Polymers

II

Synthesis of polymers.

Sources:

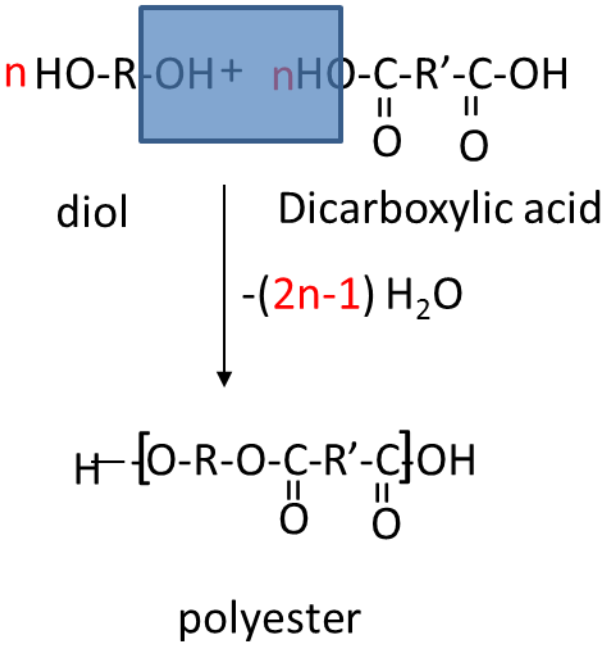
1. Polimer kimyası, Prof. Dr. Mehmet Saçak, Gazi Kitabevi, Ankara, 2002.
2. Lif ve Elyaf Kimyası, Prof. Dr. Mehmet Saçak, Gazi Kitabevi, Ankara, 2002.
3. Lecture notes: http://web.mit.edu/5.33/www/lec/poly.pdf
4. Book chapter: https://www.sciencedirect.com/topics/engineering/linear-polymer
5. https://pslc.ws/macrog/radical.htm

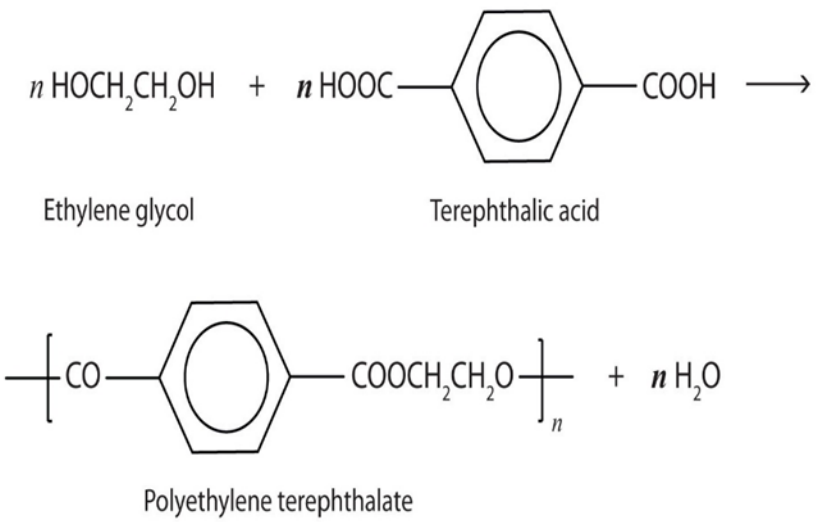
Polymerization reactions

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

- Step (condensation) polymerization
- Addition polymerization

Step (condensation) polymerization



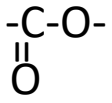
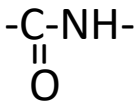
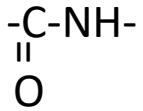
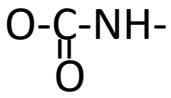
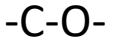


? Homework: Write an other condensation polymer

Trick (nylons)

