Polymer Science

What is it ? The Science of Large Molecules

This includes

Synthesis Characterization Polymer Physics and Physical Chemistry Polymer Engineering



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. I magine each bead is an ethylene unit;



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).



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.



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 (eg stiffness, strength)

Molecular representations

- CH_2 -





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 BEGINING.

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





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





Short chain branching

Long chain branching

Star polymers

Network Formation

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.

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*.



More Network Formation



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*.



Sequence Isomerism

In many common polymers, such as polystyrene, addition occurs almost exclusively in a headto-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



Stereoisomerism in Vinyl Polymers

Polymerization of a vinyl monomer, $CH_2 = CHX$, 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 ($-CH_2-CHCH_3$ -) chains where all the methyl (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



Stereoisomerism in Vinyl Polymers

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;

where if

$$CH_2 = CX - CH = CH_2$$

X = H we have butadiene $X = CH_3$ we have isoprene X = CI 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

 $\begin{array}{c} \mathsf{CH}_2 = \mathsf{CX} - \mathsf{CH} = \mathsf{CH}_2 \\ 1 & 2 & 3 & 4 \end{array}$

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.

$$CH_2 - CX = CH - CH_2$$

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

$$\dot{CH}_2 - CX = CH - \frac{CH}{2} - \frac{CH}{2} - \frac{CH}{2} - \frac{CX}{2} = CH - \frac{\dot{CH}_2}{4}$$

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

-A-B-B-A-A-A-B-A-A-A-B-A-B-A-B-A-A-A-B-Random Copolymers

Alternating Copolymers



Even more molecular weight !

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*,

 $[-CH_2-CH_2-] = 1$ 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 quiet 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 ?



Molecular Weight



The problem with describing the molecular weight of synthetic polymers is that there 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.







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 ?



$$\overline{M}_n = \frac{\sum N_x M_x}{\sum N_x} = \frac{[1 \times 10,000] + [4 \times 1]}{4 + 1} \sim 2,000$$



$$\overline{M}_{w} = \frac{\sum W_{x}M_{x}}{\sum W_{x}} = \frac{[10,000 \times 10,000] + [4 \times 1]}{10,000 + 4} \sim 10,000$$

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.



$$\overline{M_n} = \frac{\sum_{N_x M_x}}{\sum_{N_x}}$$

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?

Weight Average Molecular Weight

First recall the definition of weight average;

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. Eg if there are 5 chains, each of weight 10,000, then w_x is 50,000;

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

$$\overline{M}_{w} = \frac{\sum W_{x}M_{x}}{\sum W_{x}}$$

$$W_x = N_x M_x$$

$$\overline{M}_{w} = \frac{\sum W_{x}M_{x}}{\sum W_{x}} = \frac{\sum N_{x}M_{x}^{2}}{\sum N_{x}M_{x}}$$

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 =
$$\frac{M_w}{\overline{M}_n} \ge 1$$

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;

Number Average Molecular Weight

 $\overline{M}_{n} = \frac{\sum N_{x} M_{x}}{\sum N_{x}}$

$$\overline{M}_{w} = \frac{\sum N_{x} M_{x}^{2}}{\sum N_{x} M_{x}}$$

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 ratio's of these averages can be related to the moments of the distribution and tell us about its breadth and "skewedness"

MOLE (NUMBER) AND WEIGHT DISTRIBUTIONS



A *narrow* molecular weight distribution plotted according to *number* (left) and *weight* (right)

Molecular Weight - Enough Already!



Degree of Polymerization