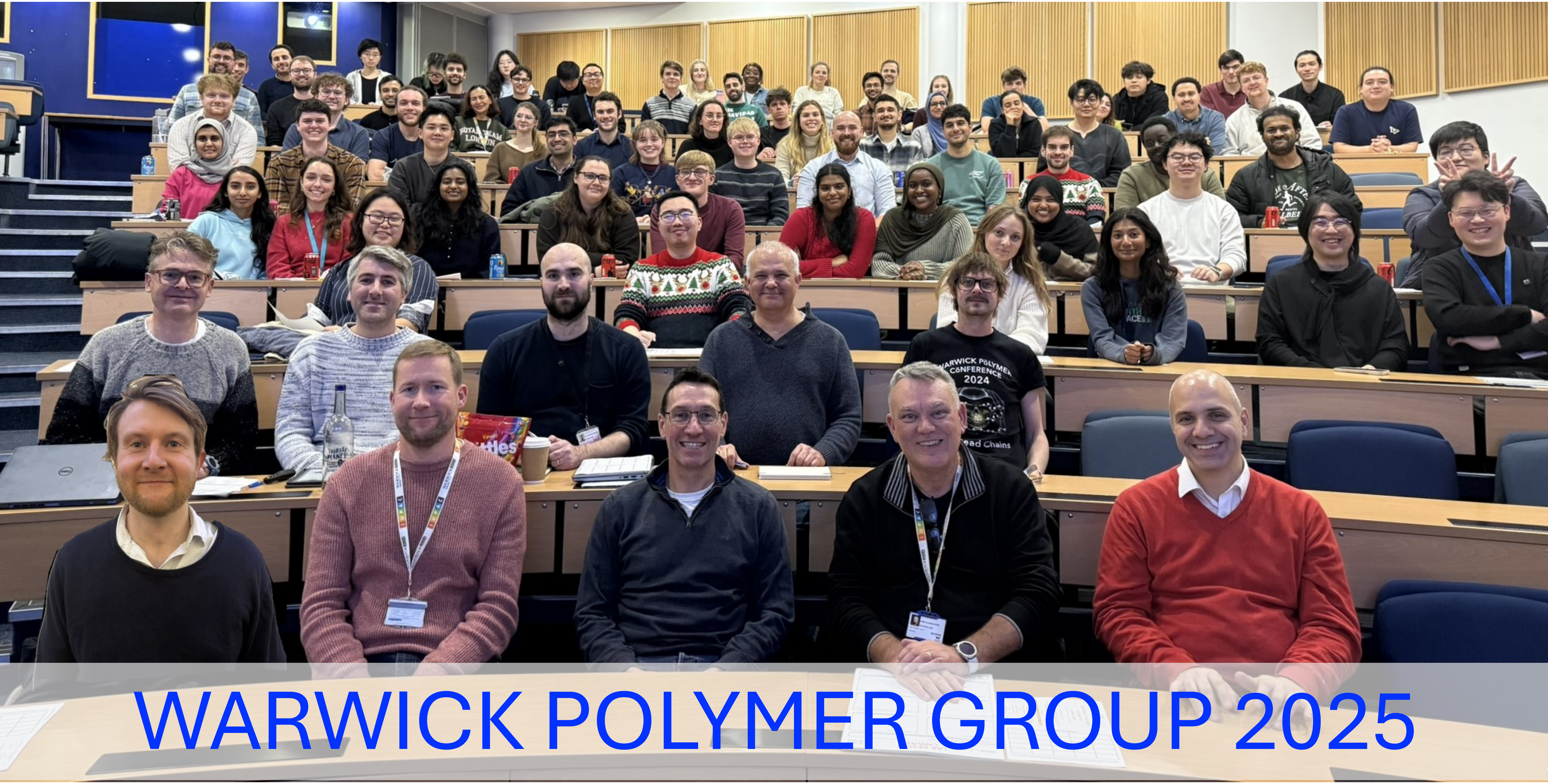
https://warwick.ac.uk/fac/sci/chemistry/research/wilson; @PWilsonTeam

University of Warwick PRESS Chemistry Session 2026



WARWICK POLYMER GROUP 2025


YOUTH FOOTBALL LEAGUE
Edwards
Specialist

Contents

By the end of the session, you'll have a better idea about:

- ❑ Important definitions in **macromolecular** chemistry
- ❑ The importance of polymers – **THE POLYMER AGE**
- ❑ Approaches to the synthesis/manufacture of polymers
- ❑ The original of polymer **properties** and how to **characterise** them
- ❑ Thermoplastic, thermosets and polymer recycling

Definitions

Monomer: the building blocks of ***all*** macromolecules

Polymer: poly = many / meros = parts

Plastic: plastikos = able to be moulded

Macromolecule: ***large***, complex molecule composed of repeating units of *monomers* held together by covalent bonds.

Biomacromolecule: biological macromolecule

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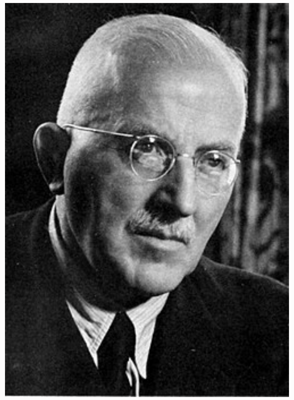
Definitions

What do we mean when we say **large and complex**?



Famous organic chemist 1 – **Herman Staudinger**

1920 – Proposes that rubber, starch, cellulose and proteins are long-chain, high molecular weight molecules composed of short repeating monomer units held together by covalent bonds. Eventually became known as ‘***Makromoleküles***’

1936 – “sooner or later a way will be discovered to prepare artificial fibers from synthetic high-molecular products, because the strength and elasticity of natural fibers depend exclusively on their macro-molecular structure – i.e., on their long thread-shaped molecules.” *Trans. Faraday Soc.* (1936) 32: 323–332

Famous organic chemist 2 – **Emil Fischer**

Along with many pre-eminent organic chemists at the time believed that high molecular weights measured arose due to self assembly and formation of non-covalent colloids composed of aggregated small molecules.

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Definitions

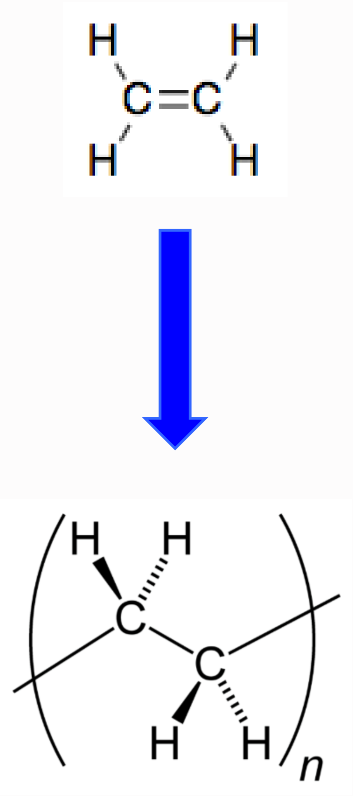
What do we mean when we say **large and complex**?

