## **Introduction to Polymer Chemistry**

What is a polymer?

#### Why are polymers important?

A polymer is a large molecule made up from identical building blocks = monomers



# Difference between small molecules and macromolecules:

## Small molecule:

- Defined structure and configuration
- Defined molecular weight: all molecules are identical
- Sharp boiling or melting point
- Solids: usually crystalline = regular structure

Up to about 1920, most scientists did not believe macromolecules could exist the idea was that small molecules simply stuck to one another to give larger aggregates.

Argument: what are the end groups? None could be detected.

#### Macromolecular Hypothesis:

### Hermann Staudinger Nobel Prize 1953

#### "Father of polymer chemistry"

coined the word "macromolecule" proposed long-chain formulas for rubber, polystyrene etc.

These have now been substantiated by physical measurements: molecular weight measurements small-angle X-ray scattering

#### Acceptance of the theory:

Wallace H. Carothers, "An Introduction to the General Theory of Condensation Polymers", *J. Am. Chem. Soc.* **1929**, *51*, 2548 – 2559.

W. H. Carothers, "Polymerization", Chem. Rev. 1931, 8, 353 – 426.

Paul J. Flory: Mechanism and theory of chain reactions, 1937. Nobel Prize 1973.

Are polymers new?

Asphalt, amber: known since ancient times Others discarded as undistillable oils, tars

Ca. 1860: Poly(ethylene glycol) **"Celluloid"**: cellulose nitrate plasticized with camphor based on cellulose, a natural polymer used for billiard balls, piano keys, later **celluloid film** 1865: discovery of cellulose acetate – safer alternative to cellulose nitrate first man-made fibres

#### Natural rubber:

1839 Goodyear discovers "vulcanisation" = cross-linking with sulphur Rise of the rubber industry 1907: **Baekeland** discovers phenol-formaldehyde polymer Solid plastic, electrical insulator, varnishes *"Bakelite"* 

early 1900's: first synthetic rubber: copolymerisation of dienes with styrene

#### Year of industrial Introduction:

1936	Poly(vinyl chloride) PVC
1936	Poly(chloroprene) "Neoprene" rubber
1936	Poly(methylmethacrylate) "Perspecs"
1937	Polystyrene
1939	Polyamide fibres: Nylon-66 -> Carothers
1941	Poly(tetrafluoroethylene) "Teflon"
1943	Polyethylene (branched)
1943	Butyl rubber
1943	Silicone polymers
1955	Linear polyethylene
1957	Polypropylene
1957	Polycarbonate

## **Classification of Polymers:**

Several different methods:

- (1) According to physical properties
- (2) According to chemical reaction

#### (1) Classification by physical behaviour: thermal treatment:

how does the material behave when heated?



## ➔ Thermoplastics

polymers which melt when heated and resolidify on cooling. Polymer types: usually LINEAR polymers

> Examples: Polyethylene, polypropylene, polyesters



## → Thermosets

polymers donot melt on heating. Eventually decompose irreversibly when heated to sufficiently high temperatures

Polymer types; usually cross-linked polymers, i.e. 3D-networks.

Examples: Bakelite, vulcanised rubber

#### (2) Classification based on chemical reaction:

how is the material formed?

### ➔ Condensation polymers

polymers prepared from monomers where the reaction is accompanied by loss of small molecules (e.g. water):

n HO-R-OH + n HOOC-R'-COOH 
$$\longrightarrow$$
  
HO-R-O-C-R'-C-O-H + (2n-1) H<sub>2</sub>O  
DO-R'-C-O-H + (2n-1) H<sub>2</sub>O  
polyester

$$nH_2N-R-NH_2+ n CIOC-R'-COCI \longrightarrow H_2O$$

$$H_2N-R-N-C-R'-C-O-H + (2n) HCI$$

$$polyamide: e.g. Nylon$$

## ➔ Addition polymers

polymers formed by addition of unsaturated polymers:

all "vinyl" polymers



These addition polymers can be formed in different ways:

by radical reactions, by anionic or cationic mechanism, or by catalysis. This is not obvious from the chemical structure of the product.

Similar:



## **Polymer Structure**



Example: Vinyl "addition" polymerisations

In practice, head-to-tail structure is almost always formed.

This polymerisation reaction has formed a series of asymmetric centres:



If <u>all</u> asymmetric carbon atoms have the <u>same</u> configuration, the polymer is called **isotactic**:





Polymers with regular alternating changes in stereochemistry are called **syndiotactic**:



syndiotactic

Polymers with **random** distribution of stereocentres is called **atactic**:



atactic

## Structural isomerism in polymers:

#### The example of polyisoprene

