### The Structure of Polymers

Do polymers melt, like crystals?



# Glass transition temperature, $T_g$ :

In an amorphous polymer below  $T_g$ , the polymer chains vibrate but move little with respect to one another.

Glass transitions are observed for <u>linear amorphous polymers</u>.  $brittle/glassy \rightarrow less rigid, rubbery$ 

Polymer chains remain entangled: properties similar to inorganic glass



 $T_g$ : enough energy is available fro polymer chain to move passed eachother: polymer softens, loses mechanical strength





### Temperature

At  $T_g$ , the <u>rate of heat uptake changes</u>.

Changes at  $T_g$ :

- coefficient of thermal expansion
- heat capacity
- refractive index
- electrical properties

All these properties depend on the degree of freedom for molecular motion within polymeric material.

➔ Glass transition is the point at which rotation around the single bonds becomes much easier.

#### Factors that affect Glass Transition:

Increased by:

• pendant groups on polymer backbone,  $\rightarrow$  they increse energy required to rotate molecule;

- rigid backbone structures, e.g. phenylene groups;
- crosslinking: prevent molecule rotation
- attractive forces between chains, e.g. H-bonding
- molecular mass: large molecules rotate less easily

• stereochemistry: regular structure pack better and rotate less easily.

Decreased by: • plasticizers: decrease interactions between chains "internal lubricants"

	$T_g$ [°C]	
Polyethylene	-20	flexible backbone
isotactic polypropylene	+5	$CH_3$ side chains
PVC	80	polar attractions
PTFE	115	very stiff backbone

## **Polymer Crystallisation**

Most small molecule compounds crystallise. In crystals the molecules occupy regular positions in the lattice.

These crystals have sharp, well-defined melting points  $T_m$ .

How can this be applied to "floppy" molecules like polymers?



Most obvious in polyethylene: regular = hard:



side-branching = loss of crystallinity = soft:





Polymers are more difficult to crystallise than small molecules:
→many degrees of freedom; rotational, translational

Areas of high stereoregularity pack closely parallel:

crystalline domains = microcrystallites

➔ rigidity and strength

Method: X-ray diffraction

shows regular reflections like that in crystals

Polymers without regular structure remain amorphous entanglements.

Crystalline domains are interrupted by irregular entanglement:

→ these domains give *elasticity*, *toughness*, *impact resistence* 

Melt behaviour of polymers more complicated than small molecule crystals range of polymer sizes

- range of polymer structures:
- co-existence of crystalline and amorphous domains

Effectively "mixtures" -> polymers melt over a wider temperature range

Microcrystallites: can affect optical properties, transparency.

Effect of Structure on  $T_m$ :



Effect of side chain structure on  $T_m$  of <u>isotactic</u> polyolefins:



### Relationship between $T_g$ and $T_m$ :

Usually, polymer structure affects both  $T_g$  and  $T_m$  in a similar way: same structural reasons (cohesive energy, molecular packing).

For most linear polymers,

$$T_g$$
 (K)  $\approx 1/2 - 2/3 T_m$  (K)

# **Determination of Polymer Molecular Weights**

→ no precise molecular weight but a *molecular weight distribution*

Typical distribution:



molecular weight

Because there is ONE maximum and the curve has no shoulders, this is called a monomodal molecular weight distribution.

Mixtures of polymers may give bi- or polymodal distributions:



### Calculating polymer molecular weights:

The *number-average molecular weight*, `M<sub>n</sub>

Polymers consist of mixtures of molecules of different weights.

Total weight w of the sample = sum of weights of each molecular species:

$$w = \sum_{i=1}^{\infty} w_i = \sum_{i=1}^{\infty} M_i N_i$$

average mol. weight by definition:



For most polymers,  $\overline{M}_n$  is close to the peak of the MW distribution curve but is NOT the maximum



molecular weight

The weight average molecular weight is important in kinetics: how many polymer chains are being formed.

Can be determined directly e.g. from concentration of end groups (by chemical tests i.e. titration, or by spectroscopy (relative intensity of end groups, NMR)

### The weight-average molecular weight

The properties of a polymer are largely determined by the longest molecules, i.e. a small mol-fraction of long chains can constitute the bulk of the polymer, while the many short chains do not amount to much total weight. To account for this, the weight-aveage MW has been defined:

 $N_i M_i$  = weight of all polymer chains with molar mass  $M_i$ weight fraction of polymer *i*:  $w_i = N_i M_i$  / sum of all polymer weights =  $N_i M_i$  /  $\Sigma N_i M_i$ 

weight fraction x Molar mass of polymer  $i = w_i M_i$  $(w_i M_i) = N_i M_i^2 / \Sigma N_i M_i$ 

For sum of all weight fractions:

$$\overline{M}_{W} = \frac{\sum_{i=1}^{\infty} N_{i} M_{i}^{2}}{\sum_{i=1}^{\infty} N_{i} M_{i}}$$

Example:

Mixture of 100 molecules of MW  $10^4$ , 20 molecules MW  $10^5$ .

$$M_{w} = \{(20 \times 10^{5} \times 10^{5}) + (100 \times 10^{4} \times 10^{4})\} / (100 \times 10^{4} + 20 \times 10^{5}) = 70,000$$

i.e. weight-average MW is closer to higher MW fraction

#### $M_{\rm w}$ is always greater than $M_{\rm n}$

 $\overline{M}_{w}$  is always greater than the peak maximum  $\rightarrow$  fewer molecules but large contribution to total weight

# The ratio $M_w / M_n$ is known as <u>"polydispersity"</u> = "molecular weight distribution"

#### also known as PD = polydispersity index

Is this important?

