

Semi-crystalline Solids - Polymers

Books

**P Lovell and RAYoung - Introduction to Polymers,
Chapman and Hall**

LH Sperling - Physical Polymer Science Wiley

G Strobl - Polymer Physics Springer (2nd ed)

Man-made polymers frequently contain both crystalline and amorphous regions, although some are completely amorphous.

A good example is polyethylene ('polythene'), which is rarely more than about 75% crystalline – and that value is high for a polymer.

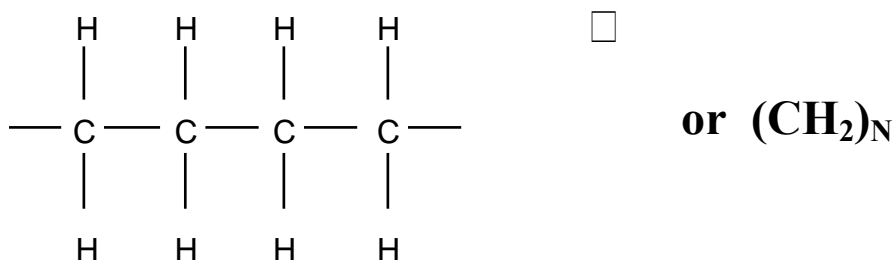
Essentially no polymers are 100% crystalline (with the exception of those produced by epitaxial means).

What are Polymers?

Polymers are long chain molecules, usually with a carbon backbone (although some are based on silicon in the backbone).

They consist of a string of repeating units called **monomers**, joined together.

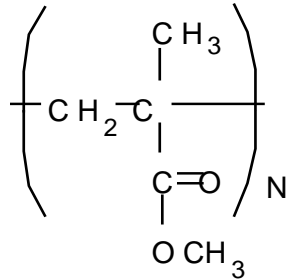
Simplest is polyethylene (polythene)



N is known as the **degree of polymerisation** and may run to thousands.

Other common polymers include perspex and nylon.

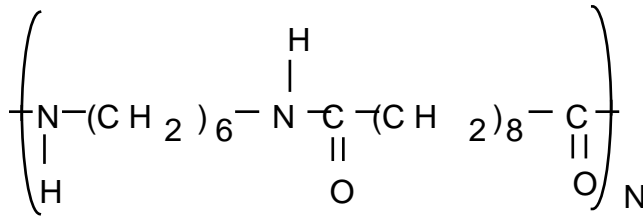
Perspex is the (British) trade mark for poly (methyl methacrylate).



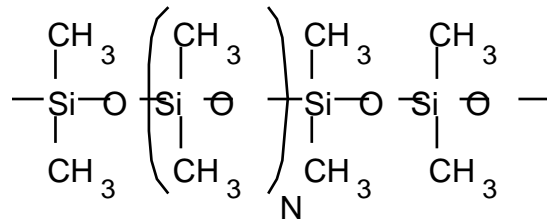
Known as Plexiglass in the USA.

Nylon (so-called because of developments made collaboratively in New York and London), has various forms depending on the number of carbons

.g nylon 6-10



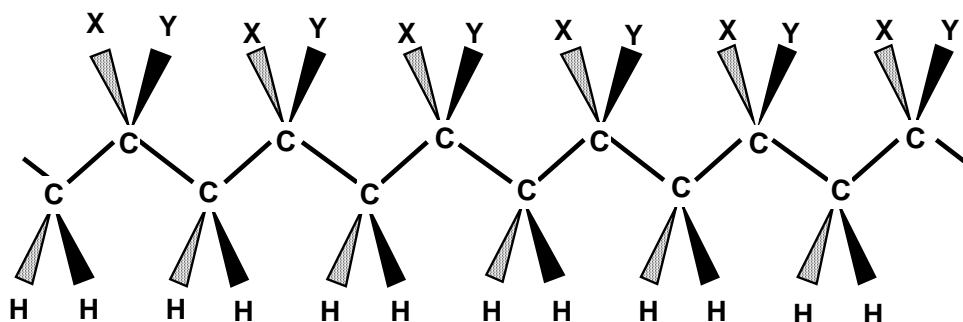
Poly dimethyl siloxane (the basis of silicone rubber):