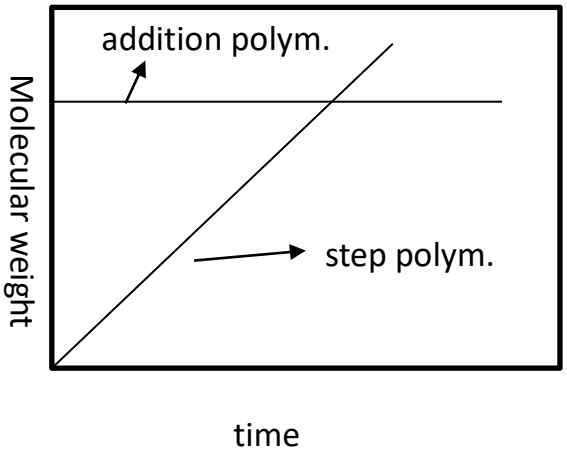
In the step polymerization, the chain growth progresses slowly and step by step. In the early stage of the polymerization, the monomer molecules are rapidly consumed. A polymer with high molecular weight could only be occurred at the final stages of the polymerization.

Some condenation polymers and characteristic bonds

Polymer	Bond
Polyester	
Polyamide	
Proteins, wool, silk	
Polyuretane	
Cellulose	

Addition polymerization

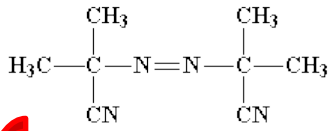
In this polymerization, the monomer molecules are added to the polymer chain rapidly and one-by-one. Due to the rapid chain growth, in the every stage of the polymerization, a polymer with high molecular weight is present.



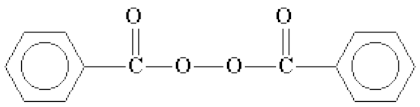
-Radical (free radicals)
-Ions (anionic/cationic)

Lif ve Elyaf Kimyası, Prof. Dr. Mehmet Saçak, Gazi Kitabevi, Ankara, 2002.

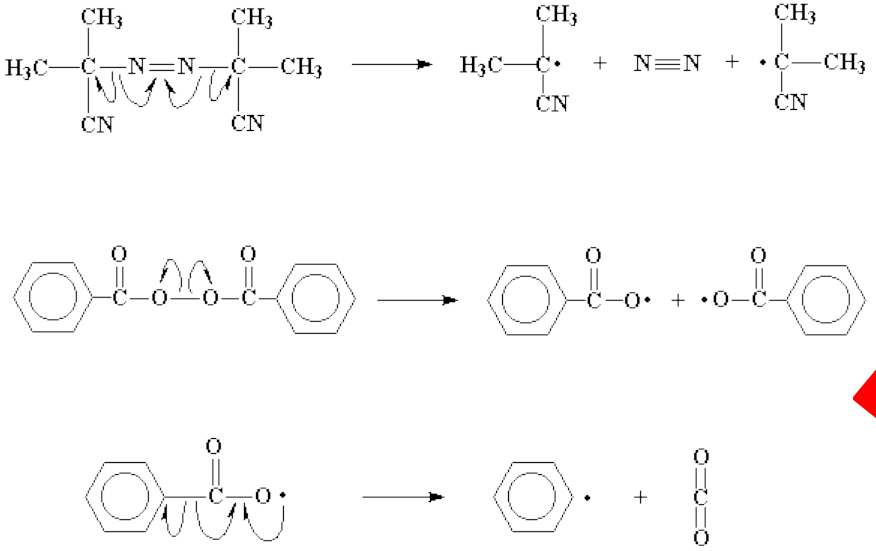
Radicalic Initiators



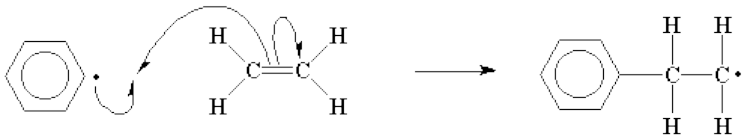
2-2'-azo-*bis*-isobutyrylnitrile
(AIBN)