There is no real definition but maybe **> 5 KDa (g.mol^{-1})** with the term ***oligomer*** often used.

We can also think in terms of a chemical structure ***repeat unit***

Do they have special **properties** because they are big?

Yes! They have interesting and tuneable ***chemical*** properties as well as ***mechanical*** properties. These properties depend upon ***molecular weight***, ***composition*** and ***architecture***.



(polyamides)

HDPE (polyethylenes) LDPE

Nylon-6,6

Kelvar

A quick question

Which of the following statements is correct?

1. ALL polymers are plastics	2. ALL plastics are polymers

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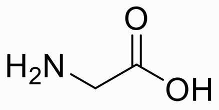
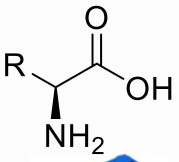
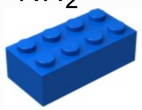
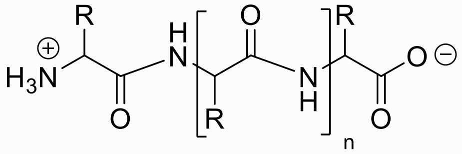
Inspired by nature - biomacromolecules

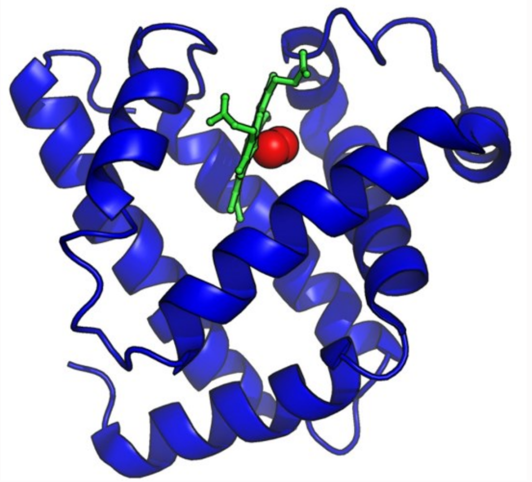





Monomers =
amino acids



Polyamide
repeating unit

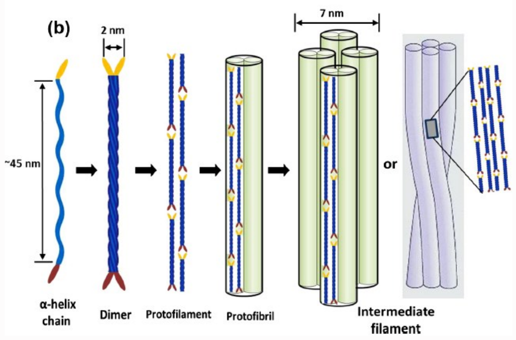


Protein / polypeptide e.g. Myoglobin

Keratins - structure

Instructions
(Biology)

≡



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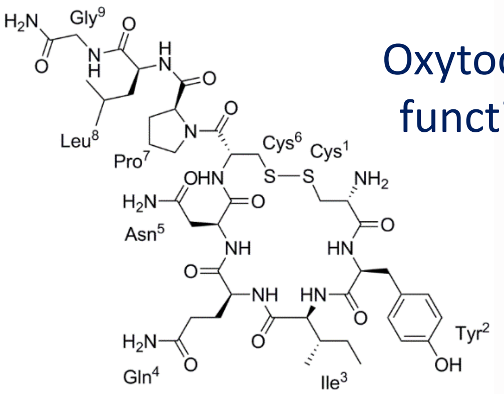

Oxytocin -
function

Exquisite control over structure, properties and function

Yr1 Introduction to chemical biology
Yr2 Macromolecules

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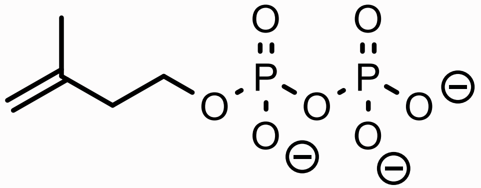
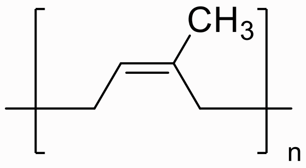
Polymers are all around us

