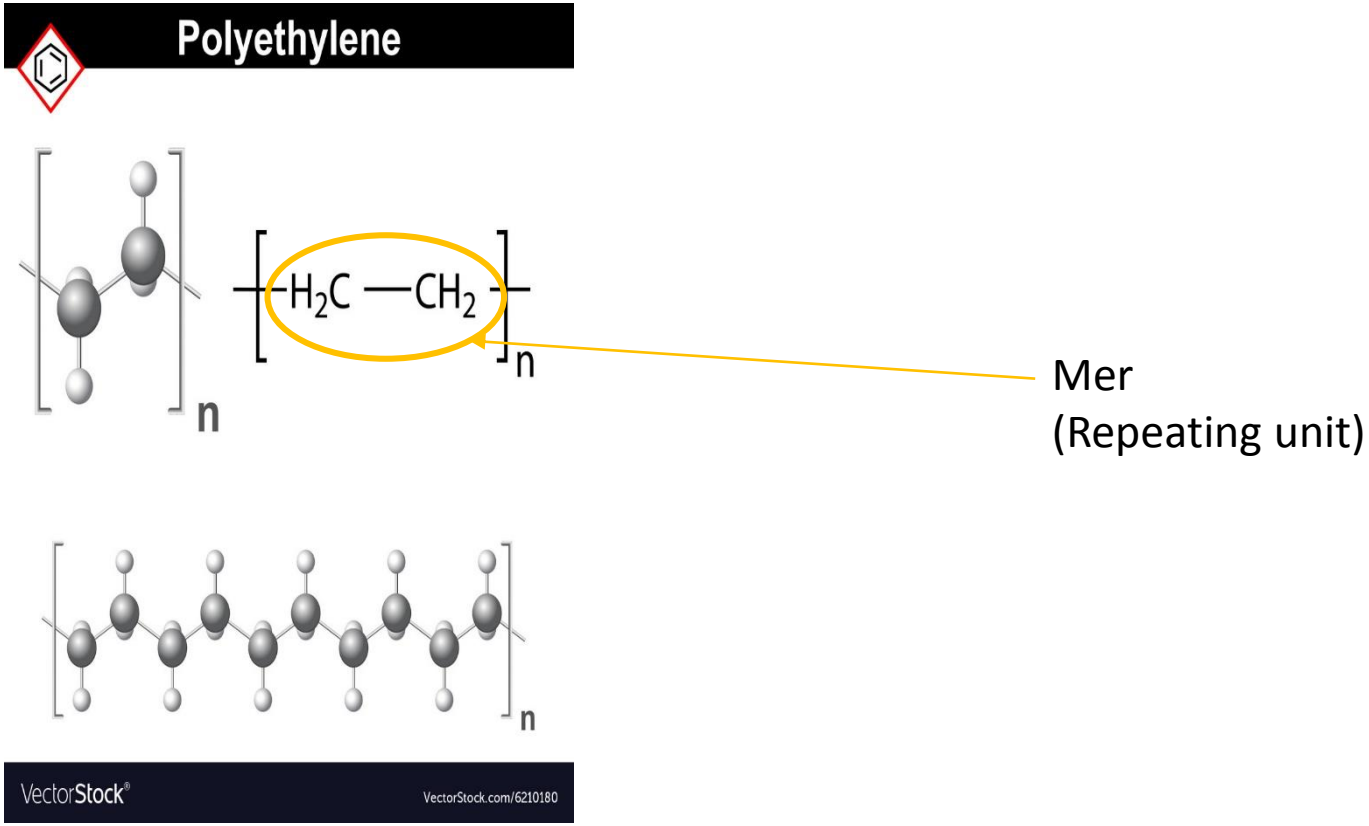
Polymers I

The types, properties, and synthesis of polymers.

