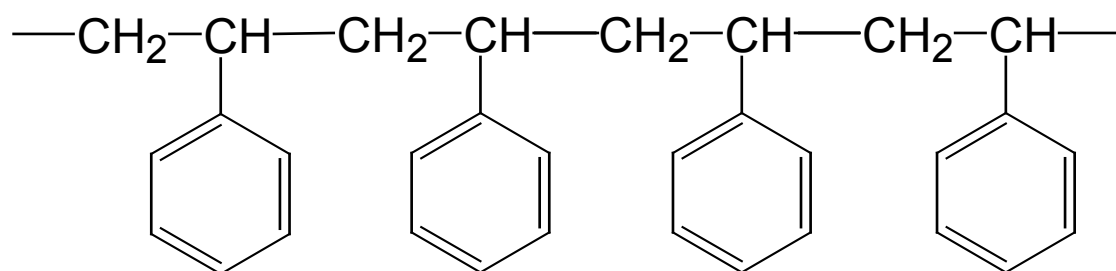


History

During the 19th century and the beginning of the 20th century, polymer substances were considered as **colloidal aggregates** of small molecules.

It was **H. Staudinger** that first proposed that polymers are connected with **covalent bonds**.

e. g. polystyrene:



Staudinger got the Nobel Prize in chemistry in 1953.

Methods for molecular weight determination.

Viscosity measurements and End group analysis.

The development of the plastic industry.

- 1866 The Parkines Company produces plastic material from cellulose nitrate and resin oil.
- 1870 J. W. Hyatt makes celluloid.
- 1908 Bækeland produces the phenol plastic bakelite (phenolic formaldehyde). This material was dominating until 1950.
- 1927 Poly(vinyl chloride)
- 1933 Fawsett and Gibson make LD-polyethylene (Amorphous, branched).
- 1953 Ziegler makes HD-polyethylene (crystalline, linear).
- 1954 Ziegler makes isotactic propylene.

Ziegler and Natta shared the Nobel Prize in chemistry in 1963.

Nomenclature and definitions.

Polymer: poly = many, mer is from meros = parts

Polymer denotes a large molecule (macromolecule) made up from many smaller parts - monomers.

Dimer - two parts; Trimer - tree parts; Oligomer - few parts (10)

Classification of polymers after their nature.

Native polymers - Biopolymers

Synthetic polymers

Modified polymers - have gone through a chemical modification

Molecular weight distribution.

Definitions.

Degree of polymerization (X) = number of monomers in the chain, $M = M_0X$.

M_0 = the molecular weight of the monomer and M = the molecular weight of the polymer.

Different kinds of molecular weight averages.

For long chain molecules, all molecules are not necessarily characterized by a chemical formula of the same weight. A population of polymer molecules (e.g. polystyrene molecules) might contain chains with different amount of styrene units (monomer) in the chains. In order to quantify the molecular weight in these cases, we need **well defined methods to calculate an average of the molecular weight**. There are several ways to define these averages, and it is important to know that **different techniques** (e. g. osmotic pressure and light scattering) can give **different types of averages**.

Monodisperse: population of macromolecules where **all molecules are identical** (the same weight).

Polydisperse: a population of **molecules of different weight**.

It is usual to use three types of **molecular weight average**: **number average**, **weight average** and **Z-average**.

In addition we will also define the **viscosity average** of the molecular weight, M_v .

Number average molecular weight.

$$\bar{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

N_i = number of molecules with the molecular weight M_i .
 \bar{M}_n is determined from osmotic pressure measurements.

Ex. 1: Assume that we have one molecule with molecular weight 1 and one molecule with molecular weight 1000.

$$\bar{M}_n = \frac{1*1 + 1*1000}{1+1} \approx 500$$

Weight average molecular weight.

$$\bar{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

$$\bar{M}_w = \frac{\sum_i c_i M_i}{\sum_i c_i}$$

where $\sum_i c_i$ is the total weight concentration of the molecules we consider in e.g. a solution.

\bar{M}_w can e.g. be determined from light scattering measurements.