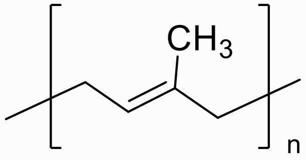
Monomer =



Natural

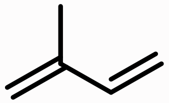
Isopentenyl pyrophosphate





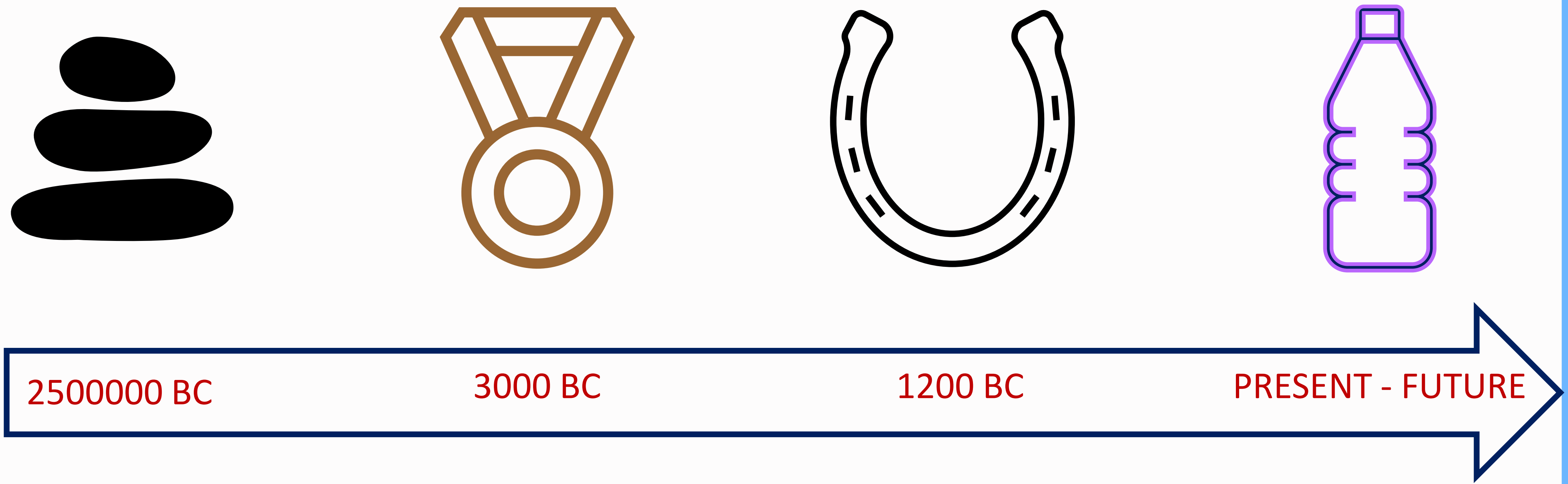
Synthetic

Monomer =



isoprene

The ages of humankind



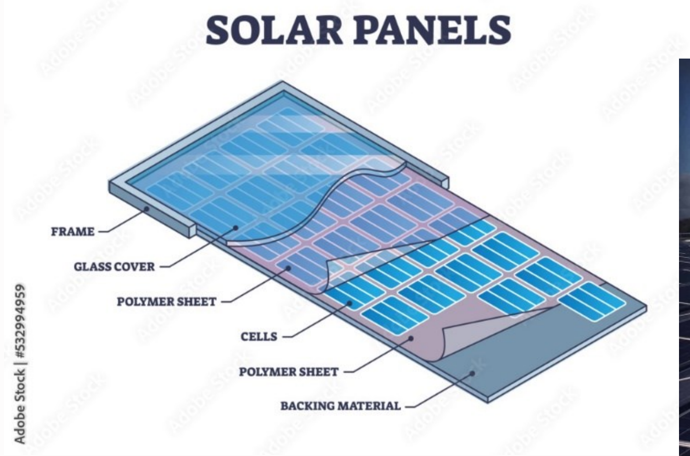
We are living in the Polymer Age

2026

1500 BC — 0 — 1800 — 1900 — 2000

Yr1 Introduction to chemical biology
Yr2 Macromolecules

We are living in the Polymer Age



Step-growth polymerisation

Yr1 Introduction to chemical biology
Yr2 Macromolecules

Chain-growth polymerisation

A quick question

Which of the following contains the highest number of molecules?

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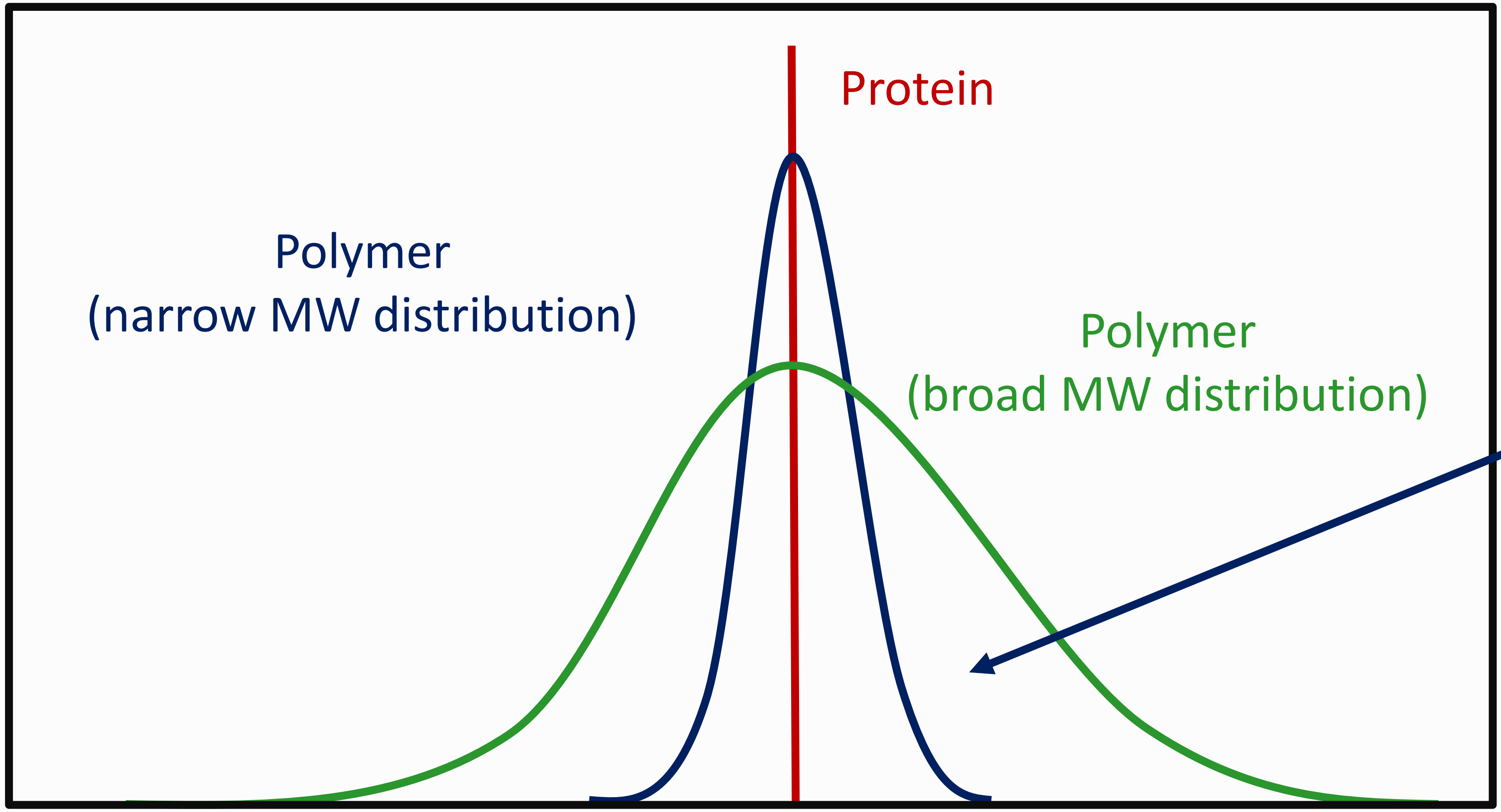
The importance of molecular weight

