Network Formation

We have seen how monofunctional molecules react once to give a slightly larger molecule and bifunctional molecules react to give chains, how would you make chains that branch and then perhaps interconnect to form networks?

- A. Use a mixture of bifunctional and monofunctional units
- B. Get a tube of Molecular Super Glue and stick a bunch of chains together
- C. Use multifunctional (f>2) monomers

Network Formation

The hydrogens in the ortho and para positions to the OH group, which by convention are not usually shown but here are indicated by a * ,can react with fomaldehyde to form (initially) oligomers.





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.



Step-Growth Polymerization ; Summary



Chain Polymerizations



Chain Polymerizations



Chain Polymerizations - a simplistic view

$$\begin{array}{c} X \\ CH_{2} = C \\ H \end{array} \xrightarrow{} CH_{2} \cdot CH_{2}$$

Chain Polymerizations



Chain Polymerizations - types or nature of the active site



Free Radical Anionic Cationic Coordintation

Characteristics of Chain Polymerizations

Need to consider;

Initiation
 Propagation
 Termination
 Chain Transfer



Free Radical Polymerization - Initiation



Free Radical Polymerization - Propagation



Free Radical Polymerization - Question

So, we have a bunch of growing chains reacting with monomers which (in a batch reaction) gradually get depleted. Obviously, the ends of two growing chains could also meet as a result of their random motions. What would happen then?

A. Nothing, the radicals would not like each other (both are characterized by having unshared negatively charged electrons at their ends)

B. They would react, terminating each chain

Free Radical Polymerization - Termination

$$\frac{\operatorname{Rest of Chain}}{\operatorname{CH}_{2}} \operatorname{CH}_{2} \operatorname{C$$

Rest of Chain
$$CH - C$$
;
 $X \rightarrow X$
Rest of Chain $CH - C$;
 $X \rightarrow X$
 $X \rightarrow X$
 $Rest of Chain CH = CHX$
 $H_2XC - CH_2^{Rest of Chain}$

Chain Transfer



Chain Transfer to Monomer - Propylene



Chain Transfer and Long Chain Branching



Short Chain Branching in Polyethylene



In addition to long branches, free radically polymerized polyethylene also has short chain branches by a process called backbiting. This is an intramolecular chain transfer reaction that occurs locally among groups near the end of the chain. The formation of a butyl branch is

 $CH_2 = CH_2$

More Short Chain Branching



Butyl branches are thought to predominate because of the six membered ring transition state (see preceding page), but amyl and hexyl branches are also formed, where hydrogens are abstracted from the sixth and seventh methylene groups from the radical end. Ethyl branches are also formed from additional intramolecular transfers.

Anionic Polymerization



Although there is an unshared electron at the end of a growing chain in free radical polymerization, there is still an equal number of protons and electrons, hence overall charge neutrality. Certain monomers can be polymerized anionically, however, such that there is an excess of one electron at the active site, hence a negative charge*.

$$\sim \sim CH_2 - CH_2 - O: + CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - O - CH_2 - CH_2 - O:$$

*Those of you that have done some electrochemistry may be confused by this, because in an electrolytic cell the anode is positively charged. But an anion is then a species that migrates towards the anode and must therefore be negatively charged. (Confusingly, in other types of cells the anode can be negative, the definition of an anode is actually in terms of an oxidation site - aren't you glad we told you that?)

Anionic Polymerization



If the active site is a carbon atom, as shown on the left, then this charged species is called a carbanion. Below is an oxanion, formed in this case during an anionic ring-opening polymerization.

$$-\sim CH_2 - CH_2 - O: + CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - O - CH_2 - CH_2 - O:$$