Introduction
to Modern Biomaterials

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Polymeric Materials - Part II

Learning Resources

www.msm,cam.ac.uk/

University of Cambridge

Department of Materials Science and Metallurgy

Teaching: DoITPoMS Project

Library of Teaching and Learning Packages for Materials Science

www.msm.cam.ac.uk/doitpoms/tlplib/index.php

THE GLASS TRANSITION IN POLYMERS (required reading)

Types of Polymers

- Thermosets
- Thermoplastics

Classification based on Processing

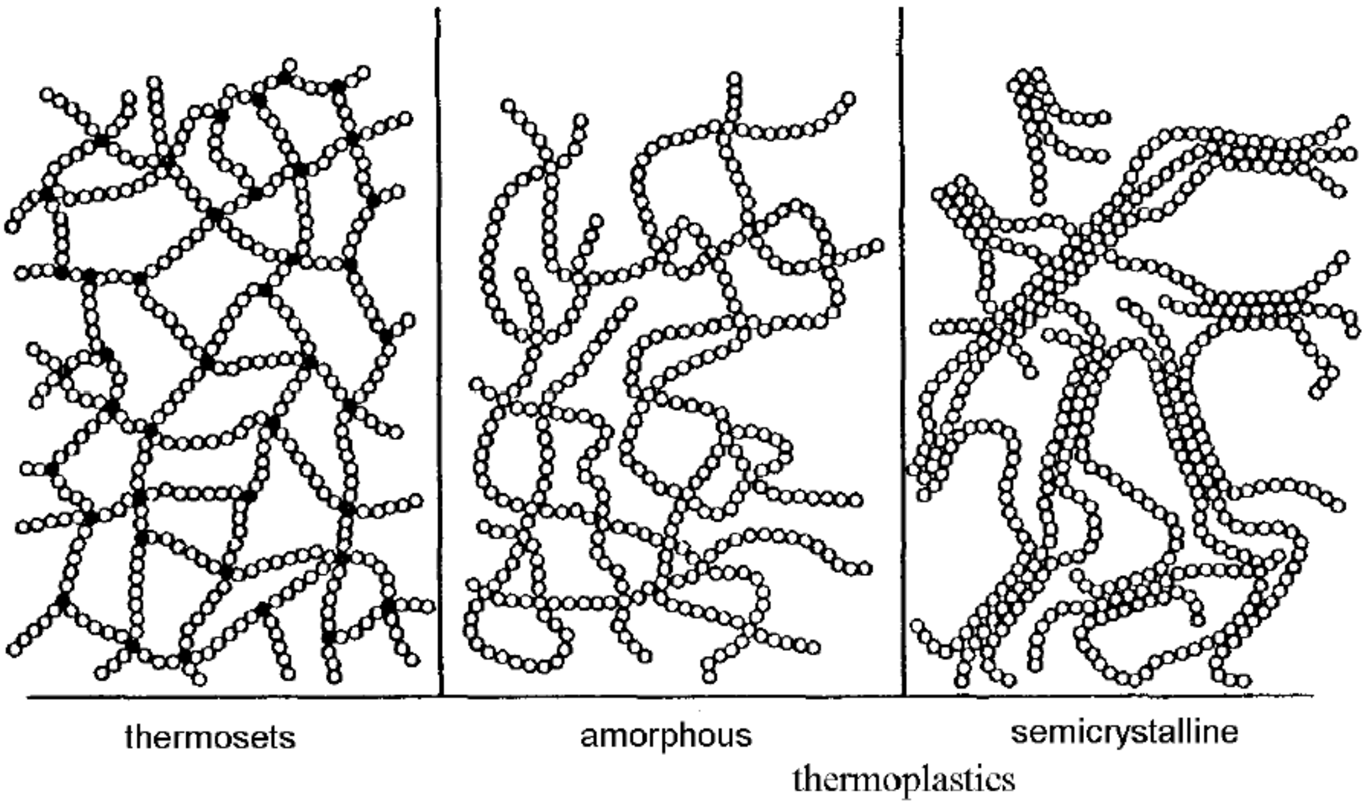
- Elastomers – Classification based on mechanical properties
- Hydrogels- Classification based on chemical properties
- Polyelectrolytes-Classification based on chemical properties
- Natural-Classification based on origin
- Biodegradable-Classification based on biostability

What makes One Polymer Different from Another?

- Strength of intermolecular forces and their sum over long polymer chains.
- Molecular weight and entanglement, which slow down motion of polymers.
- Crystallinity.
- Crosslinking.

All these properties determine the diverse states of macromolecular aggregation that polymers show.

Schematic sketch of thermosets and thermoplastics. The latter can be amorphous or a structure similar to thermosets but a lower crosslink density.



Consequences of the random coil model

- Crystallization strongly impeded by chain entanglement-only partial crystallization or glassy state upon cooling of a melt
- Entanglement gives rise to very high viscosity of polymer melts
- Entropic restoring force upon stretching of a chain- *entropy elasticity* of elastomers

Binding and Structure of Polymers

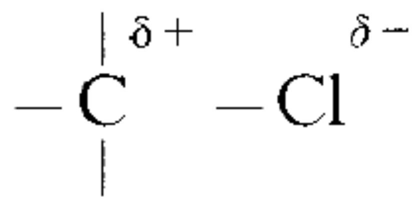
Interchain bonding: covalent

Intermolecular binding

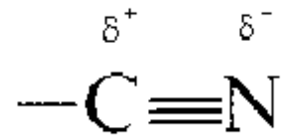
- permanent dipole (polar groups)
- induction forces: induced dipole
- hydrogen bonds
- repulsive forces (Pauli principle)
- Van der Waals interaction

Intermolecular Interactions

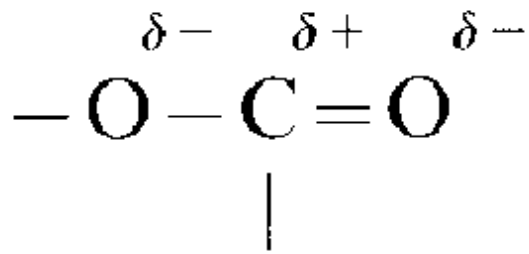
- Forces between permanent dipoles
- Different electronegativity of partners
- permanent dipole moment
- Examples of “polar groups“: e.g., in PVC



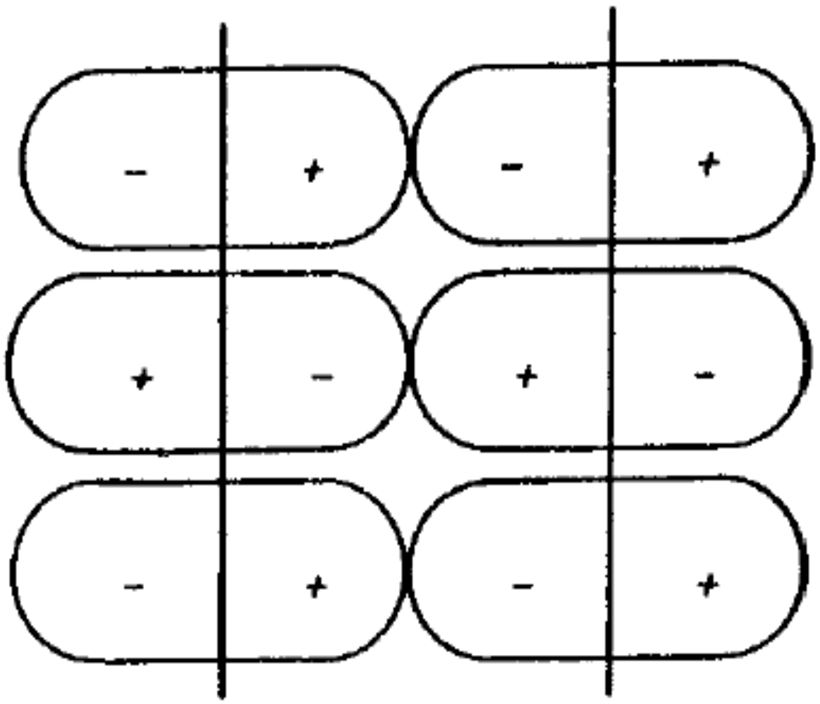
- nitrite group (less polar)

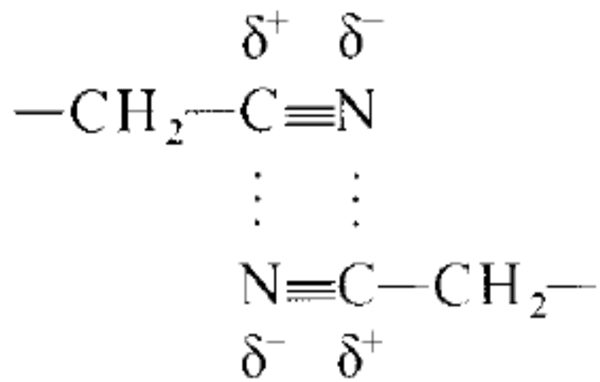


- ester group (less polar)



Dipole forces in a polymer.