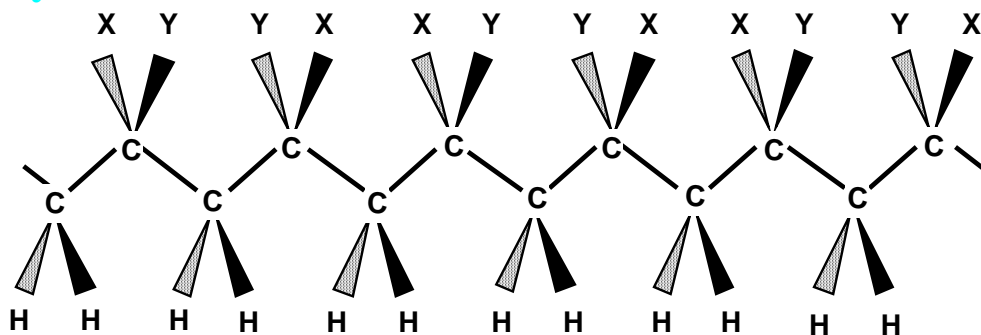
Tacticity and Stereochemistry

In practice the molecule is a 3-dimensional entity, and where the groups attached to each carbon atom are non-identical one can identify 3 ways in which the attachment can occur:

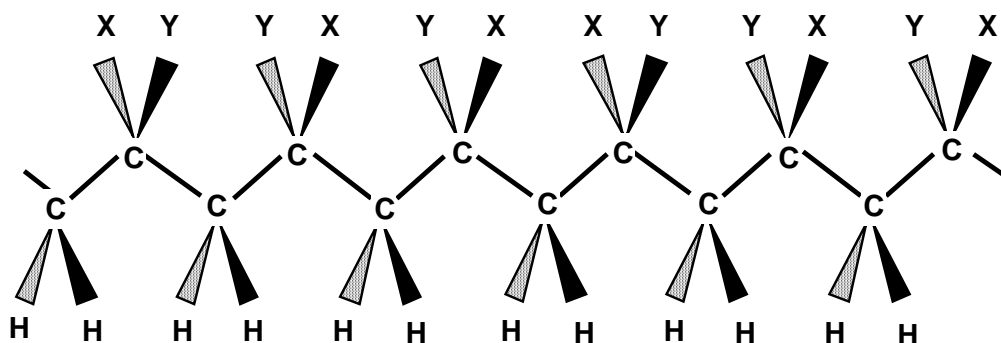
Isotactic



Syndiotactic



Atactic



Atactic polymers are generally **easy to synthesise, but these polymers cannot crystallise due to their irregularity.**

With suitable polymerisation routes, it is possible to prepare isotactic and syndiotactic polymers (at least in some cases), and these can crystallise.

Building up models of long chain molecules we can begin to see that there are **many possible conformations they can adopt.**

How can we characterise them?

How to deal with Polymers?

You might think because polymers are long, complicated objects, they might be equally complicated to deal with.

For many properties this is not true.

Many of their properties depend **much more strongly on their length (or equivalently degree of polymerisation N), than on specific chemistry.**

Also a single chain tends to interact with many other chains.

This means we can average out the interactions of surrounding chains and use so-called **mean field theory and statistical mechanics** to understand their behaviour.

This leads to so-called scaling laws.

It turns out mean field theories are better obeyed by polymers than for many simpler, atomic species.

For more information see

P-G de Gennes - Scaling Laws in Polymer Physics, Cornell UP.
Random Walks

Random walks will be familiar to you from statistical mechanics in general.

We can use this approach to derive a scaling law for the **mean end-to-end distance** of a polymer chain.

Simple model – freely jointed chain i.e. each of N segments of length a is independent.

