Polymer Science

What is it?
The Science of Large Molecules

This includes
Synthesis
Characterization
Polymer Physics and Physical Chemistry
Polymer Engineering

Poly............mer
many units
\(-M-M-M-M-M-M-M-\)
or
\(-(M)_n-\)

Some Basic Definitions

**Polymer** — A large molecule made up of small building blocks

**Monomers** — The building blocks

**Homopolymer** — What you get if the building blocks are all the same

**Copolymer** — A polymer composed of different monomers

**Blend** — A mixture of different polymers
How Big are Polymers?

Check out the chain of beads on the right. Imagine each bead is an ethylene unit:

Ethylene  \[ \text{Polyethylene} \]

Then because there are only 200 ethylene units in this chain (ie it is a 200 - mer), its molecular weight is only 5,600 (= 28 x 200).
Polyethylene as pictured above is what we call a simple homopolymer; that is, it is made up of identical units. It is also linear, as opposed to being branched like the part of a chain shown opposite. This is the type of thing we mean by microstructure. Chain microstructure can have a profound effect on things like crystallinity and hence macroscopic properties (e.g., stiffness, strength).

Chain Microstructure

So far we’ve given you a picture representation of a chain as a connected set of beads, like pearls on a string. In addition, we snuck in a picture of part of a polyethylene chain, like the one shown opposite.
Molecular representations

- CH₂ - CH₂ - CH₂ - CH₂ - CH₂ - CH₂ - CH₂ - CH₂ -
CHAIN MICROSTRUCTURE

TOPICS COVERED :-

• LINEAR CHAINS, BRANCHING
• CROSS - LINKING AND NETWORK FORMATION
• SEQUENCE ISOMERISM
• STERIOISOMERISM IN VINYL POLYMERS
• DIENE POLYMERS
• COPOLYMERS AND BLENDS
PHILOSOPHICAL APPROACH

ILLUSTRATE THE CONNECTION BETWEEN STRUCTURE AND PROPERTIES RIGHT FROM THE BEGINNING.

TO DO THIS WE NEED TO REMIND OURSELVES ABOUT THE NATURE OF CRYSTALLINITY

RANDOM COIL
Like “cooked spaghetti”

CRYSTALLINE
Like “uncooked spaghetti”
{Real polymer crystals are more complicated than this, as we will see}
THE EFFECT OF CRYSTALLINITY ON MATERIALS’ PROPERTIES

We will be asking how crystallinity affects

• Strength
• Stiffness
• Toughness
• Barrier Properties
• Solubility
• Transparency
• Thermal Properties
• Etc
The Elements of Polymer Microstructure

**Linear and Branched Polymers**

- Ethylene
  - High Pressure Free Radical Polymerization
  - Zeigler-Natta Catalysts
  - Affects Ability to Crystallize

**High Density Polyethylene (HDPE)**
- Essentially Linear

**Low Density Polyethylene (LDPE)**
- Significantly Branched

*(A) Part of a Linear Polyethylene Molecule
(B) Part of a Branched Polyethylene Molecule*
Branching and network formation

The type of branching we’ve considered so far is actually short chain branching. Long chain branching can also occur and by doing some clever chemistry one can even make star polymers, where a number of long chain branches are joined apparently at a single point, but actually in a well defined junction zone.
Branching can also lead to the formation of densely connected networks. For example, if we start with a Y shaped molecule, where each arm of the Y has a reactive group that is capable of reacting with and connecting to any other group on another Y, then as the reaction proceeds we would build up molecules of various sizes. The unreacted ends of these larger molecules would also continue to react, ultimately forming a network of interconnected units. We say that the Y shaped molecule is **trifunctional**.

**Tetrafunctional** (four reactive groups) molecules can also react to form networks (e.g. X shaped).

What would happen if you reacted bifunctional molecules?
Bifunctional Molecules

All you would be able to make from bifunctional molecules is linear chains!

More on this later when we discuss polymerization. But for now, back to network formation.
An example of forming a network from a trifunctional molecule is the reaction of phenol with formaldehyde.
Network Formation

Here is what a small part of such a network would look like. Phenolic resins like this were first made around the turn of the twentieth century by Leo Baekeland, who modestly called the resulting materials Baekelite.
Networks can also be made by taking linear polymer chains and linking them together using covalent bonds. We call this cross-linking.
Network formation by cross-linking

An example of cross linking is the reaction of natural rubber or poly(isoprene) with sulfur (or, as we prefer, sulphur).