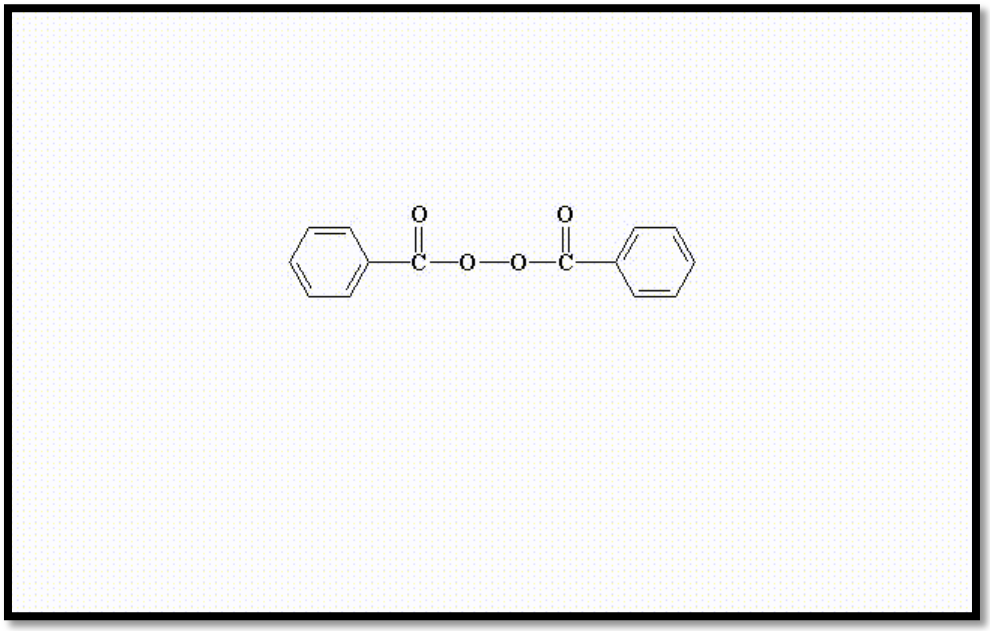
benzoyl peroxide



https://pslc.ws/macrog/radical.htm



Initiation with Benzoyl peroxide



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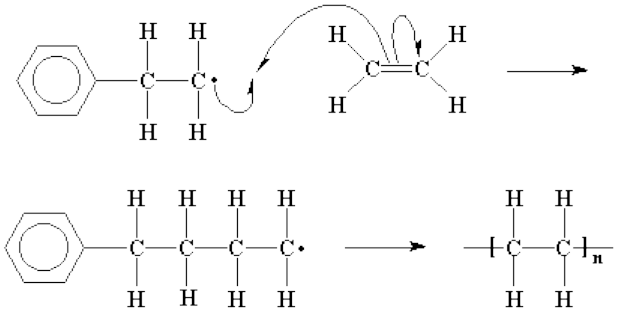
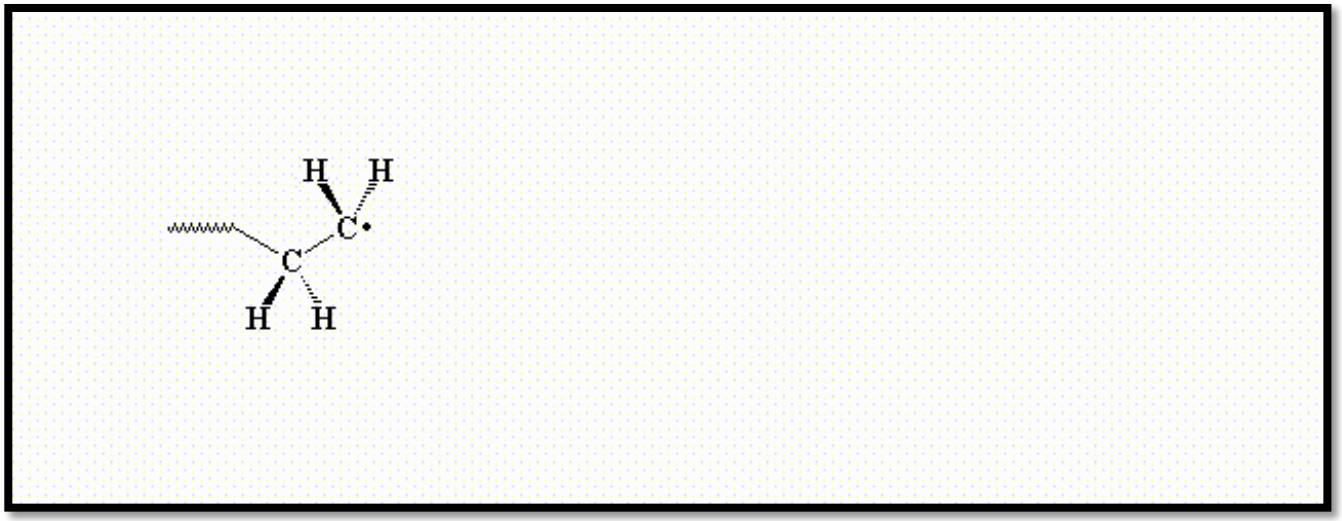