End-to-end distance

$$\underline{\mathbf{r}} = \underline{\mathbf{a}}_1 + \underline{\mathbf{a}}_2 + \underline{\mathbf{a}}_3 + \underline{\mathbf{a}}_4 + \dots + \underline{\mathbf{a}}_N = \sum_{i=1}^N \underline{\mathbf{a}}_i$$

Mean $|\mathbf{r}|^2$ is

$$\langle \mathbf{r} \cdot \mathbf{r} \rangle = \left\langle \left(\sum_{i=1}^N \underline{\mathbf{a}}_i \right) \cdot \left(\sum_{j=1}^N \underline{\mathbf{a}}_j \right) \right\rangle$$

$$\therefore \langle \mathbf{r}^2 \rangle = \sum_i \sum_j \underline{\mathbf{a}}_i \cdot \underline{\mathbf{a}}_j = N a^2 + \sum_{i \neq j} \langle \underline{\mathbf{a}}_i \cdot \underline{\mathbf{a}}_j \rangle$$

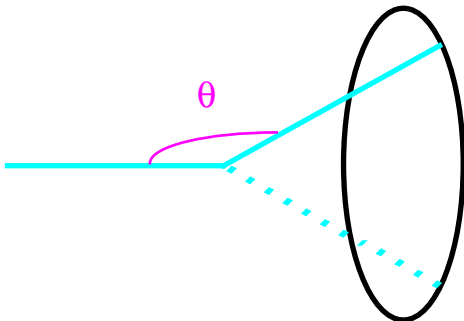
Since there are no correlations between segments

$$\langle \mathbf{r}^2 \rangle = N a^2$$

scaling law for random walk

In practice this is a very unphysical model for a chain.

The chemistry of the chain means that there are fixed angles between segments.



$$\text{Then } \langle \underline{\mathbf{r}}_i \cdot \underline{\mathbf{r}}_{j-1} \rangle = a^2 \cos \theta$$

For segments m apart

$$\langle r_j \cdot r_{j-m} \rangle = a^2 \cos^m \theta$$

Correlations therefore die away along the chain.

There will be subunits (multiple segments) which are uncorrelated, and these can then be used as the basic building blocks.

g links/subunit, each described by vector \underline{c}_i ;
 N/g subunits per chain.

$$\langle r^2 \rangle = \frac{N}{g} \langle c^2 \rangle = Nb^2$$

b is known as the statistical step length

$b > a$ clearly. How much greater is a measure of how strong the correlations are along the chain.

This can be described by the characteristic ratio C_∞ .

$$C_\infty = \frac{b^2}{a^2}$$

Tells you about how stiff/straight the chain is.

C_∞ can be worked out from the chemical details of the chain (bond angles etc).

This is an example of how we can **find universal behaviour** for polymers, even though the chemical specificity clearly matters too. We can find **scaling laws** in terms of the general quantities

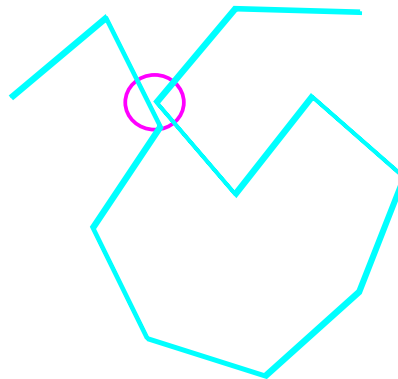
e.g. $\langle r^2 \rangle = Nb^2$

but what b is depends on the specific polymer.

Our model is still too simple.

Correlations along a chain may die out quite fast, but a chain may still loop back on itself.

Two remote segments can interact with one another.



This interaction may be energetically favourable or unfavourable, and depending on this the chain statistics are correspondingly affected.

- The interaction is **unfavourable**. Then the segments will tend to keep away from each other and the chain will **swell**: a "**self-avoiding walk**".

Mean field theory (due to Flory) says in this case

$$\langle r^2 \rangle^{1/2} = N^\nu a$$

where $\nu = 3/5$ (ie greater than 0.5).

Modern renormalisation group methods give $\nu = 0.588$. Experimentally very difficult to distinguish between these two values of ν .

These statistics apply in a so-called '**good solvent**'.