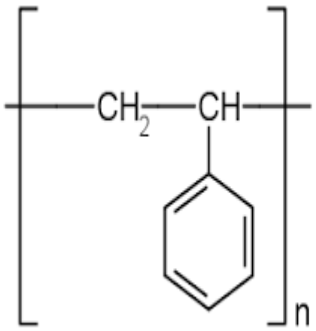
Sources:

1. Polimer kimyası, Prof. Dr. Mehmet Saçak, Gazi Kitabevi, Ankara, 2002.
2. Lif ve Elyaf Kimyası, Prof. Dr. Mehmet Saçak, Gazi Kitabevi, Ankara, 2002.
3. Lecture notes: http://web.mit.edu/5.33/www/lec/poly.pdf
4. Book chapter: https://www.sciencedirect.com/topics/engineering/linear-polymer
5. https://pslc.ws/macrog/radical.htm

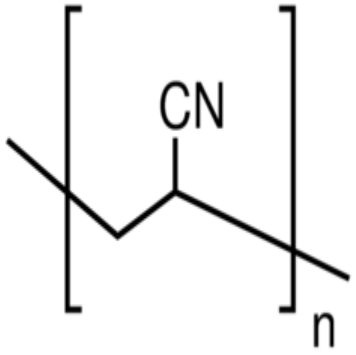
- Polymers are large molecules that are built up by the covalent bonding of small molecules (monomers). A polymer may consist of ten to thousands of monomer molecules. The monomer molecules are covalently bound to each other with polymerization reactions to give yield a polymer. For the definition of a polymer molecule, a polymer chain term is frequently used.



- Homopolymer if a polymer consists of one type of monomer, then its called homopolymer, but if it contains more than two different monomers with chemical structures, we call it as copolymer.

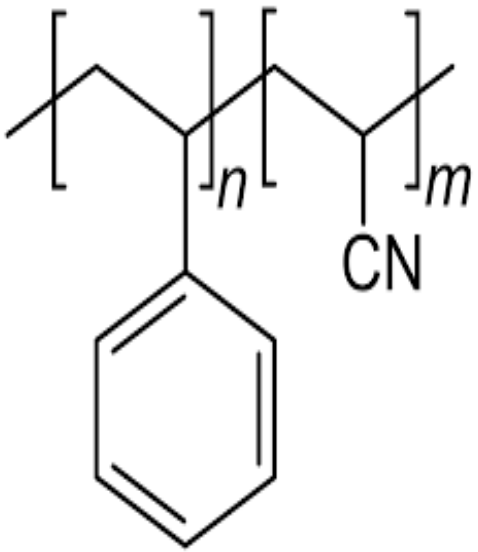


polystyrene



polyacrylonitrile

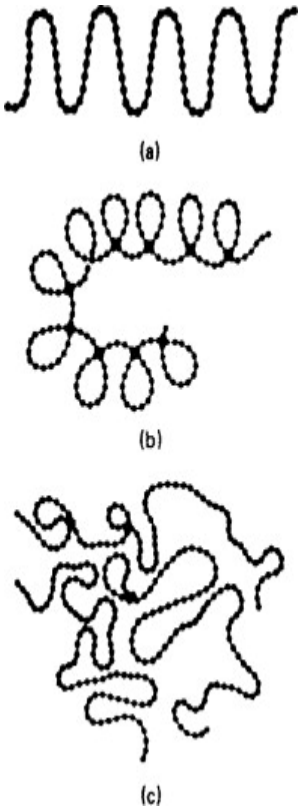
Homopolymer



copolymer

- Lineer polymers: A linear polymer is a long continuous chain of carbon–carbon bonds with the remaining two valence bonds attached primarily to hydrogen or another relatively small hydrocarbon moiety.*

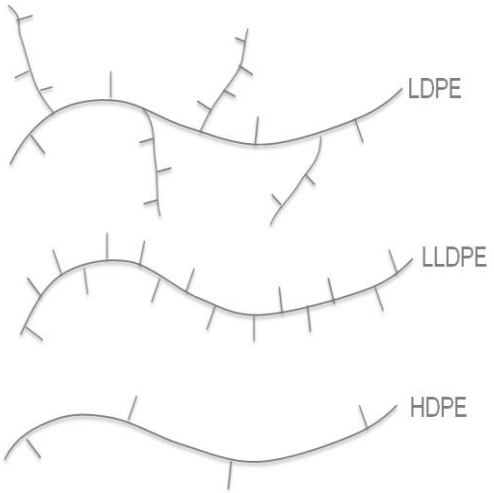
Lineer polymers can be easily dissolved in an apropriate solvent , and many times shaped after melting.