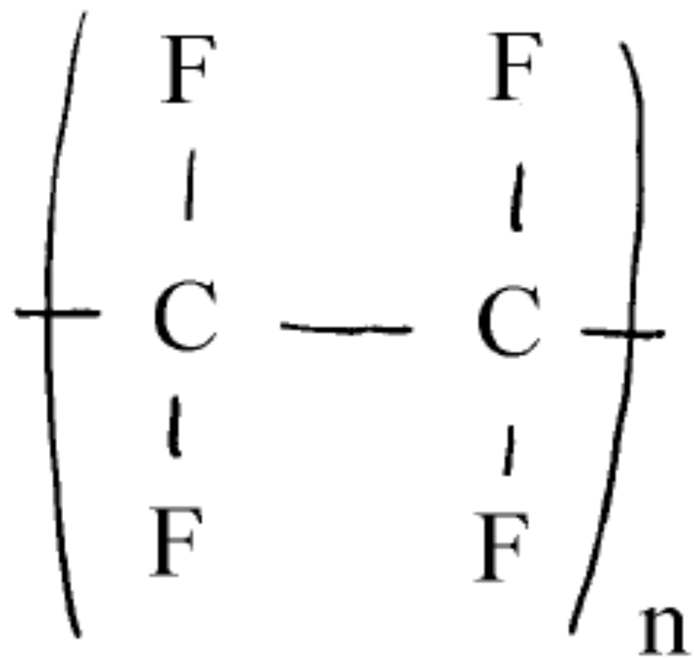


Effect of Polar Groups:

- lower solubility (except in strongly polar solvents)
- higher softening temperature (glass temperature Tg).

Almost no external dipole moment for symmetrical arrangement of dipoles!

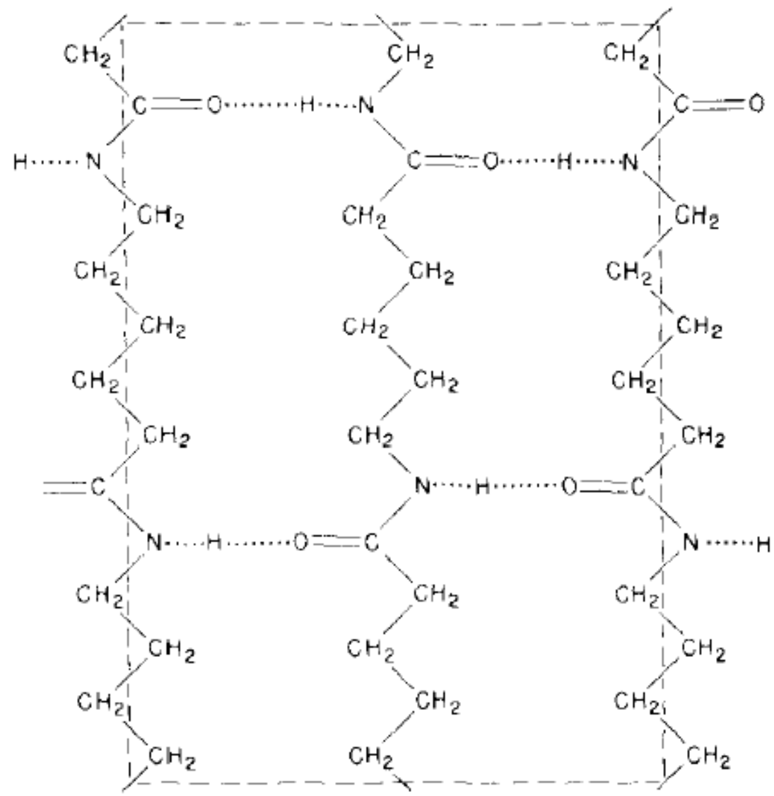
PTFE



Hydrogen bonds

only for F, O, N as strongly electronegative partner

- Illustration of hydrogen bonds in polyamid 6 (PA6)
- Particularly strong in polyamides and polyurethanes



Thermoplastics

- thermoplastic polymers are defined as materials that soften, melt, and flow when heat is applied; the adhesives solidify when cooled.
- Majority of familiar plastics
- Can be reprocessed

Thermoplastics

Amorphous

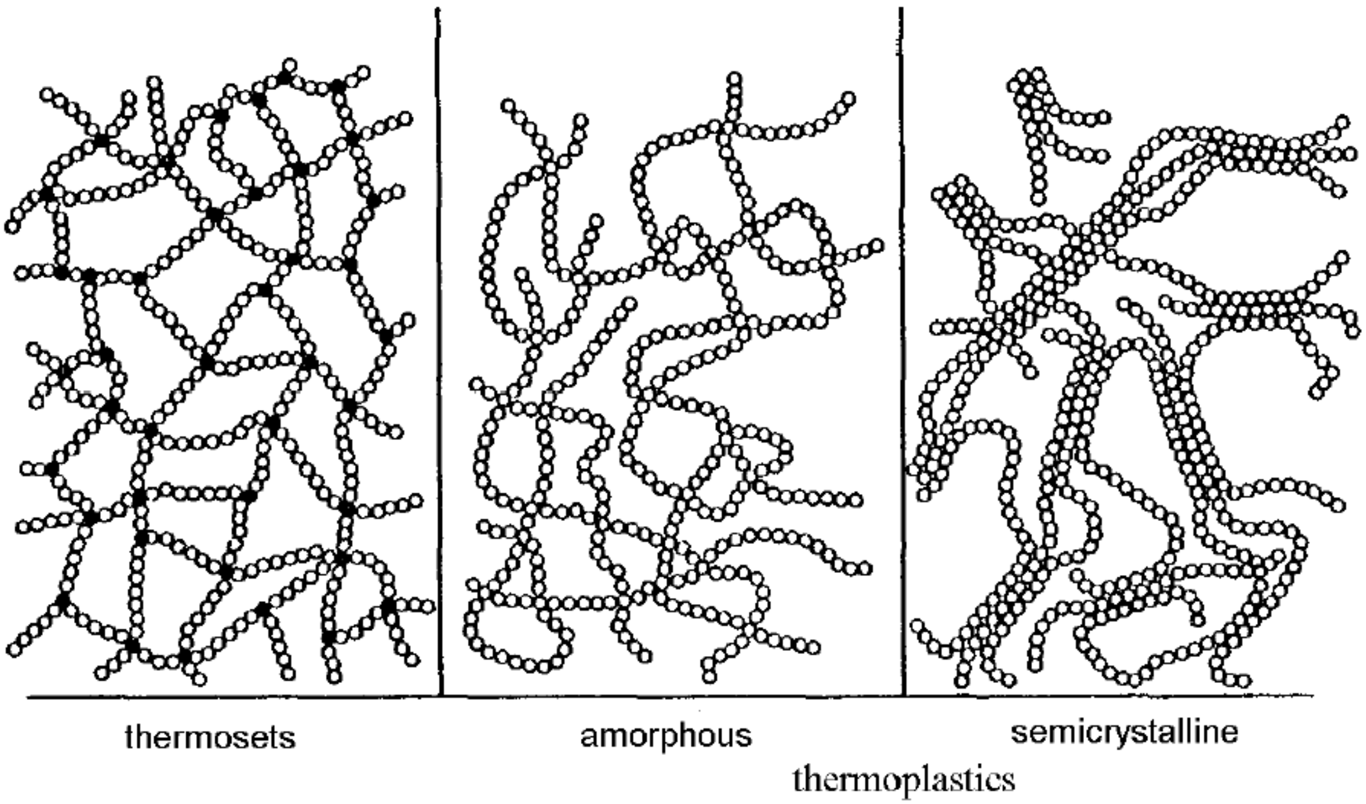
- Random structure
- Good clarity
- Broad melt temperature
- Low mold shrinkage (<0.005 in./in.)
- Acrylic, polycarbonate, PETG,polystyrene, PVC, TPU,