The sulfur interconnects the chains by reacting with the double bonds. This process was originally discovered by Charles Goodyear, who called it vulcanization (note that the linkages shown on the right actually consist of short chains of sulphur atoms).
Isomerism in Polymers

Now we move on to another topic under the general heading of microstructure, namely isomerism. There are various types of isomerism that occur in nature and to us they find their most fearsome form in describing the structure of various sugars.

Two molecules are said to be isomers if they are made up of the same number and types of atoms, but differ in the arrangement of these atoms.

Fortunately the types of isomerism we will consider are not as complex or involved. Specifically, we will consider:

1. Sequence isomerism
2. Stereoisomerism (in vinyl polymers)
3. Structural isomerism (in diene polymers)
Sequence Isomerism

When a monomer unit adds to a growing chain it usually does so in a preferred direction. Polystyrene, poly(methyl methacrylate) and poly(vinyl chloride) are only a few examples of common polymers where addition is almost exclusively what we call head-to-tail.

\[
R^* + CH_2=CHXY \quad R^* + CH_2=CHXY \quad R^* + CH_2=CHXY \\
\quad T \quad H \quad T \quad H \quad T \quad H
\]

- \( R^* + CH_2=CHXY = (HT) \)
- \( R^* + CH_2=CHXY = (TH) \)

\( R^* + CH_2=CHXY \)
Sequence Isomerism

In many common polymers, such as polystyrene, addition occurs almost exclusively in a head-to-tail fashion.

Obviously, steric factors play a role here, the bloody great benzene rings on adjacent units would strongly repel during the polymerization process if they were head-to-head.
Sequence Isomerism

In other polymers, particularly those with smaller substituents, head-to-head and tail-to-tail placements can occur.

A good example is poly(vinylidene fluoride), -CH$_2$-CF$_2$- . Check out the illustrations below. The yellow balls are the fluorine atoms.

- All head-to-tail units
- Some head-to-head and tail-to-tail units
Polymerization of a vinyl monomer, $\text{CH}_2=\text{CHX}$, where $X$ may be a halogen, alkyl or other chemical group (anything except hydrogen!) leads to polymers with microstructures that are described in terms of tacticity. The substituent placed on every other carbon atom has two possible arrangements relative to the chain and the next $X$ group along the chain. These arrangements are called racemic and meso, just to annoy you and make your life difficult.
Stereoisomerism in Vinyl Polymers

Parts of polypropylene (\(-\text{CH}_2\text{-CHCH}_3\)-) chains where all the methyl (\text{CH}_3) substituents are on the same side (we’ve colored their carbon atoms red) are shown schematically below. We call this arrangement isotactic, so this polymer is isotactic polypropylene.

Part of an isotactic polypropylene chain seen from the side

The same chain seen more from the top
Here are two more polypropylene chains, both shown as if we were looking down from “on top”. One of these consists of units that are all racemic to one another and is called syndiotactic. The other has a random arrangement of units and we call such chains atactic. Which one is the atactic chain, A or B?
TACTICITY IN SOME COMMERCIALLY IMPORTANT POLYMERS

POLYSTYRENE - ATACTIC
POLYPROPYLENE - LARGELY ISOTACTIC
PVC - LARGELY ATACTIC
  some syndiotactic sequences?
PMMA - ATACTIC
So far we’ve described sequence and stereoisomerism. Now we come to structural isomerism and is seen in the synthesis of polydienes from conjugated dienes:

\[ \text{CH}_2 = CX - \text{CH} = \text{CH}_2 \]

where if

- \( X = H \) we have butadiene
- \( X = \text{CH}_3 \) we have isoprene
- \( X = \text{Cl} \) we have chloroprene

The polymers made from these monomers are important because they (and also many copolymers that incorporate these units) are elastomers or rubbers. Poly(isoprene), for example, is natural rubber, poly(chloroprene) is neoprene (you know, what wet suits are made of). However, natural rubber is a particular structural isomer of poly(isoprene), cis-1,4-poly(isoprene).

