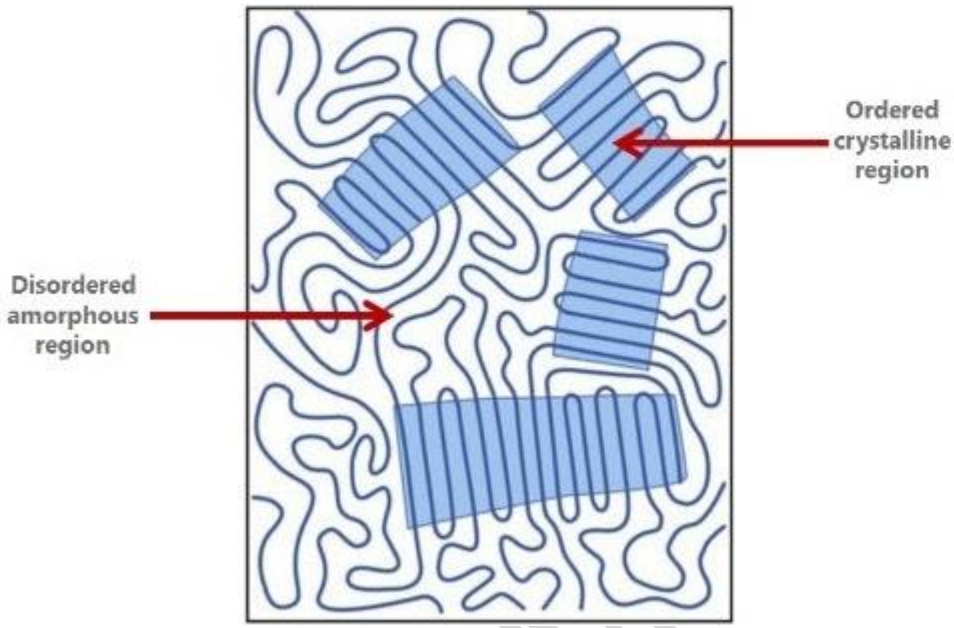
Crystallinity of Polymers

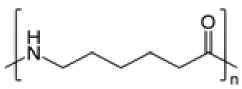
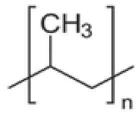
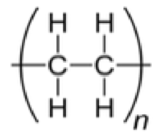
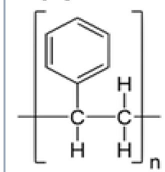


Crystallization of polymers is a process associated with **partial alignment** of their molecular chains. These chains fold together and form **ordered regions called lamellae**, which compose larger **spheroidal structures named spherulites.**

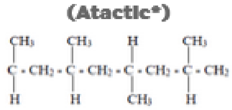
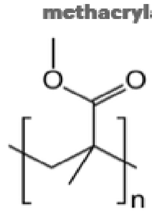
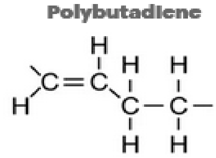
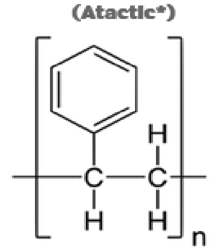
Polymers can crystallize upon **cooling from melting**, **mechanical stretching or solvent evaporation.** Crystallization affects **optical, mechanical, thermal and chemical properties** of the polymer. The **degree of crystallinity** is estimated by different analytical methods and it typically ranges between **10 and 80%,** with crystallized polymers often called **"semi-crystalline"**.

When hardness and rigidity are required, a polymer with greater **crystallinity may be preferred**.

Crystalline Polymers

	Nylon 	Polypropylene (Isotactic*) 	Polyethylene 	Polystyrene (Syndiotactic*) 
Monomer(s):	adipic acid & hexamethylene diamine	propylene	ethylene	styrene
T_m:	260°C (500°F)	174°C (345°F)	137°C (279°F)	270°C (518°F)
Uses:	thermoplastics, fibers	thermoplastics, fibers	thermoplastics, fibers	thermoplastics
Polymerization:	acid catalyzed condensation polymerization	Zieglar-Natta polymerization	free radical chain polymerization	metallocene catalysis polymerization