Number fraction of chains with mass M

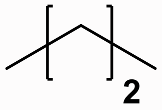


Properties come from here

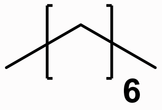
Molecular Weight

The importance of molecular weight

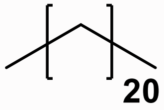
Ethane GAS MWt = 28 $g.mol^{-1}$



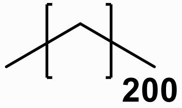
Butane GAS MWt = 58

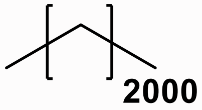


Octane LIQUID MWt = 114

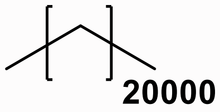


Wax MWt = 306

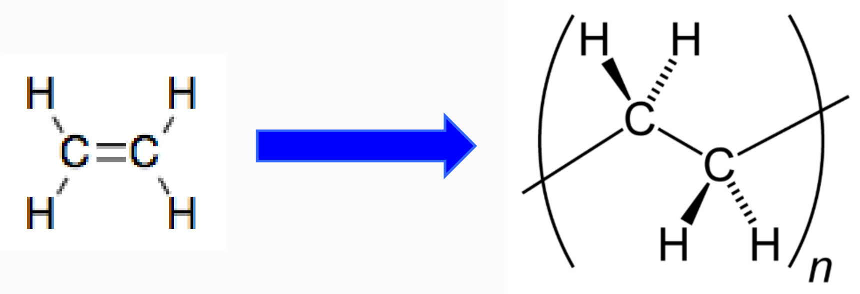


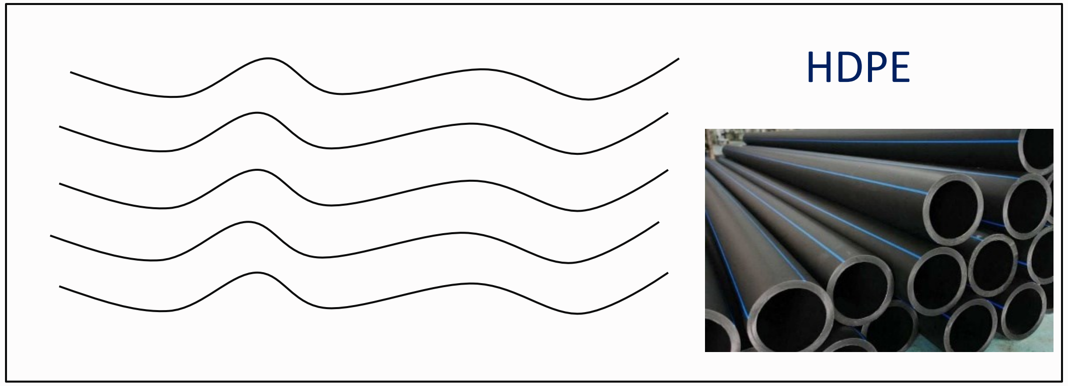


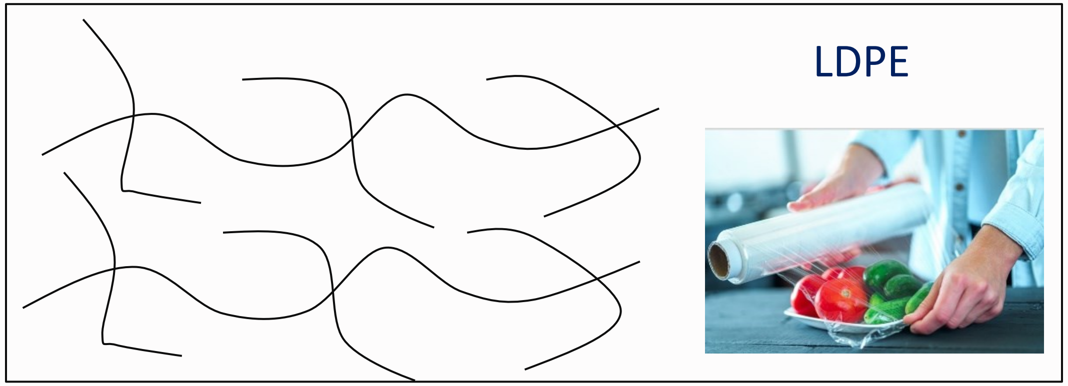
Polyethene Plastic MWt = 28,000



Polyethene Plastic MWt = 280,000







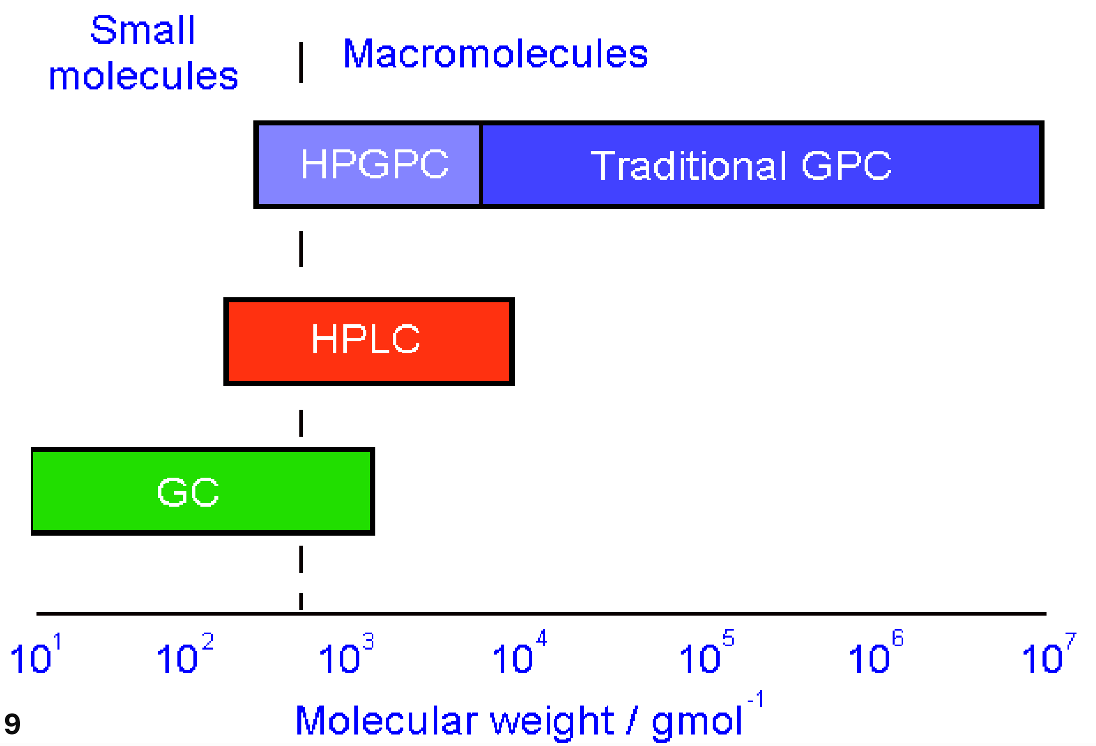
Yr1 Introduction to Polymers in Molecules and Materials Across the Periodic Table
Yr2 Macromolecules, **Yr3** Advanced Polymers from Macromolecular Engineering