Simplified representation of various linear polymer configurations

*Hanna Dodiuk, Sidney H. Goodman, in Handbook of Thermoset Plastics (Third Edition), 2014

Branched polymers: Resemble linear polymers with the addition of shorter chains hanging from the polymer main chain. Since these shorter chains can interfere with efficient packing of the polymers, branched polymers tend to be less dense than similar linear polymers. Since the short chains do not bridge from one longer backbone to another, heat will typically break the bonds between the branched polymer chains and allow the polymer to be a thermoplastic, although there are some very complex branched polymers that resist this 'melting' and thus break up before softening, i.e., they are thermosetting.*



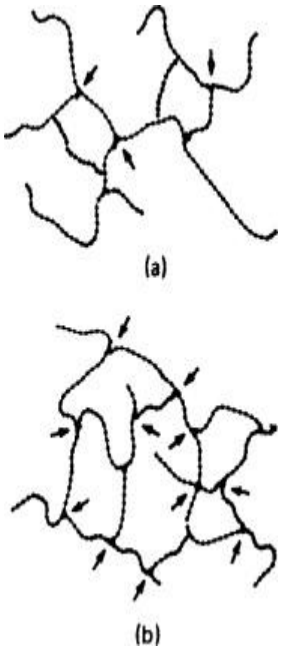
https://polymerdatabase.com/polymer%20physics/Branched%20Polymers.html

*https://www.e-education.psu.edu/matse81/node/2210

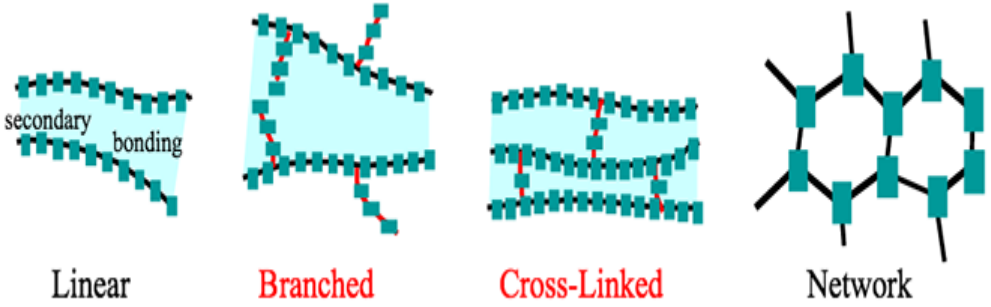
Cross-linked polymers

A cross-linked polymer is formed as a result of the chemical interaction between linear polymer chains or the build-up from monomeric resinous reactants of a 3-D fish-net configuration. The process of interaction is called *crosslinking* and is the main distinguishing element of a *thermosetting polymer*.

The "thermo" implies that the crosslinking proceeds through the influence of heat energy input, much crosslinking occurs at room temperature (25°C, 77°F) and below. The "setting" term references the fact that an irreversible reaction has occurred on a macro-scale. The network polymer formed has an "infinite" molecular weight with chemical interconnects restricting long chain macromovement.*



(a) Lightly crosslinked network polymer.
(b) Highly crosslinked network polymer.



*Hanna Dodiuk, Sidney H. Goodman, in Handbook of Thermoset Plastics (Third Edition), 2014

Molecular weight

- The molecular weight of polymer is the molar mass of the polymer chain. During the synthesis of a polymer, the length of a polymer chian can not be controlled. Consequently, in the different stages of the polymerization, polymers with different chain lengths are present.
- To clearly characterise polymer properties, an average molecular weight is used.
- Different average values can be defined depending on the statistical method that is applied.