Thermoplastics

Semi-crystalline

- Linear alignment of chains
- Harder, less flexible
- Unique melting point
- High mold shrinkage (>0.01 in./in.)
- Polyethylene (LDPE / MDPE /HDPE), polypropylene, PTFE, Polyamide, PEK, TPU

Schematic sketch of thermosets and thermoplastics. The latter can be amorphous or a structure similar to thermosets but a lower crosslink density.



(Thermo)plastics

- Glass transition at *T*g: onset of long-range chain mobility
- If semicrystalline plastics: melting intervall of crystallites at *T*m
- - *T* > *T*g: mouldable into any shape
- - *T* < *T*g: range of usage
- ·Soluble

Thermosets

- A thermosettingpolymer, as the name suggests, becomes set into a given network, normally through the action of a catalyst—heat, radiation, or a combination of these factors—during the process of cross-linking.
- As the name suggests, *cross-linking* is the process of forming cross-links between linear polymer molecules (*curing* is another term commonly used).
- As a result of this process, thermosets become infusible and insoluble.
- Thermosetting resins (e.g., epoxies, polyesters, and phenolics) are the basis of many structural adhesives for load-bearing medical applications, as well as for the precision joining of electronic parts.

Thermosets

- Hard, strong, rigid
- Excellent heat resistance
- Cannot be reprocessed

Crystalline

- Epoxy, phenolic, polyester,

Amorphous

- Rubber, silicone, polyurethane

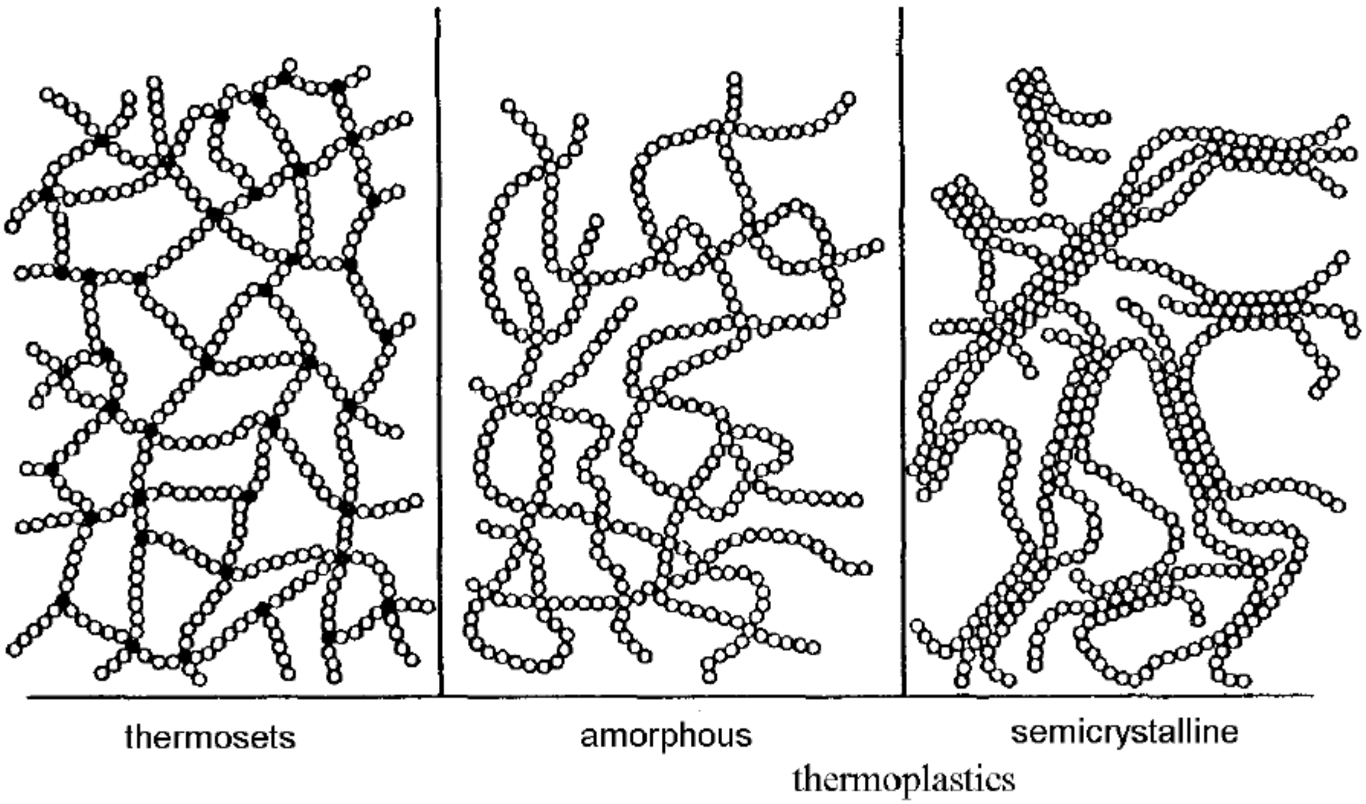
Thermosets

- Not meltable
- Not soluble
- Not swellable
- Processing generally prior to crosslinking

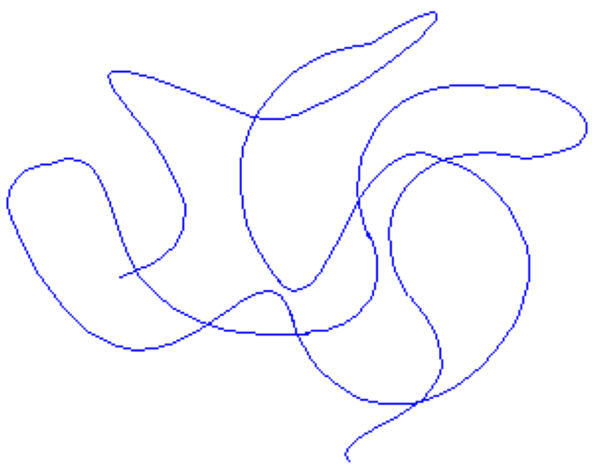
Elastomers

- Not meltable
- Not soluble
- Swellable
- Used at $T > Tg$ (Tg often reduced by plasticizers).

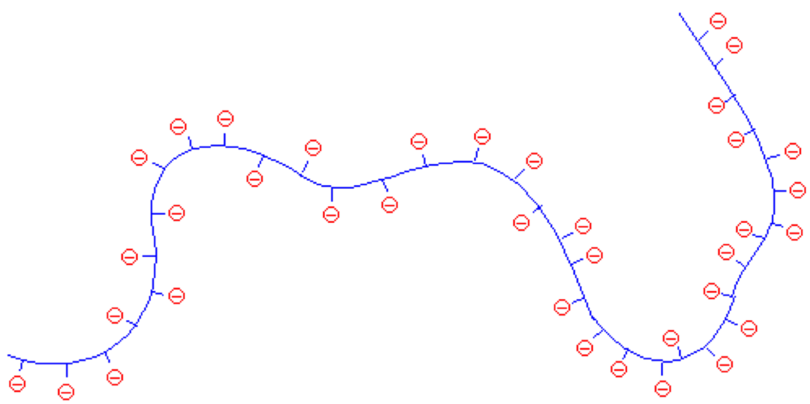
Schematic sketch of thermosets and thermoplastics. The latter can be amorphous or a structure similar to thermosets but a lower crosslink density.