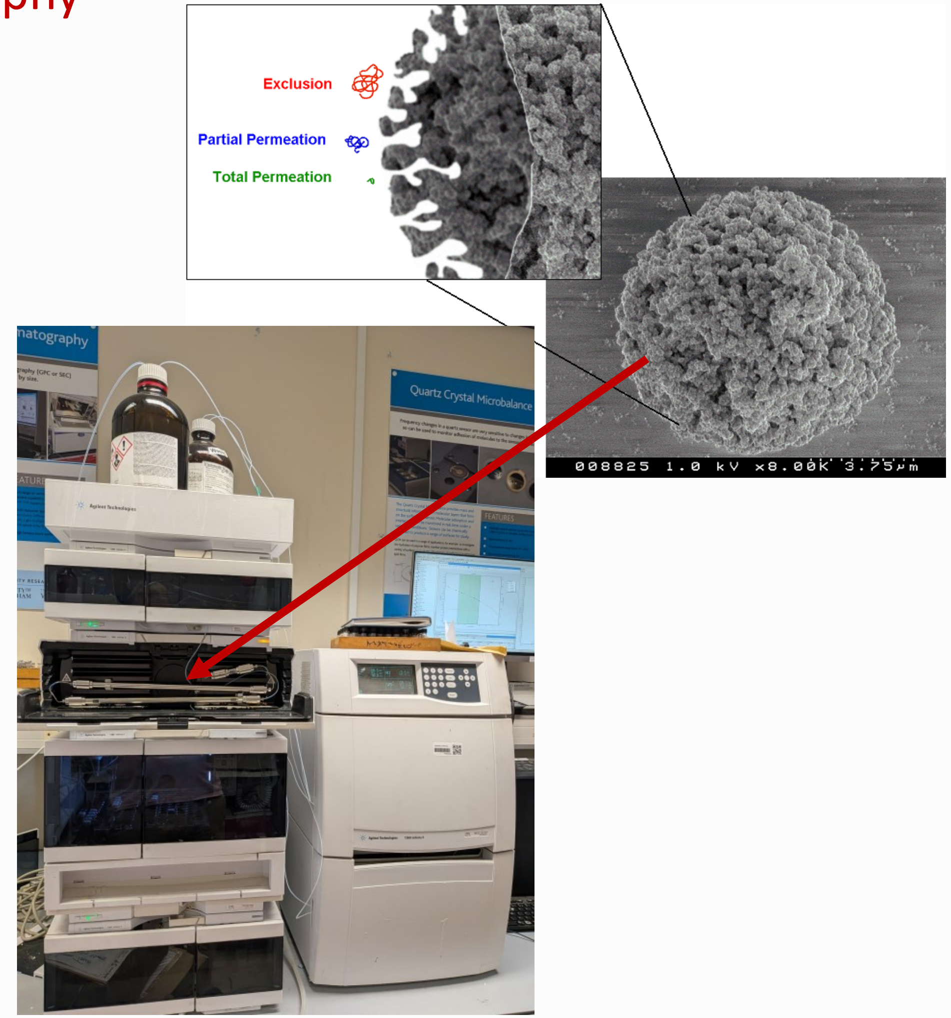
Measuring the molecular weight of polymers

Methods of molecular separation using chromatography

Interactive adsorption, partition, ion exchange, etc

Non-interactive GPC, SEC, GFC





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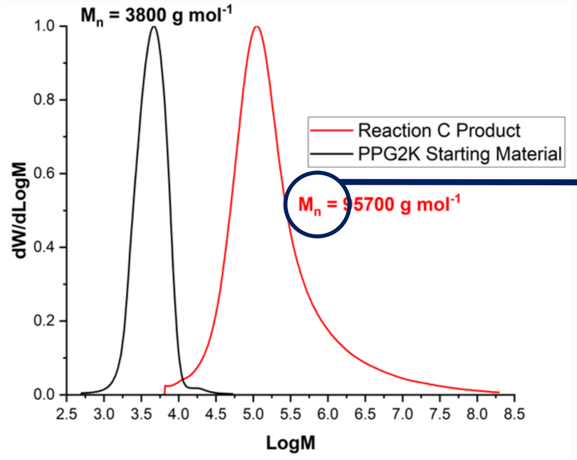
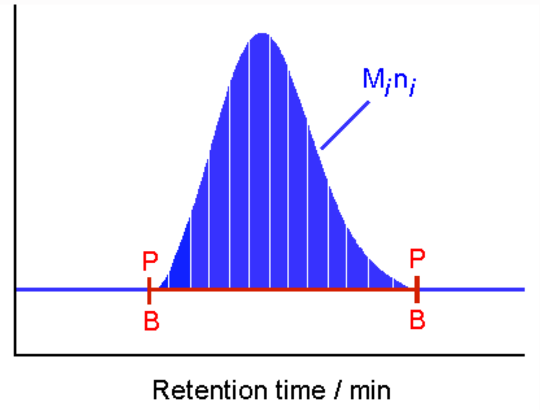
Measuring the molecular weight of polymers

GPC chromatogram converts retention time to molecular weight via calibration curves



Long retention time = low molecular weight

Short retention time = high molecular weight



Number average molecular weight (M_n), obtained by weighting each molar mass by the number of molecules of that molar mass present in the molecule.

$$M_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{1}{N} \sum N_i M_i$$

Weight average molecular weight (M_w), considers the weight fraction i.e. $\sum w_i M_i$ where;

$w_i = c_i/c$

$c_i = N_i M_i$

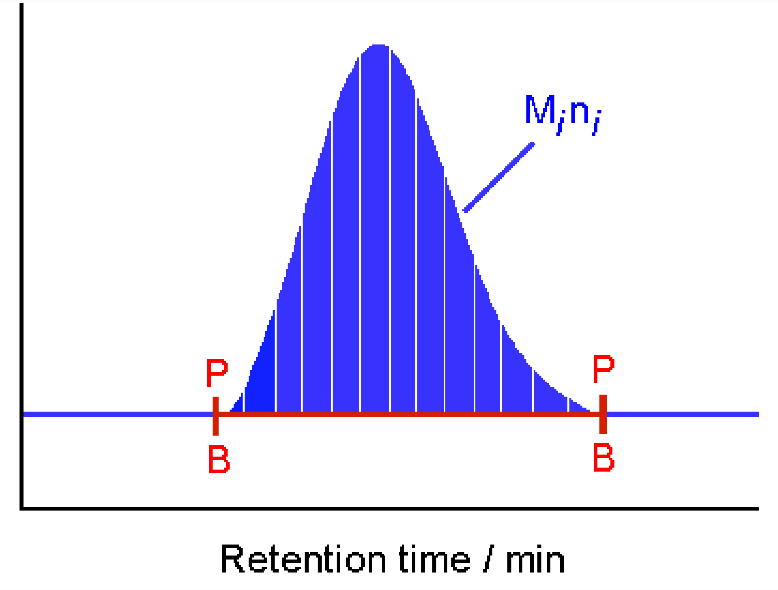
$c = \sum c_i = \sum N_i M_i$

$$M_w = \frac{\sum N_i M_i M_i}{\sum N_i M_i}$$

Dispersity ($Đ$) is the ratio of these molecular weights – $Đ = M_w / M_n$ and tells us about that molecular weight distribution. Note $Đ > 1.0$