Ex. 2: We use the same two molecules as on Ex. 1.

$$\bar{M}_w = \frac{1*1^2 + 1*1000^2}{1*1 + 1*1000} = 999.0$$

Z-average molecular weight.

$$\bar{M}_Z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2}$$

\bar{M}_Z can e.g. be determined from combined diffusion and sedimentation measurements.

Ex. 3: With the same two molecules as before:

$$\bar{M}_Z = \frac{1 * 1^3 + 1 * 1000^3}{1 * 1^2 + 1 * 1000^2} = 1000$$

Viscosity average molecular weight.

$$\bar{M}_V = \left[\frac{\sum_i N_i M_i^{1+a}}{\sum_i N_i M_i} \right]^{1/a}$$

where a is the exponent in Staudinger-Mark-Houwinks equation: $[\eta] = k \cdot M^a$ ($[\eta]$ = intrinsic viscosity). For a flexible polymer in a good solvent, $a \approx 0.7$.

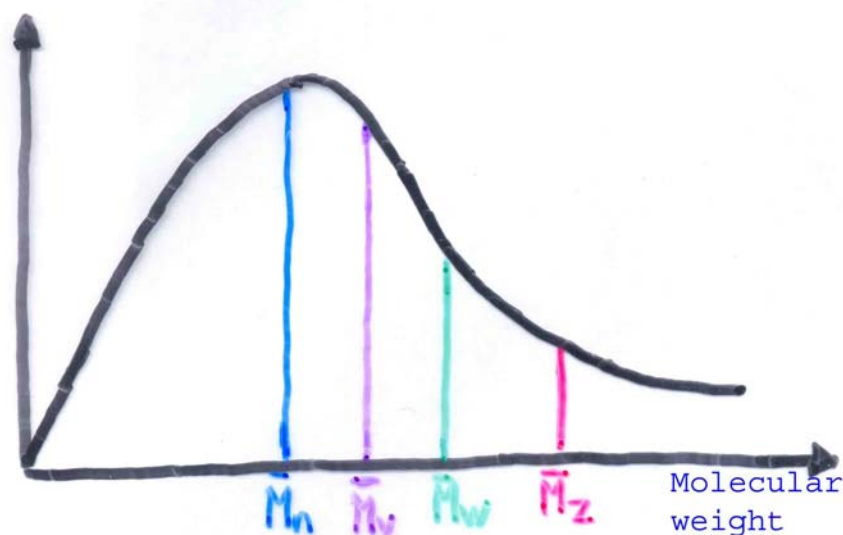
M_V is determined by viscosity measurements.

Ex. 4: With the same two molecules as before:

$$\bar{M}_V = \left[\frac{1 \cdot 1^{1+0.70} + 1 \cdot 1000^{1+0.70}}{1 \cdot 1 + 1 \cdot 1000} \right]^{1/0.70} = 998.5$$

Schematic illustration of molecular weight distributions.

Molecular weight distribution curve.



Random distribution: $\bar{M}_n : \bar{M}_v : \bar{M}_w : \bar{M}_z = 1 : 2 : 3$

Monodisperse distribution: $\bar{M}_n = \bar{M}_v = \bar{M}_w = \bar{M}_z$

Polydisperse distribution: $\bar{M}_n < \bar{M}_v < \bar{M}_w < \bar{M}_z$

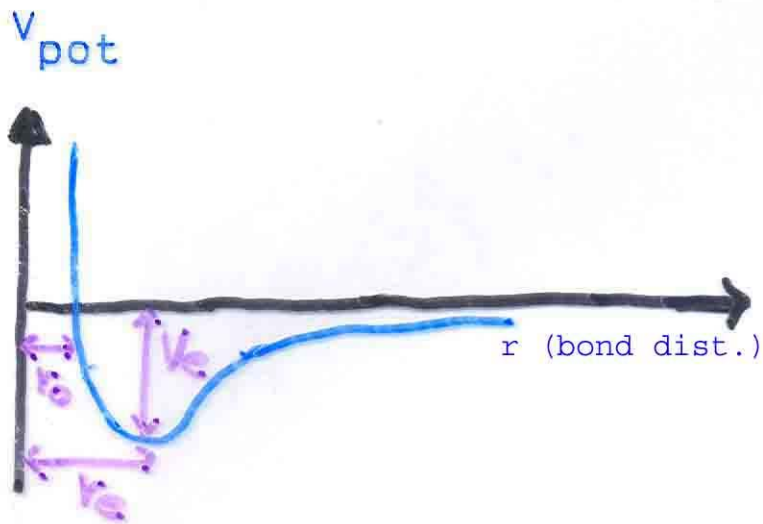
A measure of the molecular weight distribution: $\frac{\bar{M}_w}{\bar{M}_n} \geq 1$
(Polydispersity index).