Polyelectrolytes



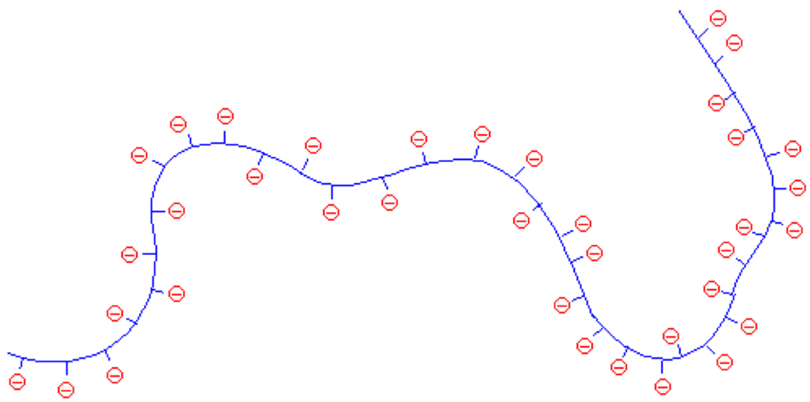
A polymer molecule tangled in a random coil.



A polyelectrolyte expands because it's like charges repel each other

Polyelectrolytes

- But when the polymer chain is covered with negative charges (which repel each other), the polymer can't be bunched in on itself. So the chain stretches out, like this.
- This makes the solution (remember we're talking about polyelectrolytes *in solution*) more viscous.
- Think about it.
- When the polyelectrolyte chain stretches out it takes up more space, and is more effective at resisting the flow of the solvent molecules around it.



A polyelectrolyte expands because it's like charges repel each other

Reversibility of the Process

- If one take a solution of a polyelectrolyte in water, and throws in a lot of salt.
- The NaCl will separate into Na+ and Cl- ions.
- In the case of a negatively charged polyelectrolyte like poly(acrylic acid), the positively charged Na+ ions will get in between the negative charges on the polymer, and cancel them out in effect. When this happens, the polymer chain collapses back into random coil again.

Salt makes polyelectrolytes in solution collapse into random coils.

Polymerization

- Starts with monomers
- The Addition-Condensation System

Addition Polymerization

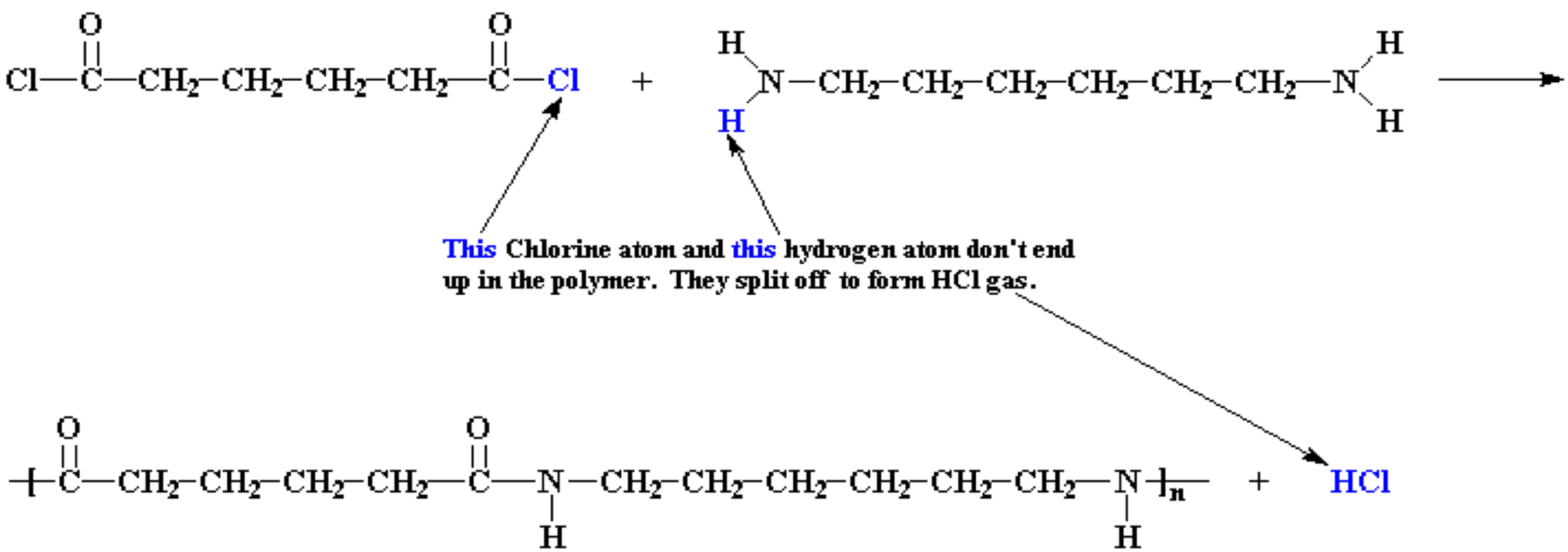
- polymerization where the entire monomer molecule becomes part of the polymer.
- ethylene is polymerized to make polyethylene.

Ethylene has two carbon atoms and four carbon atoms, and the polyethylene repeat structure has two carbon atoms and four hydrogen atoms. None gained, none lost.

Condensation Polymerization

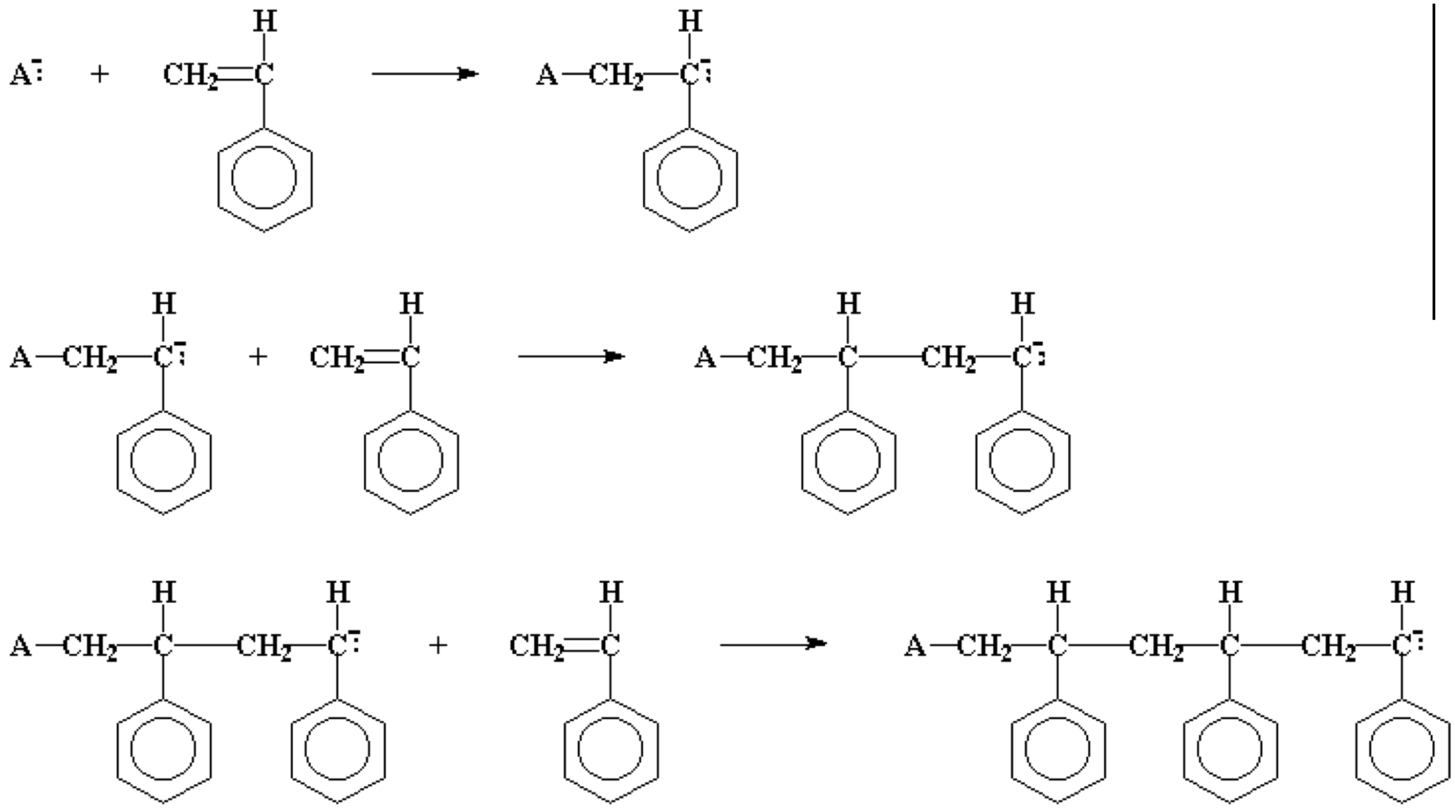
- Reaction where part of the monomer molecule is kicked out when the monomer becomes part of the polymer.
- The part that gets kicked out is usually a small molecule like water, or HCl gas.
- The polymerization of Nylon 6,6
- Because there is less mass in the polymer than in the original monomers, we say that the polymer is *condensed* with regard to the monomers.