propagation



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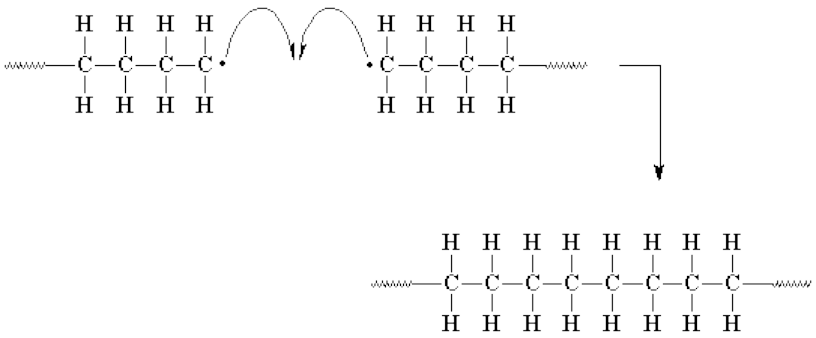
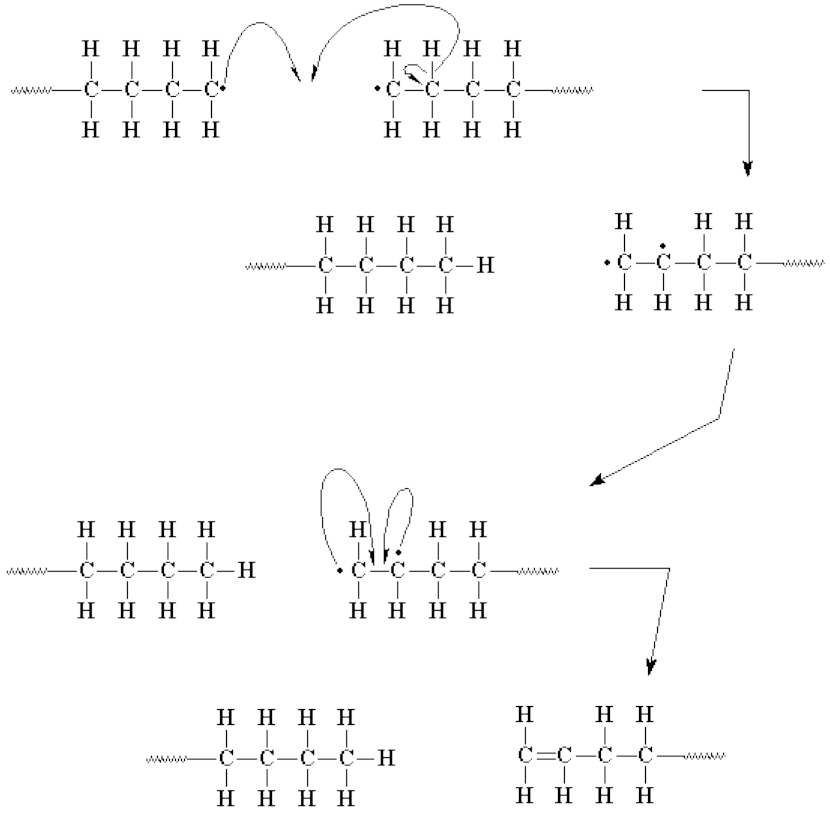