It can be obtained by multiplying the mass of each repeating unit (M_0) by the degree of polymerisation and then adding the mass of end groups. For a linear polymer, it is rare that all polymer chains have the same mass. There is always a distribution existed.

$$—[CH_2\text{-}CH_2]_{1000}—$$

$$M_n=(28/N_A)*1000*N_A=2800$$

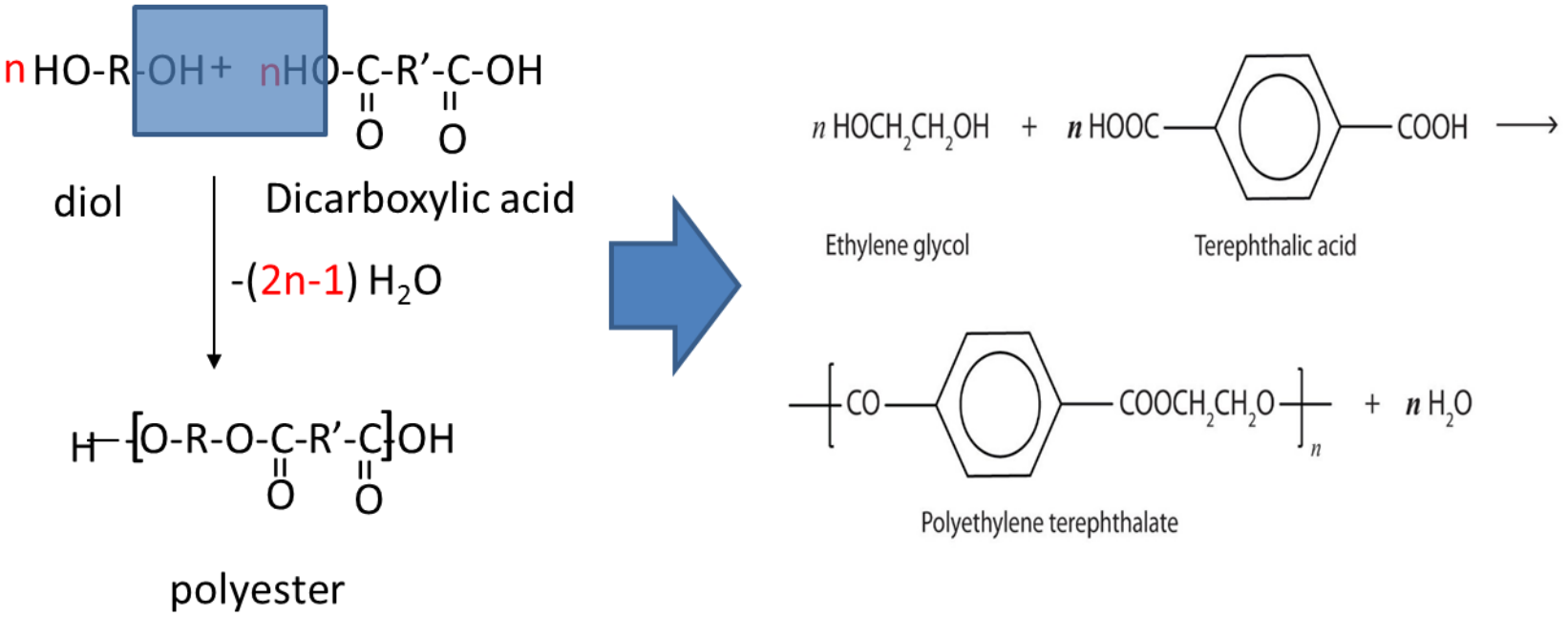
$$D_p= M_n/M_{mon}$$ Dp: degree of polymerization

Polymerization reactions

? Homework: what's the difference between conventional condensation reaction and condensation polymerization

- Step (condensation) polymerization
- Addition polymerization

Step (condensation) polymerization



? Homework: Write an other condensation polymer

Trick (nylons)

In the step polymerization, the chain growth progresses slowly and step by step. In the early stage of the polymerization, the monomer molecules are rapidly consumed. A polymer with high molecular weight could only be occurred at the final stages of the polymerization.

Some condenation polymers and characteristic bonds

Polymer	Bond
Polyester	-C(=O)-O-
Polyamide	-C(=O)-NH-
Proteins, wool, silk	-C(=O)-NH-
Polyuretane	O-C(=O)-NH-
Cellulose	-C-O-