Nylon 6,6 is made from adipoyl chloride and hexamethylene diamine

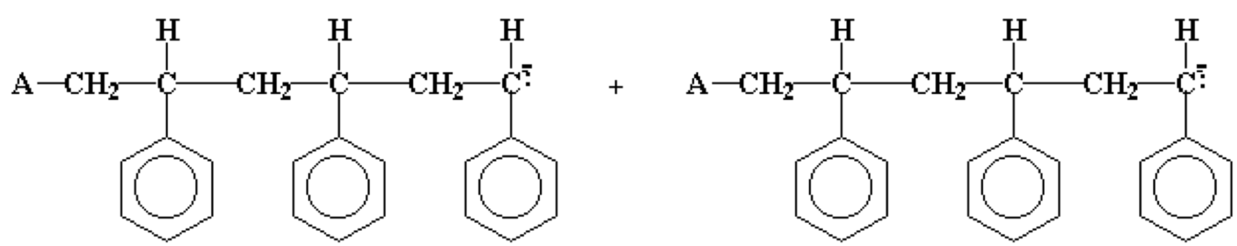


Chain Growth Polymerizations

- monomers become part of the polymer one at a time.



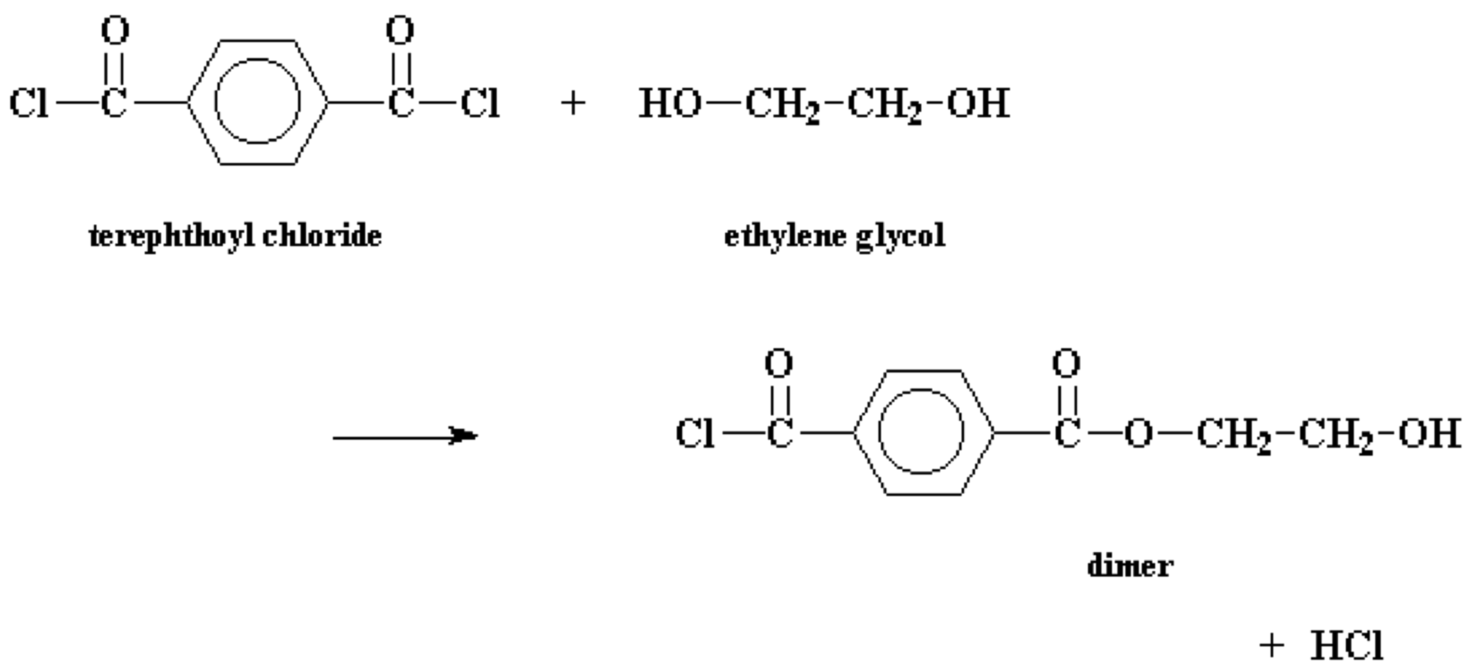
A chain growth polymerization: in the anionic polymerization of styrene, only styrene monomer can react with the growing polystyrene chain. Two growing chains won't react with each other.



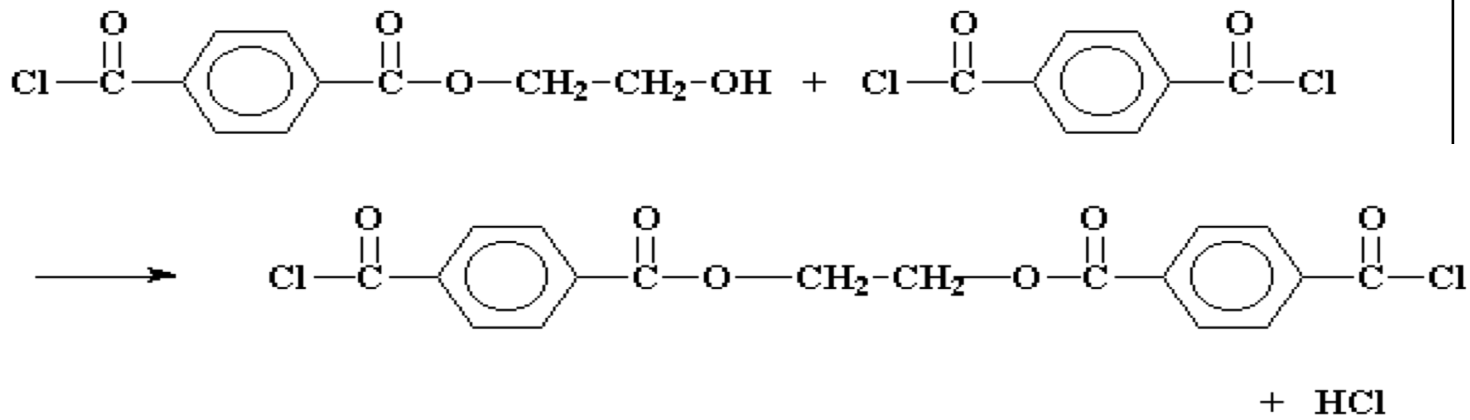
Step Growth Polymerizations

- This is a little more complicated, whereas chain growth polymerizations add one monomer at a time; multiple reaction products are possible.
- Let's take a look at the step growth polymerization of two monomers, terephthoyl chloride and ethylene glycol, to make a polyester called poly(ethylene terephthalate).