Using the molecular weight equations

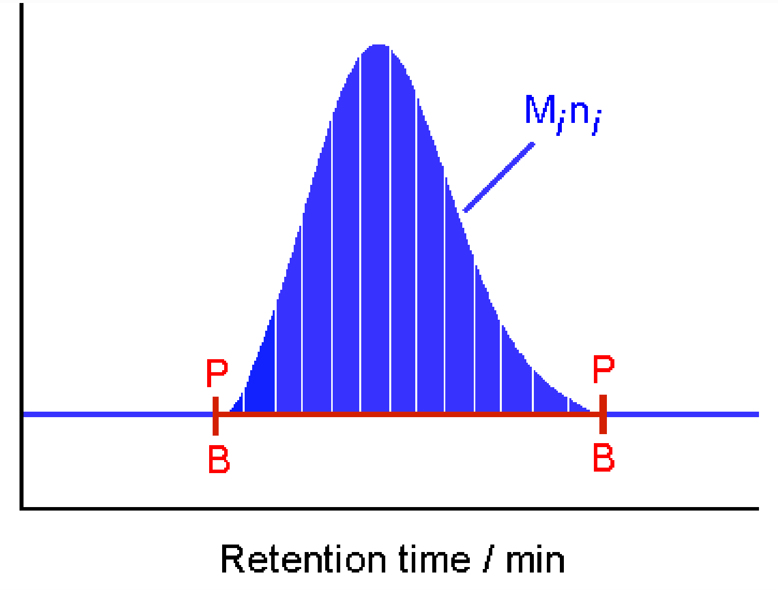
Calculate M_n, M_w, $Đ$ for the following population of polymer chains



MWt (Mi)	Area (Ni)
10000	10
20000	20
30000	40
40000	20
50000	10

Using the molecular weight equations

Calculate M_n, M_w, $Đ$ for the following population of polymer chains



MWt (M_i)	Area (N_i)	N_iM_i	$N_iM_iM_i$
10000	10	100000	1×10^9
20000	20	400000	8×10^9
30000	40	1200000	36×10^9
40000	20	800000	32×10^9
50000	10	500000	25×10^9

$\sum N_i = 100$

$\sum N_iM_iM_i = 102 \times 10^9$

$\sum N_iM_i = 3000000$

$M_n = 30000$ g.mol^{-1}
$M_w = 34000$ g.mol^{-1}
$Đ = 1.13$

22

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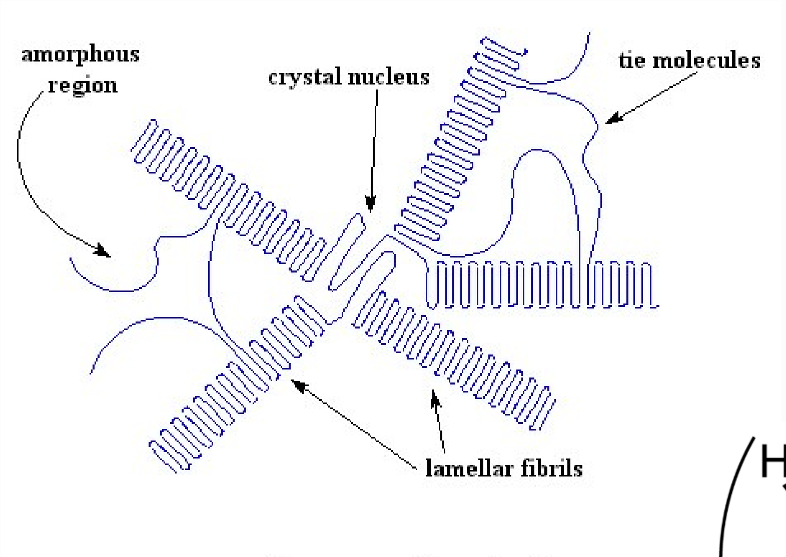
Thermal properties – polymers in the solid state

Recall – polymers have interesting properties that depend upon ***molecular weight***, ***composition*** and ***architecture***.

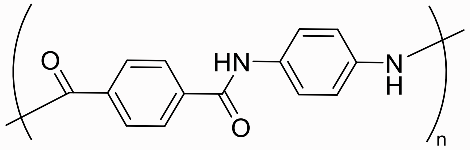
In the solid-state they can be ***amorphous***, ***crystalline*** or ***semi-crystalline***

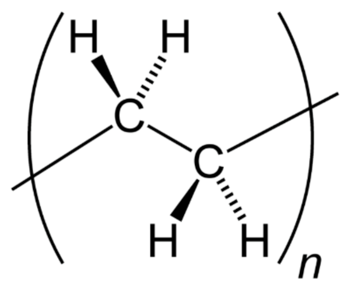


a polymer crystalline spherulite

Crystallinity of polymers depends upon ***thermodynamic*** and ***kinetic*** factors.

If polymers have good packing properties then they can be very tough as all volume is taken up my "molecule" e.g. HDPE and Kevlar





Thermal properties – amorphous polymers

Amorphous bulk polymer has chains arranged in less than a well-ordered state and exhibit a ***glass transition temperature T_g***.

In simple terms this is the temperature at which material transitions from the solid/***glassy*** state to a softer/***rubbery*** state.

T_g is a second order thermal transition and T_m a first order thermal transition. Common method to measure these properties is ***Differential Scanning Calorimetry (DSC).***

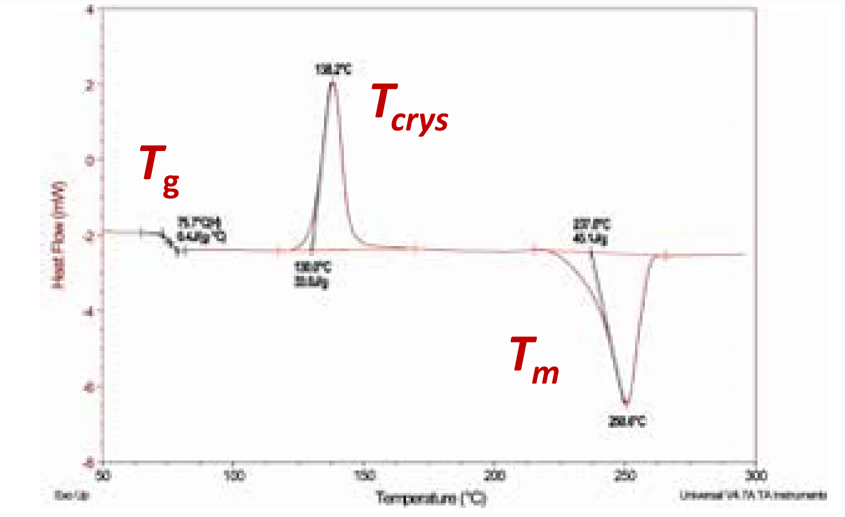
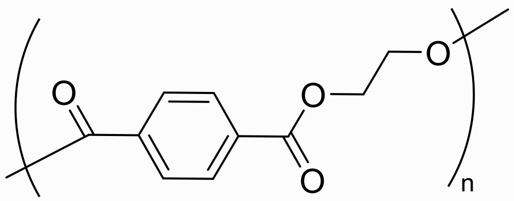