Termination-combination



Termination-disproportion

https://pslc.ws/macrog/radical.htm

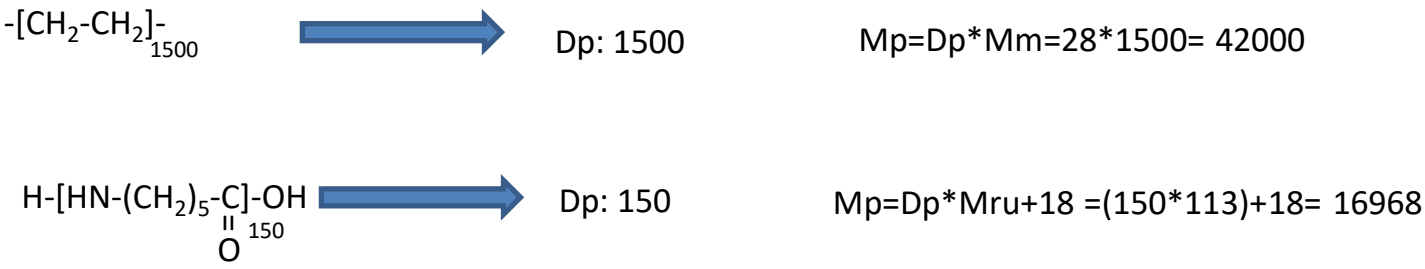
? Homework: Write an example for an other addition polymer

? Homework: compare the properties of addition and step polymerizations.

Dp concept for step and addition polymers

The definition for Dp concept differs for addition and step polymers.

* Dp can be defined as average number of monomer molecules per chain (repetitive unit)



* Dp is defined as number of average structural unit per chain

? Homework: Calculate the molecular weight of polyethylene adypat whose Dp value is 100.

Trick: $H\text{-}[O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}(C{=}O)\text{-}(CH_2)_4\text{-}(C{=}O)]_{100}\text{-}OH$

The stereochemistry* of polymers

configuration

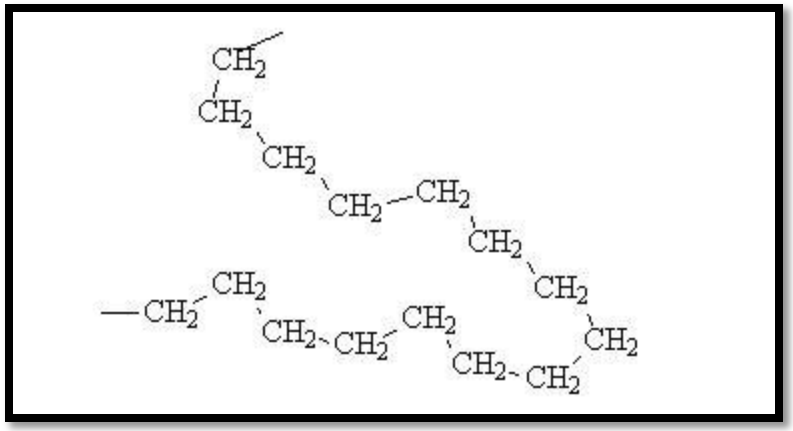
*the branch of polymer chemistry concerned with the three-dimensional arrangement of atoms and molecules and the effect of this on chemical reactions.

Structural isomerism

- $[-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-]_n$ ⟶ C_2H_4 ⟵ $[-CH_2-CH_2-O-]_n$