Anionic polymerized polystyrene fractions usually have $\frac{\bar{M}_w}{\bar{M}_n} < 1.1$

For a random distribution: $\frac{\bar{M}_w}{\bar{M}_n} = 2$

Different intermolecular bonds.

Illustration of intermolecular interaction energy.



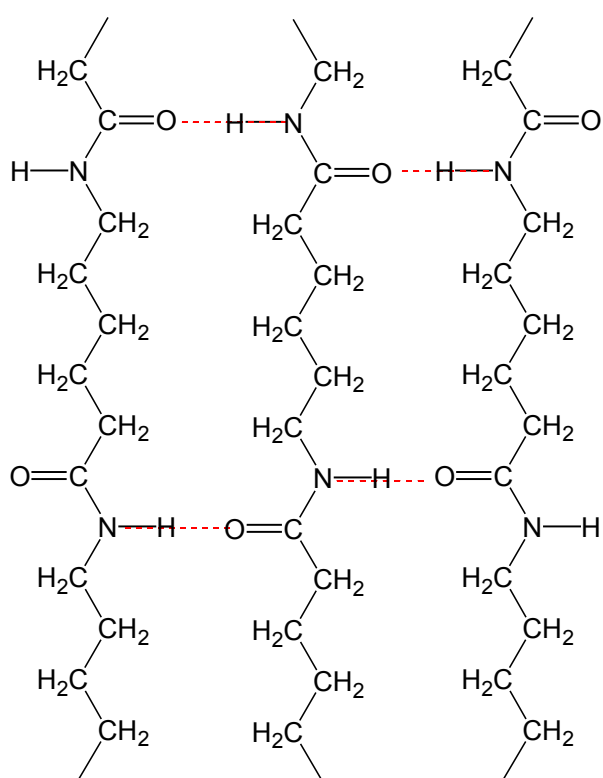
Lennard-Jones potential:

$$V(r) = 4V_e \left[\left(\frac{r}{r_0} \right)^{-12} - \left(\frac{r}{r_0} \right)^{-6} \right]$$

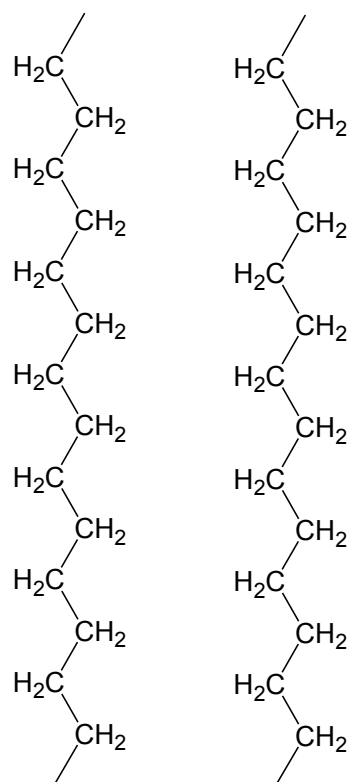
Hydrogen binding

Strongest bonding: biopolymers.

Molecules containing OH, COOH, NH₂, CONH₂ may form hydrogen bonds to molecules containing N, O, F and S.



Nylon 6; mp. 220 °C

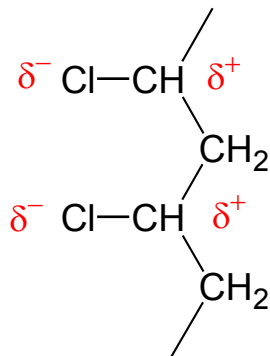


Polyethylene; mp. 140 °C

Dipole bonds:

Attractive forces between permanent dipoles in the molecules.