Terephthoyl chloride and ethylene glycol react to form an ester dimer

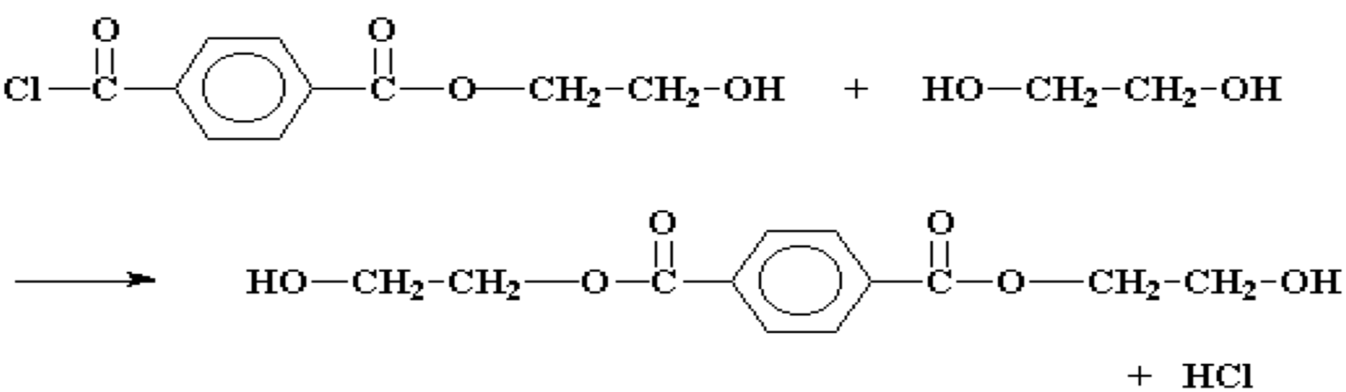


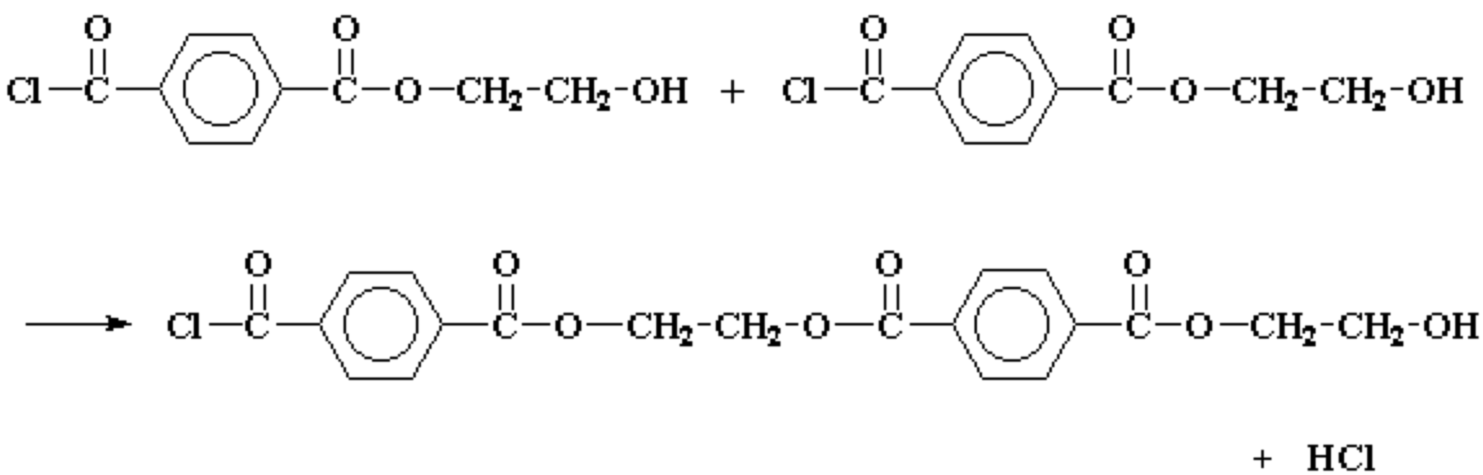
Our little dimer can react with a molecule of terephtoyl chloride...



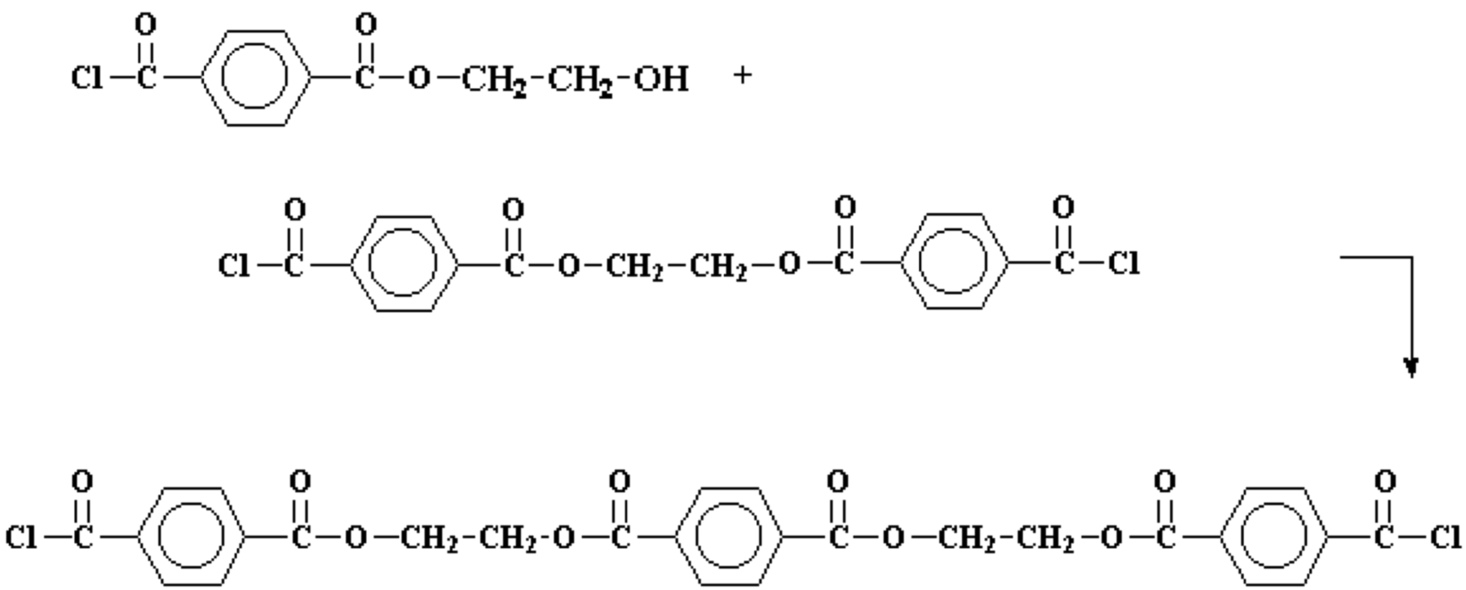
Or...

It can react with a molecule of ethylene glycol.





Two of our dimers are ganging up to form a tetramer.

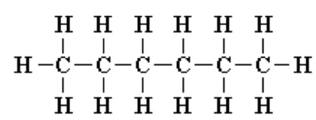


Merger Mania!