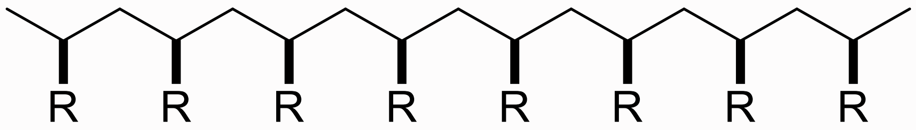
Figure 1: DSC Scan of Polyethylene Terephthalate: Heat Flow versus Temperature

PET

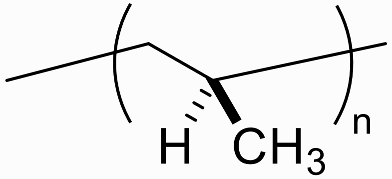


T_g – glass transition (endothermic)
T_{crys} – 'cold' crystallisation (exothermic)
T_m – melting temperature (endothermic)

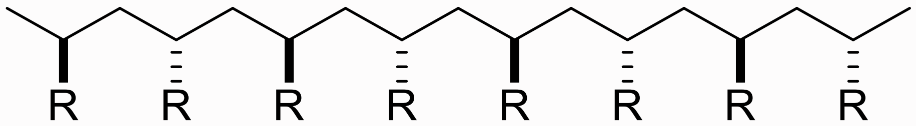
Stereochemistry also matters



isotactic



Commercial ***polypropylene*** synthesised by TM mediated polymerisation and is mainly ***isotactic*** = ***high crystallinity***



syndiotactic

Stereochemistry/tacticity allows good chain packing

Random is referred to as ***atactic***

T_m ~ 170 °C (isotactic)
T_m ~ 140 °C (syndiotactic)
Atactic = amorphous

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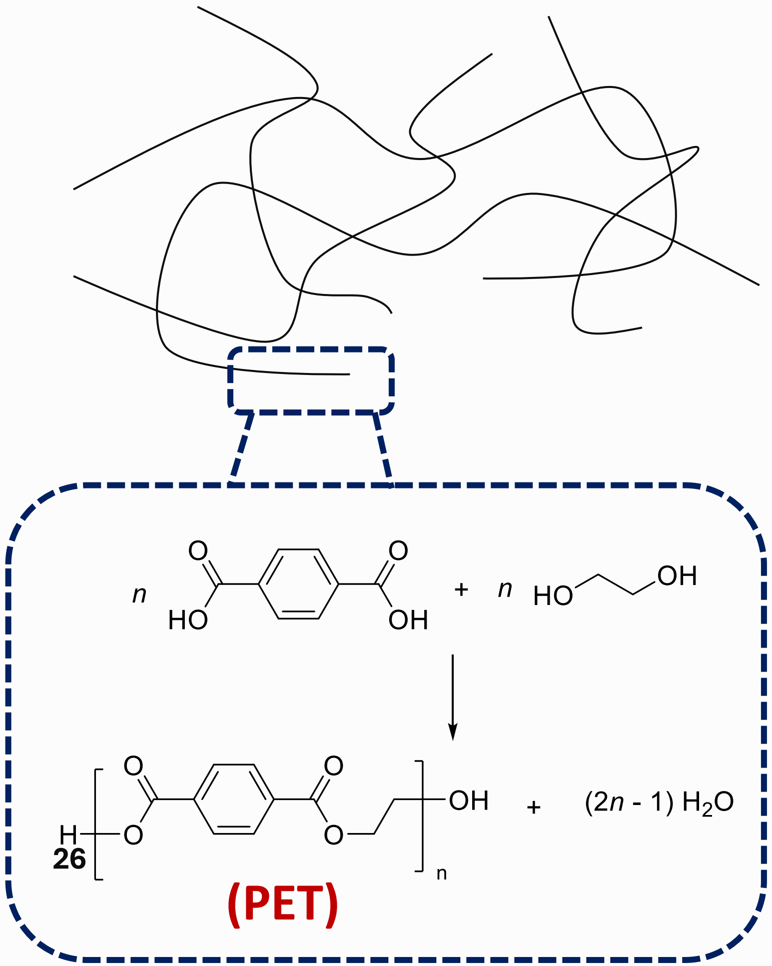
Thermoplastics vs Thermosets

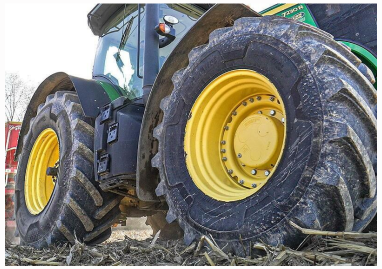
THERMOPLASTIC: poly(ethylene terephthalate) **(PET)**

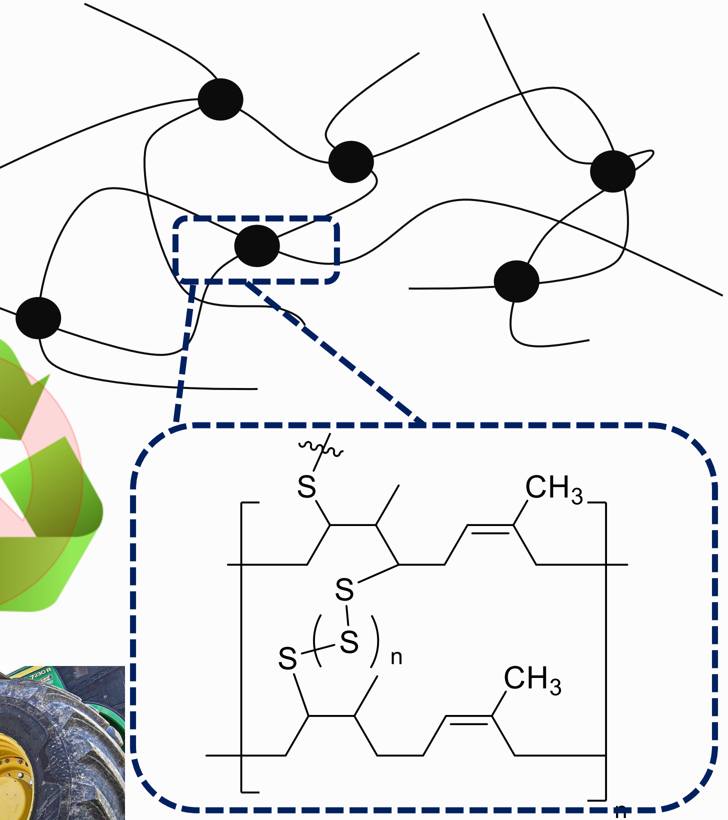
A polymer that can ***soften and harden reversibly*** on changing the temperature