Ex.



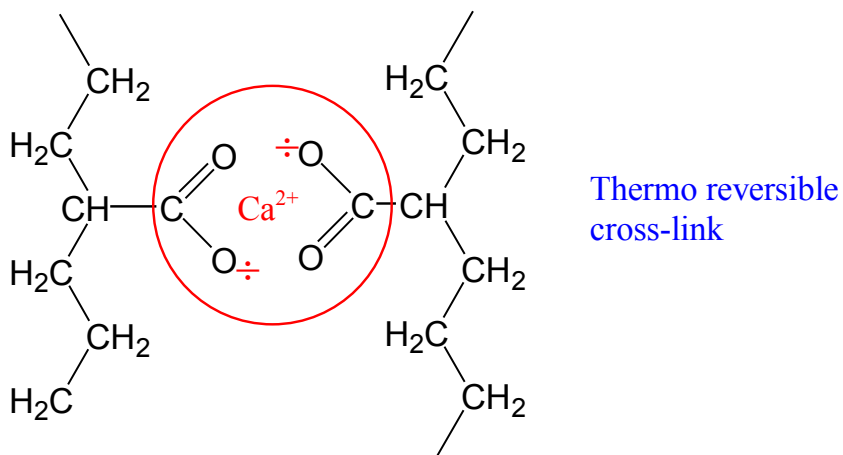
PVC

Ionic bonds:

Attractive forces between charged (ionized) groups in the molecules.

Is often present in ionomers.

Ex.



Ionomer polyethylene co-polymer ethylene-acrylic acid.

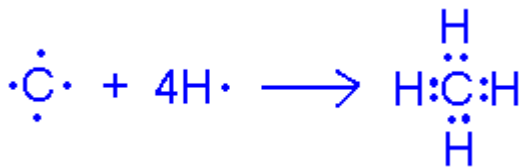
Dispersion forces:

Van der Waals forces; weak forces.

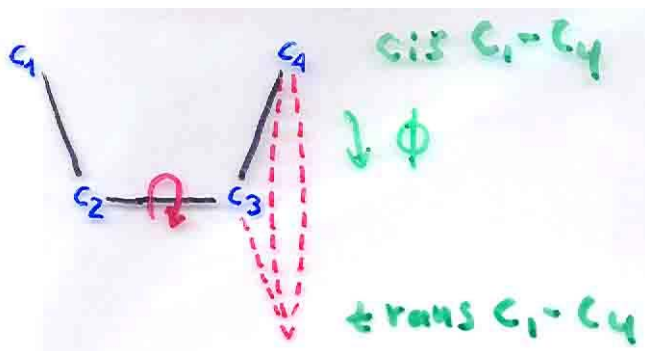
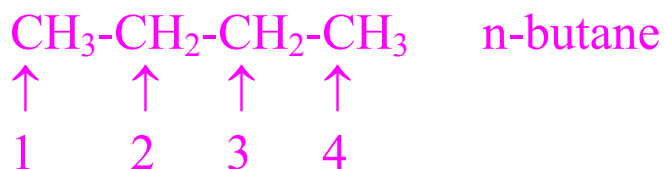
Induced dipoles in the atoms electron clouds induce attraction between the molecules. Dispersion forces exist in all polymers.

Covalent bonds:

In reality intramolecular bonds.



The flexibility of polymer molecules.



cis C₁-C₄ = 2.6 Å; trans C₁-C₄ = 3.8 Å.

Nobel Prizes related to polymer science.

- 1953 H. Staudinger “For his discoveries in the field of macromolecular chemistry” (chemistry).
- 1963 K. Ziegler and G. Natta “For their discoveries in the field of the chemistry and technology of high polymers” (chemistry).
- 1974 P. J. Flory “For his fundamental achievements, both theoretical and experimental, in the physical chemistry of macromolecules” (chemistry).
- 1991 P.-G. de Gennes “For discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex form of matter, in particular to liquid crystals and polymers” (physics).
- 2000 A. J. Hegger, A.G. MacDiarmid, and H. Shirakawa “For the discovery and development of conductive polymers” (chemistry).