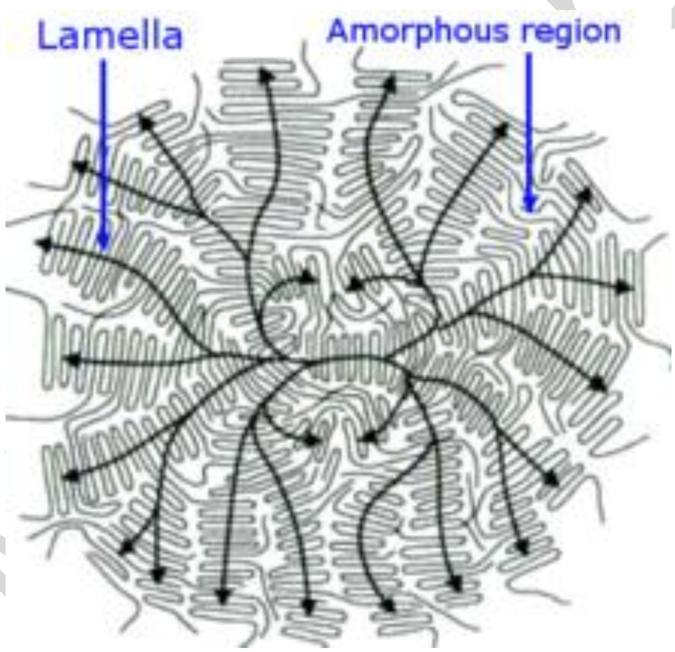
Amorphous Polymers

	Polypropylene (Atactic*) 	Poly(methyl methacrylate) 	Polybutadiene 	Polystyrene (Atactic*) 
Monomer(s):	propylene	methyl methacrylate	butadiene	styrene
T_g:	-17°C (1.4°F)	120°C (248°F)	-106°C (-159°F)	100°C (212°F)
Uses:	elastomers	thermoplastics	tires, belts, hoses, gaskets, and seals	thermoplastics
Polymerization:	Metallocene catalysis polymerization	free radical vinyl polymerization	Ziegler-Natta polymerization, free radical polymerization	free radical vinyl polymerization

Amorphous Polymers

Amorphous polymers can be defined as polymers that **do not exhibit any crystalline structures** in X-ray or electron scattering experiments. They form a broad group of materials, including glassy, brittle and ductile polymers. Many applications of **polymers and polymer coatings need flexibility** at low to ambient temperatures. That's where amorphous polymers are the right choice.

Lamella: A lamella is a **small plate or flake**, and may also be used to refer to collections of fine sheets of **material held adjacent to one another**. The term lamella is often used as a way to describe **crystal structure of some materials**.



Schematic model of a spherulite. Black arrows indicate direction of molecular alignment

Spherulites: In polymer physics, spherulites (from Greek sphaira = ball and lithos = stone) are spherical semi-crystalline regions inside non-branched linear polymers. Spherulite diameter may vary in a wide range from a few **micrometers to millimeters**. Spherulites are composed of **highly ordered lamellae**, which result in higher density, hardness, but also brittleness when compared to disordered regions in a polymer. The **lamellae are connected by amorphous regions** which provide elasticity and impact resistance.

Effects of Spherulites

- Formation of spherulites affects many **properties of the polymer material**; in particular, **crystallinity, density, tensile strength and Young's modulus** of polymers **increase** during spherulization.
- **Stronger intermolecular interaction** within the lamellae accounts for **increased hardness, but also for higher brittleness**.
- The **amorphous regions between the lamellae within the spherulites** give the material certain **elasticity and impact resistance.**

Crystallization Mechanisms

1) Solidification from the melt

Polymers are composed of long molecular chains which **form irregular, entangled coils** in the melt. Some polymers **retain such a disordered structure upon freezing** and readily convert into amorphous solids. In other polymers, the chains **rearrange upon freezing and form partly ordered regions.** Such alignment is hindered by **the entanglement**. Therefore, within the ordered regions, the polymer chains are **both aligned and folded**. Those regions are therefore neither crystalline nor amorphous and are classified as **semi crystalline**. Examples of semi-crystalline polymers are **linear polyethylene (PE)**, **polyethylene terephthalate (PET), polytetrafluoroethylene (PTFE) or isotactic polypropylene (PP)**.

2) Nucleation

Nucleation starts with **small, nanometer-sized areas** where as a result of heat motion some chains or their segments occur parallel.

Apart from the thermal mechanism, **nucleation is strongly affected by impurities**, **dyes, plasticizers, fillers and other additives** in the polymer. This is also referred to as **heterogeneous nucleation**. Many of the good **nucleating agents are metal salts of organic acids,** which themselves are crystalline at the solidification temperature of the polymer solidification.

3) Crystal growth from the melt

Crystal growth is achieved by the **further addition of folded polymer** chain segments and only occurs for **temperatures below the melting temperature (Tm)** and above **the glass transition temperature Tg**. **Higher temperatures destroy** the molecular arrangement and **below the glass transition temperature**, the movement of molecular **chains is frozen**. This process affects mechanical properties of the polymers and decreases their volume because of a more compact packing of aligned polymer chains.

4) Crystallization by stretching

The arrangement of the molecule chains upon crystallization **by stretching**. The above mechanism **considered crystallization from the melt**, which is important for **injection molding of plastic components**. Another type of crystallization occurs upon extrusion **used in making fibers and films**.

In this process, the polymer is **forced through, e.g., a nozzle that creates tensile stress** which partially aligns its molecules. Such alignment can be considered as crystallization and it affects the material properties. For example, the strength of the **fiber is greatly increased in the longitudinal direction**. **Polymer strength is increased** not only by extrusion, but also by blow molding, which is used in the production of **plastic tanks and PET bottles**. Some polymers which do not crystallize from the melt, can be partially aligned by stretching.

5) Crystallization from solution

Polymers can also be crystallized from **a solution or upon evaporation** of a solvent. This process depends on the **degree of dilution**: in dilute solutions, the molecular chains have **no connection with each other and exist as a separate polymer coils in the solution**. Crystallization from **solution may result in the highest degree of polymer crystallinity**. For example, highly linear polyethylene can form platelet like single crystals with a thickness on the order 10–20 nm when crystallized from a dilute solution.

6) Confined Crystallization

When polymers **crystallize from an isotropic**, **bulk of melt or concentrated solution**, the crystalline lamellae (10 to 20 nm in thickness) are typically organized into a **spherulitic morphology**.

The unique crystal orientation of confined polymers imparts **anisotropic properties** (A material is anisotropic in the broad sense if its properties, when measured at the same location, change with direction).