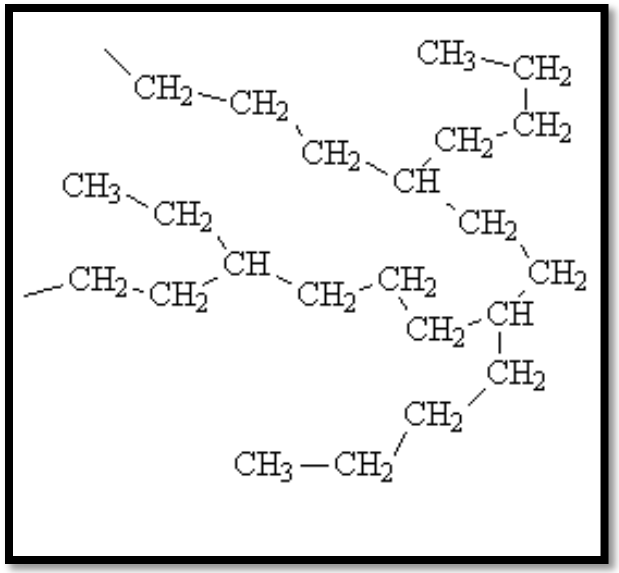
poly(vinyl alcohol)
Tm: 260 °C

poly(ethylene oxide)
Tm: 60 °C



Chain-type isomerism

HDPE



LDPE

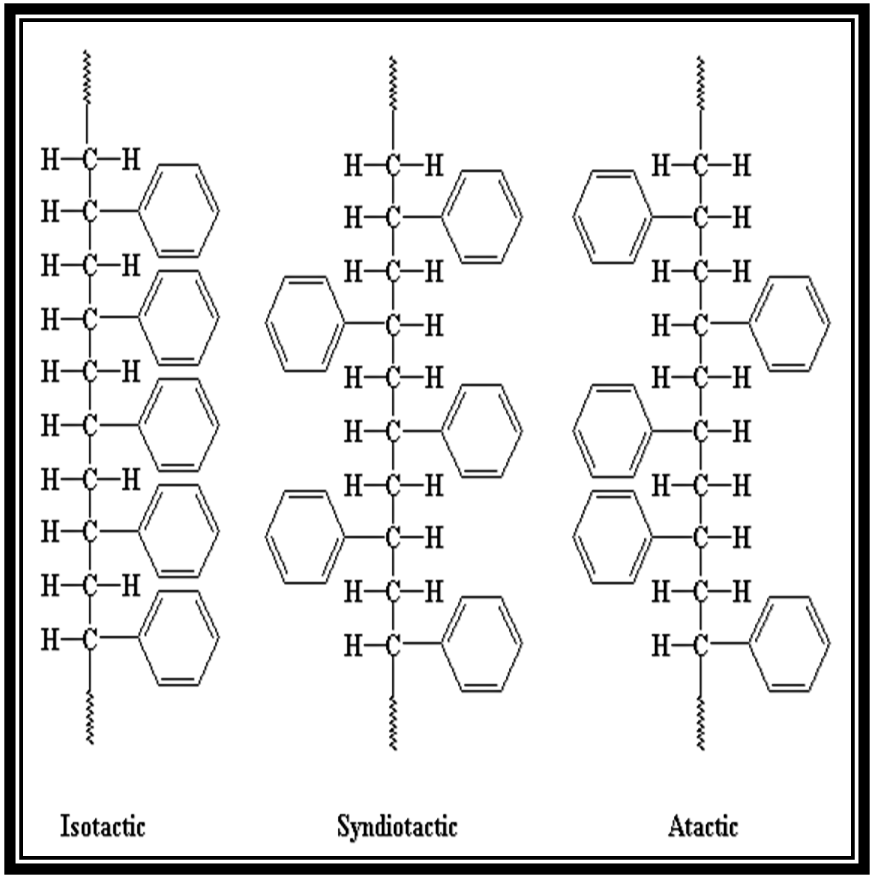
The other configuration types of polymers:

- ***Head to tail and tail to tail arrangement***
- ***Tacticitiy***
- ***Geometrical isomerism*** (valid for the polymers containing = bonds on the main chains, cis- or trans- isomerism)

Tacticity

**sequence of the –R groups of polymer chains consisting of CH_2=CHR vinyl monomers

Syndiotactic and isotactic polymers are prone to the crystallinity due to their high arranged geometry.