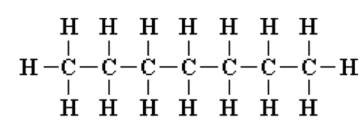
The dimer joins the trimer to form a pentamer. Will the madness never stop?

Molecular Weight

- Let's think about a small molecule, say, hexane. Hexane has a molecular weight of 86.
- Every hexane molecule has a molecular weight of 86.
- Now if we add another carbon to our chain, and the appropriate amount of hydrogen atoms, we've increased our molecular weight to 100.



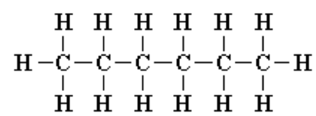
Hexane has one molecular weight, 86.



Lengthening the carbon chain by one carbon turns hexane into a completely different compound, heptane, molecular wieght = 100.

Molecular Weight

- That's fine, but the molecule is no longer hexane. It's heptane!
- If we have a mixture of some molecules of hexane and some of heptane, the mixture won't act like pure heptane, nor will it act like pure hexane.
- The properties of the mixture, say its boiling point, vapor pressure, etc., will be neither those of pure hexane nor pure heptane.



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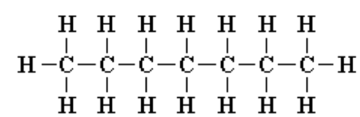


Lengthening the carbon chain by one carbon turns hexane into a completely different compound, heptane, molecular wieght = 100.

Dispersity

- Consider a protein-a protein in a polymer of amino acids linked a linear sequence, and like classic small molecules, it has a specific molecular weight and can be said to be monodisperse.
- However, commercial synthetic polymers, such as HDPE, are made up of molecules of different molecular weight.
- The numerical number for n, or the degree of polymerization (DP).
- Thus, the average molecular weight of a polydisperse polymer is equal to the product of the DP and the molecular weight of the repeating unit or mer.

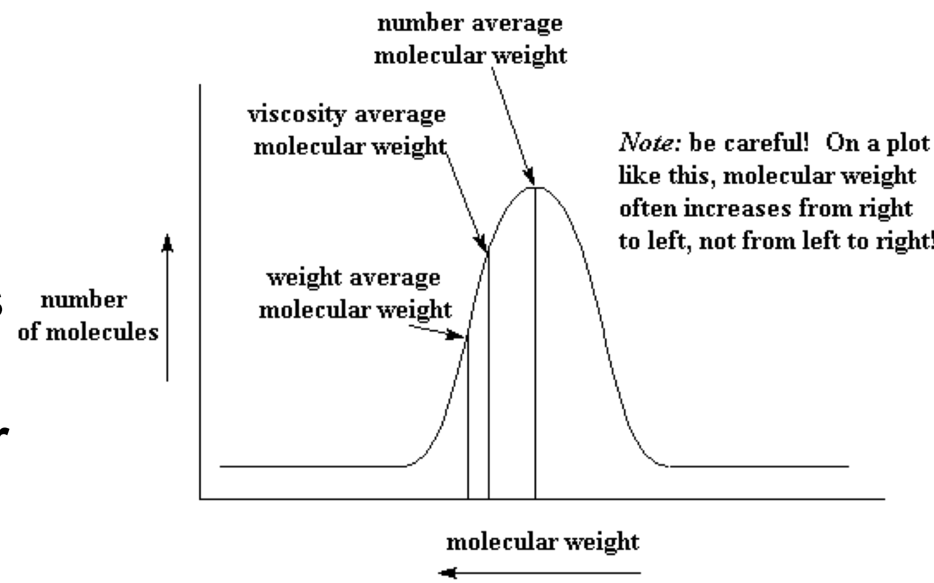
But Polymers are Different.

- Imagine polyethylene.
- If we have a sample of polyethylene, and some of the chains have fifty thousand carbon atoms in them, and others have fifty thousand and two carbon atoms in them, this little difference isn't going to amount to anything.
- If you really want to know the truth, one almost never finds a sample of a synthetic polymer in which all the chains have the same molecular weight.
- Instead, we usually have a bell curve, a *distribution* of molecular weights.

Molecular Weight

The Number Average Molecular Weight, *Mn*

- the total weight of all the polymer molecules in a sample, divided by the total number of polymer molecules in a sample



The Weight Average Molecular Weight, *Mw*

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

Where N is the number of moles in the sample with mass M, and N*M is the mass of the sample.

Molecular Weight

1. Number Average Molecular Weight (Mn)

$$Mn = \frac{\text{weight}}{\text{molecules}} = \frac{\sum NxMx}{\sum Nx}$$

2. Weight Average Molecular Weight (Mw)

$$Mw = \frac{\sum CxMx}{\sum Cx} = \frac{\sum (NxMx)(Mx)}{\sum NxMx} = \frac{\sum NxMx^2}{\sum NxMx}$$

3. Polydispersity

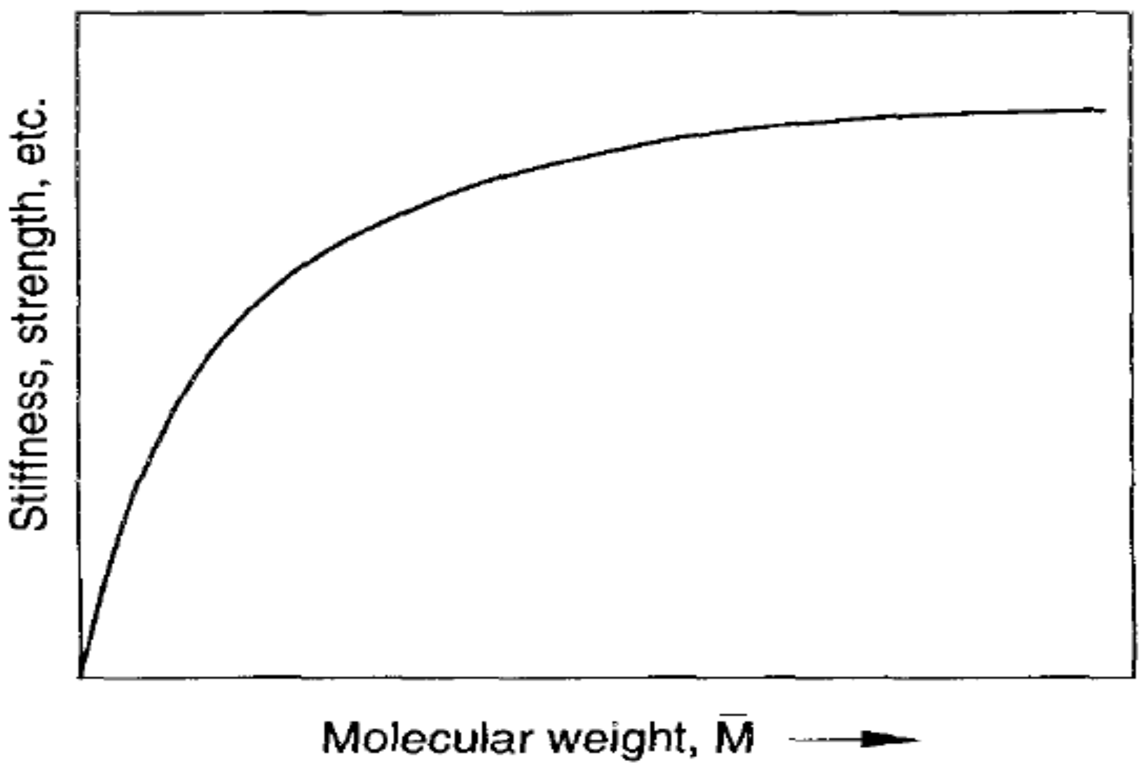
Polydispersity = Mw/Mn

Influence of Increasing Molar Mass on Properties

Increasing molar mass leads to			
higher strength	higher impact strength	higher chemical resistivity	reduction in flowability and resistance to melt fracture

Reasons			
higher interchain forces, more entanglements	lower degree of crystallization at higher chain length, more entanglements	higher interchain forces, degradation not so detrimental since high level	more entanglements

Influence of Molecular Weight on Mechanical Properties.