So what on earth does cis mean and where do the numbers come from?
Let's start with the numbers. This is pretty easy - we just label the carbon atoms of the monomer in order

\[ CH_2 = CX - CH = CH_2 \]

1 2 3 4

Now let's break one of the bonds in one of the double bonds and leave the carbon atoms still attached by a single bond. This leaves an “unshared” electron on each of the carbon atoms involved.

\[ CH_2 - CX - CH = CH_2 \]

Now let's do the same for the other double bond

\[ CH_2 - CX - CH - CH_2 \]

Obviously we can now connect the middle dots to make a new double bond, leaving unshared electrons “hanging out” on carbon atoms 1 and 4.

\[ CH_2 - CX = CH - CH_2 \]
Structural Isomerism

Two such units can become attached through their carbon atoms, 1 and 4

\[
\text{CH}_2 - CX = CH - \boxed{\text{CH}_2 - \text{CH}_2} - CX = CH - \text{CH}_2
\]

1 2 3 4 1 2 3 4

This can be repeated, building up a chain with 1,4 linkages. Of course, this step - by step breaking and reforming of bonds is not what happens in a real reaction, we’ve just constructed this picture to give you an understanding of where the 1,4 part of the nomenclature comes from. It should also now be immediately clear that we can add units by just “breaking” (ie reacting) one of the double bonds (1,2 or 3,4) and incorporating those units into the chain.
The various possibilities are shown opposite, where we have used neoprene as an example. There is still one thing we haven’t explained, however. There are two types of 1,4 units, cis and trans. This simply refers to the arrangement of carbon atoms around the double bond.
Copolymers

Random Copolymers

Alternating Copolymers

Block Copolymers

Graft Copolymers
Commercially produced polyethylene’s often have molecular weights in the hundreds of thousands. To give you a feel for this, imagine that each ethylene unit has a length of 1 inch instead of a couple of angstroms,

\[ \text{-CH}_2\text{-CH}_2\text{-} = 1 \text{ inch} \]

then the length of a fully stretched out chain of molecular weight 420,000 would be almost one quarter of a mile! These are very big molecules indeed.
A last (for now !) comment on molecular weight

One final problem - all synthetic polymers have a distribution of chain lengths (ie when we synthesize a polymer we end up with a bunch of chains of different length, ranging from the very short to the very long). As a result, we usually have to define an average molecular weight, which is not quite as easy as it sounds, because there are different types of averages. Also, certain experimental measurements will give you one average, while others may give you another. There is also one technique that can give you the entire distribution! More on these later.
MOLECULAR WEIGHT

WHY IS IT IMPORTANT?

TENSILE STRENGTH vs. MOL. WT.

MELT VISCOSITY vs. MOL. WT.
Molecular Weight

CH₄          16
CH₃ - CH₃    30
CH₃ - CH₂ - CH₃  44
CH₃ - CH₂ - CH₂ - CH₃  58
CH₃ - (CH₂)₆ - CH₃  114
CH₃ - (CH₂)₃₀ - CH₃  450
CH₃ - (CH₂)₃₀₀₀₀ - CH₃  420030

Gases
Liquids
"Semi-solid"
Solids
Increasing Molecular Weight
The problem with describing the molecular weight of synthetic polymers is that there is always a distribution of chain lengths. The solution would seem to be simple - let's just define an average. For example, if we started with 100 monomers in a pot (or, more realistically, 100 moles of monomer) and polymerized these to give 5 chains (or 5 moles of chains), then the average "length" of the chain, or degree of polymerization, would be 20; 100 divided by 5. If the weight of each unit in the chain were 100 units, the average molecular weight would be 20,000. But this says nothing about the distribution. Do we have one chain 96 units long and 4 unreacted monomers, or chains of length 18,19,20,21 and 22? Or some other distribution?