Yes -  $M_w$  /  $\overline{M}_n$  is useful as a means to characterise a polymer.

### <u>NOTE: ` *M<sub>w</sub>* /` *M<sub>n</sub>* is only meaningful if the molecular weight distribution is monomodal</u>

In some cases all polymer molecules grow at the same rate and are of equal length. In that case,  $\overline{M}_{w} = \overline{M}_{n}$  and polydispersity = 1.

This is often the case in a *"living" polymerisation*.

In living polymerisation there is no chain termination: the polymer keeps growing as long as there is monomer left.

If polymer chain growth is accompanied by <u>chain termination</u>, it can be shown that theoretical limiting value of  $\overline{M}_w / \overline{M}_n = 2.0$ .

Broad PD of 4 - 10 is often wanted to improve processability of polymer: better melt extrusion behaviour.

### Measurement of molecular weight

Many methods. The most common:

#### 1. End-Group Analysis

Polymers must terminat in some way. The end groups are usually different from main chain.

Comparing end group concentration to bulk of polymer gives  $M_n$ .

For example:



unsaturated chain end:

titration (e.g. with Br<sub>2</sub>)

or by NMR: integration of  $H_2C=CH$ - signals compared to  $CH_2$  signals of main chain.

#### 2. Properties that depend on number of molecules ("colligative

properties"): also yields  $M_n$ .

- lowering of vapour pressure
- boiling point elevation
- freezing point depression
- <u>osmotic pressure</u>

These methods are now less common.

Both end group analysis and measurement of colligative properties are difficult to apply to large molecules: depend on <u>number</u> only.

#### 3. Solution Viscosity

Important method: cheap, easy to set up, quick, informative.

→ See lab experiment

Capillary viscometer: flow time of a know volume of solution t relative to flow time of neat solvent,  $t_0$ :

relative viscosity  $\eta_r = \eta/\eta_0 \cong t/t_0$ 

specific viscosity  $\eta_{sp} = (\eta - \eta_0)/\eta_0 \cong (t - t_0)/t_0$ 

intrinsic viscosity

 $[\eta] = (\eta_{sp}/c)_{c=0}$  $= [(\ln\eta_r) / c]_{c=0}$ 

i.e. <u>intrinsic viscosity extrapolates to zero concentration</u>: value is concentration-independent. Depends on solvent used.

Simplified approximation:  $[\eta] \approx (\ln \eta_r) / c$  at c = 0.5 g / dL is often used as simple, single-point measurement.

Empirical relationship between molecular weight and viscosity:

### $[\eta] = K' M^a \rightarrow \rightarrow valid for linear polymers only$

*K*' and *a* = constants, determined from plotting  $(\ln\eta_r) / c$  against *c*. a varies usually from 0.5 - 1.0commonly a = 0.6 - 0.8*K*' =  $5 \times 10^{-4}$  to 0.5*K*', *a* = function of solvent as well as polymer type. *K*' and *a* are tabulated for large numbers of polymers. This allows the determination of the vsicosity average molecular weight,  $M_v$ :

$$[\eta] = K' \ M_v^a$$

 $M_{v}$  is usually 10-20% below  $M_{w}$ . Can be used to approximate  $M_{w}$  with [ $\eta$ ].

This equation becomes inaccurate for molecular weights < 50,000.

Several theories exist to give improved correlations.

<u>Summary</u>: Measurement of  $[\eta]$  gives quick information on  $M_v$  in the majority of cases. Useful characterisation number.

# 4. Gel Permeation Chromatography (GPC) = Size Exclusion Chromatography (SEC)

Method for separating molecules by size: gives molecular weight distributions.

Dilute solutions of polymers are passed through porous gel column.

Gel pores similar in size to macromolecules:



Small molecules diffuse into many small pores: use longer pathway. Eluted last. Large molecules can only go through large channels.

Detector: usually refractive index.

Relative method: requires calibration with polymer of known molecular weight (usually polystyrene).

GPC curve = plot of polymer concentration against elution time, gives information about:

- Nature of mol. weight distribution: monomodal, bimodal, etc.
   existence of low-molecular weight trail
- `*M*<sub>n</sub>, `*M*<sub>w</sub>

# Light scattering:

often also used as detector for GPC

absolute method: does not need recalibration

<u>Amplitude of scattered light  $\propto$  polarisability</u>, hence  $\propto$  mass of particle. Intensity of scattered light  $\propto$  (mass)<sup>2</sup>

➔ heavy molecules contribute more to scattering than light ones

#### $\Delta \tau = H c M_w$

 $\Delta\tau$  = excess turbidity of solution compared to pure solvent

*c* = concentration of polymer

H = function of refractive index