https://pslc.ws/macrog/tact.htm

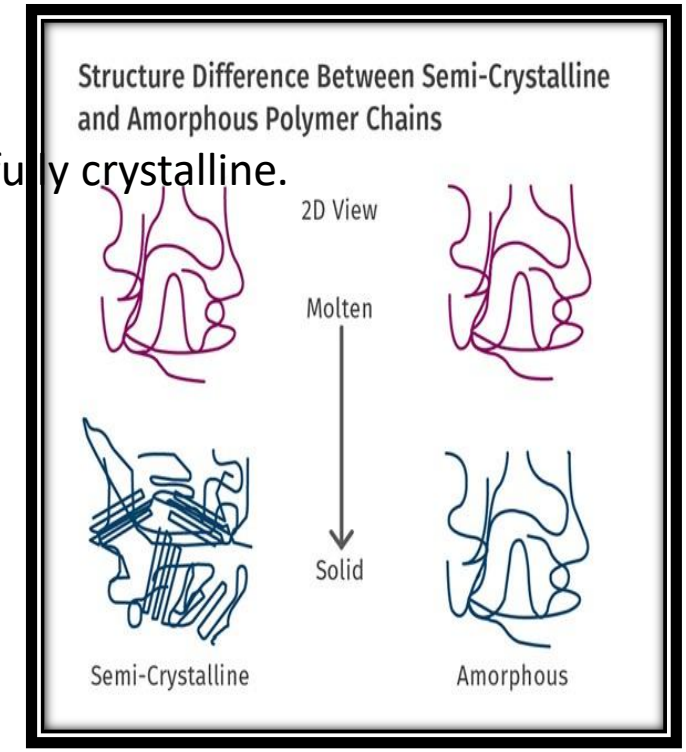
Crystallinity

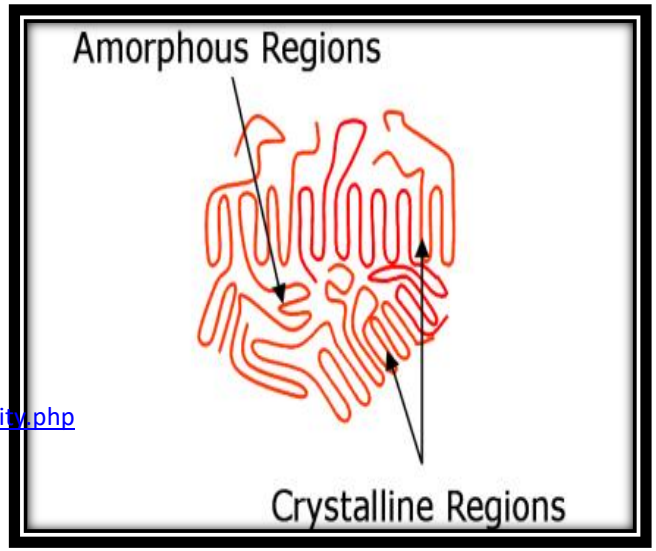
Polymers can be fully amorphous, semi-crystalline, and fully crystalline.

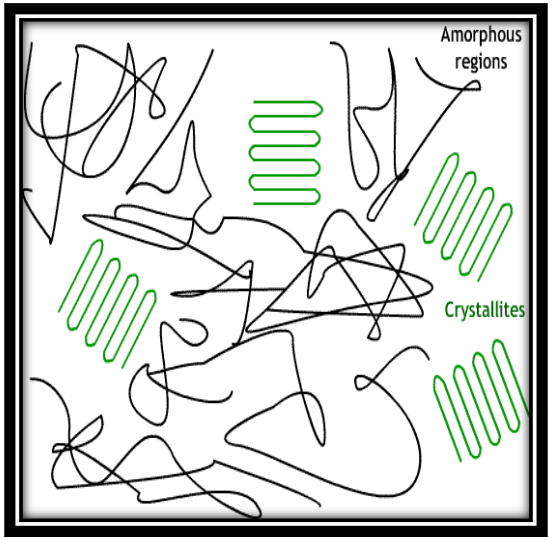
Amorphous polymers….> polymer chains are randomly mixed with each other

Fully crystalline polymers…> polymer chains that are packaged orderly take a geometry suitable for crystal structure