Also, what we have calculated is something called a number average, which is defined mathematically opposite. If you're not used to dealing with summations, this looks horrible. To give you a feel for how it works, and also introduce a different average - the weight average - let's consider a ridiculous example.

$$M_n = \frac{\sum N_x M_x}{\sum N_x}$$
Molecular Weight - Definition of Number
Average and Weight Average

Behold an elephant with four mosquito’s on its bum. If the elephant weighs 10,000 lbs., and the mosquito’s 1 lb. each. What would be the average weight of each of the things or species present?
Molecular Weight - Definition of Number Average and Weight Average

\[ M_n = \frac{\sum N_x M_x}{\sum N_x} = \frac{[1 \times 10,000] + [4 \times 1]}{4 + 1} \approx 2,000 \]
Molecular Weight - Definition of Number Average and Weight Average

\[
\bar{M}_w = \frac{\sum W_x M_x}{\sum W_x} = \frac{[10,000 \times 10,000] + [4 \times 1]}{10,000 + 4} \approx 10,000
\]
Molecular Weight - Definition of Number Average and Weight Average

Consider a sample with 5 (moles of) chains of “length” (degree of polymerization or DP) 100, (i.e. has 100 monomer units in the chain), 5 (moles of) chains of length 150 and 5 (moles of) chains of length 200.

For this simple example it should be easy to see that the average DP of the sample is 150.

If the molecular weight of each unit in the chain were 100, the number average molecular weight would then be 15,000.

\[
\overline{M_n} = \frac{\sum N_x M_x}{\sum N_x}
\]
Molecular Weight - Definition of Number Average and Weight Average

Here's how the equation works:

\[ \overline{M_n} = \frac{\sum N_x M_x}{\sum N_x} = \frac{[5 \times 10,000] + [5 \times 15,000] + [5 \times 20,000]}{5 + 5 + 5} \]

\[ = \frac{50,000 + 75,000 + 100,000}{15} = 15,000 \]

What about weight average molecular weight?
First recall the definition of weight average:

\[
\bar{M}_w = \frac{\sum W_x M_x}{\sum W_x}
\]

Now note that the total weight of species x present is just the molecular weight of each chain of type x multiplied by the number of chains of this type. E.g. if there are 5 chains, each of weight 10,000, then \(w_x\) is 50,000;

\[
W_x = N_x M_x
\]

We can now substitute in the equation at the top to obtain a different form of the equation for weight average:

\[
\bar{M}_w = \frac{\sum W_x M_x}{\sum W_x} = \frac{\sum N_x M_x^2}{\sum N_x M_x}
\]
Weight Average Molecular Weight

This gives us;

\[
\overline{M}_w = \frac{\sum W_x M_x}{\sum W_x} = \frac{\sum N_x M_x^2}{\sum N_x M_x} = \frac{5 \times 10,000^2 + 5 \times 15,000^2 + 5 \times 20,000^2}{5 \times 10,000 + 5 \times 15,000 + 5 \times 20,000} = 16,111
\]

Note that the weight average is larger than the number average. This is always true, except in the case when all the chains are the same length (as in proteins, where the number and sequence of amino acids is specified by the cell’s machinery). We call the ratio of the two averages the polydispersity of the system. It is a measure of the breadth of the distribution.

Polydispersity = \[ \frac{\overline{M}_w}{\overline{M}_n} \geq 1 \]
Molecular Weight of Polymers - What Average?

We have seen that average molecular weight is not unique. It turns out that there are more than two ways to define an average. Look at the definitions of number and weight average again:

\[
\overline{M_n} = \frac{\sum N_x M_x}{\sum N_x} \quad \text{Number Average Molecular Weight}
\]

\[
\overline{M_w} = \frac{\sum N_x M_x^2}{\sum N_x M_x} \quad \text{Weight Average Molecular Weight}
\]

You can see that we can go from number to weight average by multiplying each of the terms inside the summations by \(M_x\). Higher order averages can be constructed in the same way. Eg the z-average:

\[
\overline{M_z} = \frac{\sum N_x M_x^3}{\sum N_x M_x^2}
\]

The ratios of these averages can be related to the moments of the distribution and tell us about its breadth and "skewness"
MOLE (NUMBER) AND WEIGHT DISTRIBUTIONS

A narrow molecular weight distribution plotted according to number (left) and weight (right)
Molecular Weight - Enough Already!

Molecular Weight

\[ M_n = 108,500 \]
\[ M_w = 118,200 \]