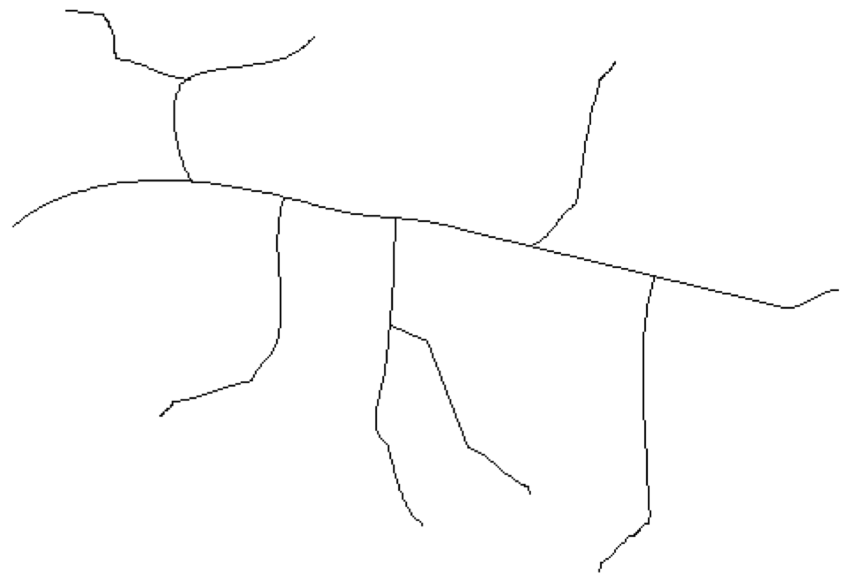


Experimental Determination of Molecular Weight

- Gel Permeation Chromatography
- Laser Light Scattering
- Viscometry

Branched Polymers

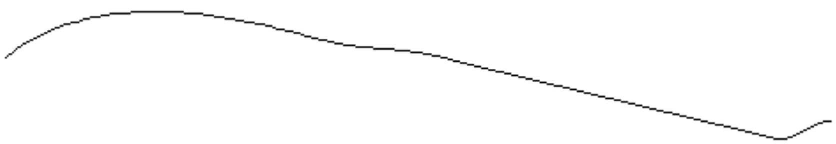
- Not all polymers are linear
- Some thermoplastic polymers, like polyethylene, can be made in linear or branched versions.



a branched polymer

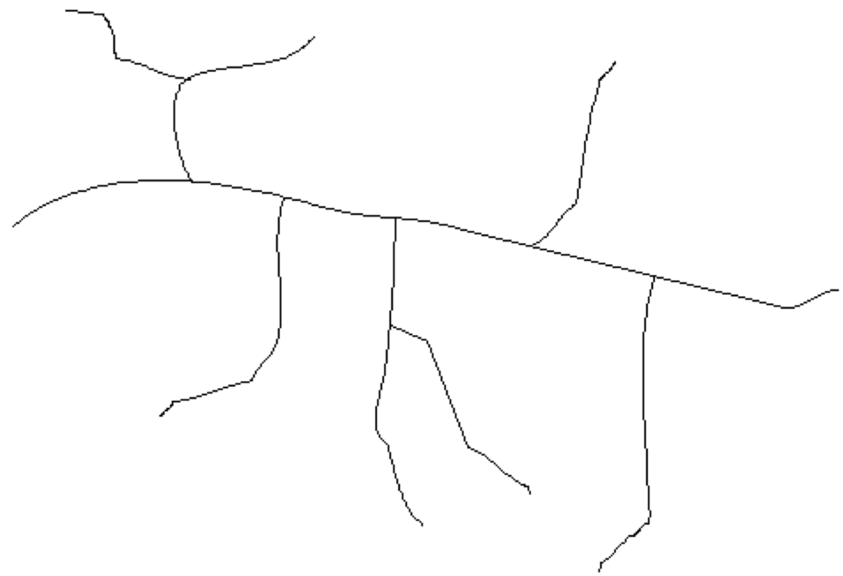
HDPE vs LDPE

HDPE



a linear polymer

LDPE

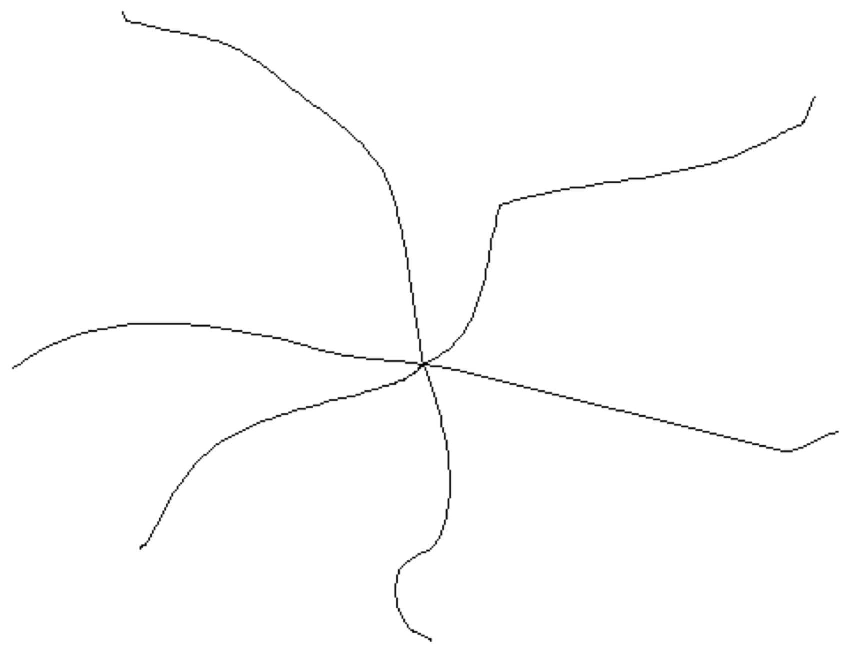


a branched polymer

The branching increases the volume and thus reduces the density of the polymer.

Star Polymers

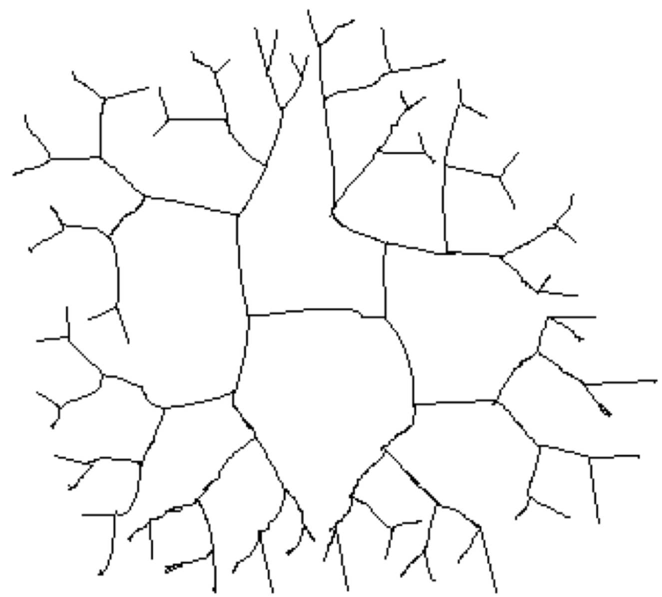
- Sometimes the ends of several polymer chains are joined together at a common center.
- Polymers like this are called *star polymers*.
- They're often used as additives or as coating materials.



a star polymer

Dendrimer

- Sometimes there is no backbone chain at all.
- Sometimes a polymer is built in such a way that branches just keep growing out of branches and more branches grow out of those branches.
- These are called *dendrimers*, from the ancient Greek word for "tree".



a dendrimer