Textile fibers are in the semi-crystalline structure





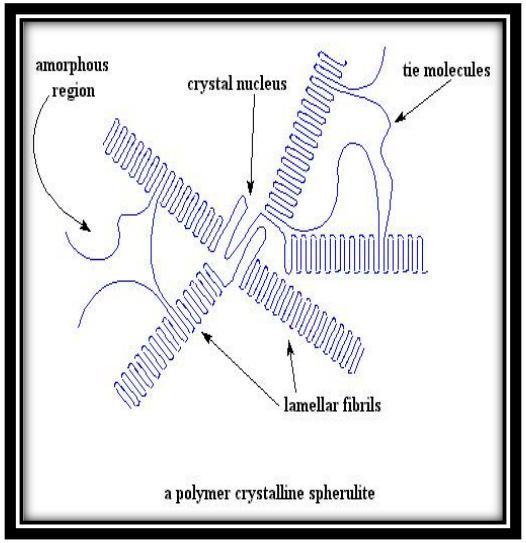


https://www.doitpoms.ac.uk/tlplib/polymerbasics/crystallinity.php

http://www.materials.unsw.edu.au/tutorials/online-tutorials/5-crystalline-or-amorphous

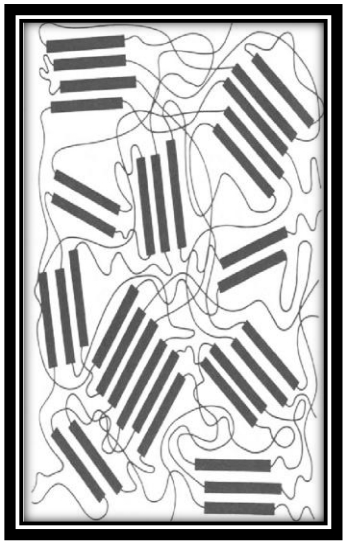
The crystalline models used in the semi-crystalline polymers

Spherulite model



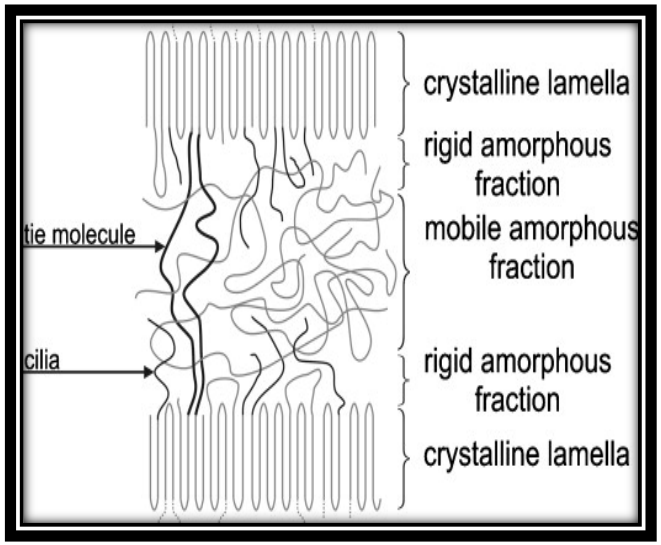
https://pslc.ws/macrog/crystal.htm

Fringed micelle model



[Influences of the Glassy and Rubbery States on the Thermal, Mechanical, and Structural Properties of Doughs and Baked Products](), Slade and Levine, 1987

Lamella model



Wietzke, Steffen & Jansen, Christian & Reuter, Marco & Jung, Taekgeun & Hehl, Judith & Kraft, Dietmar & Chatterjee, Sangam & Greiner, Andreas & Koch, Martin. (2010). Thermomorphological study of the terahertz lattice modes in polyvinylidene fluoride and high-density polyethylene. Applied Physics Letters. 97. 022901 - 022901. 10.1063/1.3462312.

Factors effecting crystallinity

- **The units take part in the main polymeric backbone**

++The simple and symmetric units containing polymers such as PE, PTFE tend to crystallinity. The other groups such as –CO-, -COO-, -CONH- are also prone to the crystallinity.

- **The tacticity of the polymer chain**

++syndiotactic and isotactic polymers are prone to the crystallinity.

- **Branching**

--Adversely affects the crystallinity

- **The interactions between polymer chains**

++The secondary forces such as H-bonds, polar interactions get closer the polymer chains and this leads to the orderly arrangement of the polymer chains.