THERMOSET: vulcanised rubber

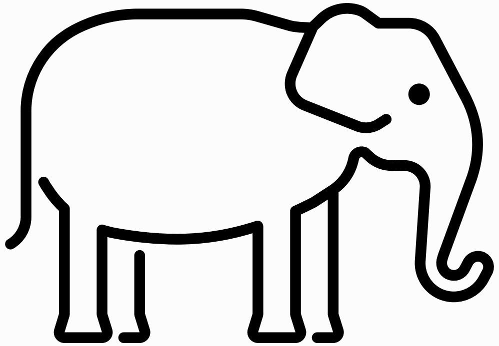
A polymer that is ***irreversibly crosslinked*** via a curing reaction







Thermoplastics vs Thermosets



- 8 -14 MT of plastic annually
- 46000 pieces of plastic per square mile (low estimate)
- 5.25 T microplastic particles

Solution: education, reuse & recycle

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Contents

By the end of the session, you'll have a better idea about:

- ❑ Important definitions in **macromolecular** chemistry ✓
- ❑ The importance of polymers – **THE POLYMER AGE** ✓
- ❑ Approaches to the synthesis/manufacture of polymers ✓
- ❑ The original of polymer **properties** and how to **characterise** them ✓
- ❑ Thermoplastic, thermosets and polymer recycling ✓

Polymers

Fantastic ~~Plastics~~

and how to find and (re)use them

Laboratory Workshop

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https://warwick.ac.uk/fac/sci/chemistry/research/wilson; @PWilsonTeam
University of Warwick PRESS Chemistry Session 2026

Identifying polymers – a lab workshop activity

Properties

Thermal analysis – DSC, thermogravimetic analysis (TGA) ✓
Mechanical testing – elongation/compression for modulus / strength ✓

Molecular weight

Gel-permeation chromatography aka size-exclusion chromatography ✓

Chemical structure, composition and architecture

^{1}H Nuclear Magnetic Resonance (NMR) Spectroscopy **(activity 1)**

Fourier Transform Infra-red Spectroscopy (FTIR) **(activity 2)**

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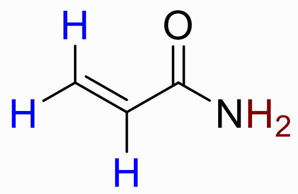
Identifying polymers – ^{1}H NMR spectroscopy

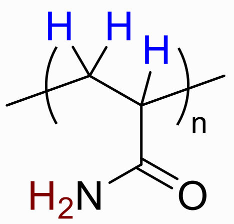
Principles

Some atomic nuclei possess nuclear ***spin*** and can therefore interact with a magnetic field. For example, a proton ^{1}H has spin of ½ and can align with the applied field +1/2 or against it -1/2. The energy between these states depends on the field strength and the nuclear environment.

Nuclei can be ***shielded*** or ***deshielded*** by neighbouring atoms and/or functional groups. Useful for following reaction progress in some polymer syntheses – chain growth polymerisation of acylics



Acrylamide (monomer)



Polyacrylamide

Task – use ^{1}H-NMR to identify the blue protons and how they change as a result of polymerisation

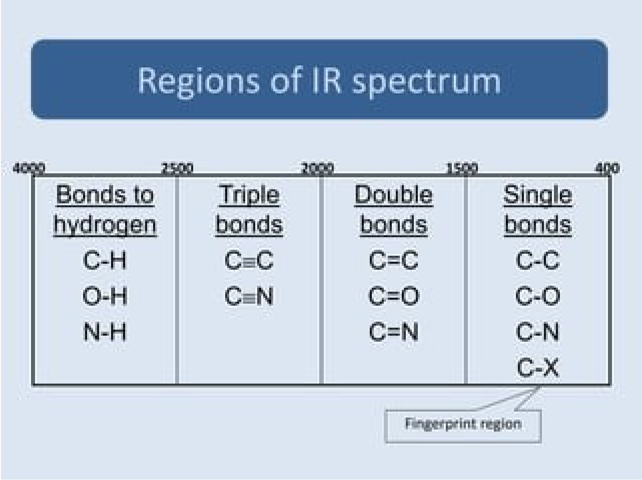
Identifying polymers – FTIR

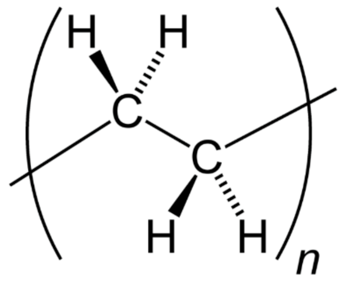
Principles

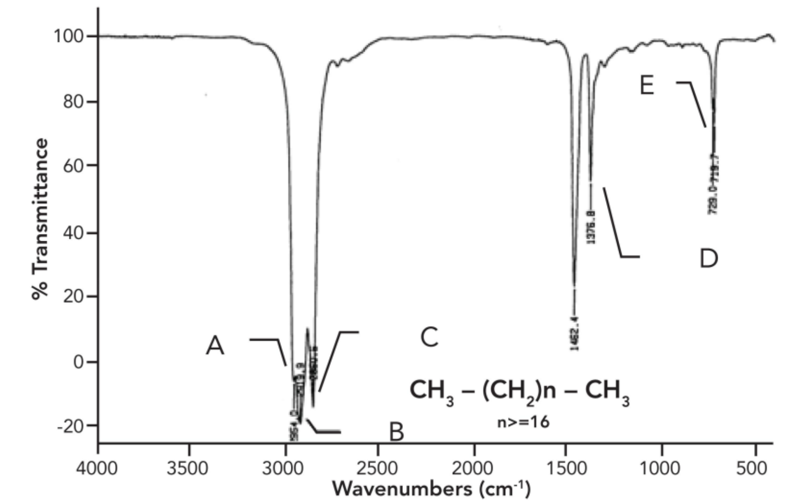
Infrared radiation can stimulate bond stretching and bending. Different bonds and functional groups require different energy related to bond strength and the mass of the atoms constituting the bond.

v = frequency of bond vibration/stretch
f = force constant (bond strength)
μ = reduced mass ($m_1 m_2/m_1 + m_2$)

$$v = \frac{1}{2\pi c}\sqrt{\frac{f}{\mu}}$$







A	2954	CH_3 Asymmetric stretch
B	2920	CH_2 Asymmetric stretch
C	2860	CH_2 Symmetric stretch
D	1377	CH_3 Umbrella bending mode
E	729, 720	Split CH_2 rocking vibration

Task – use FTIR to identify the unknown polymer samples