Polymers in solid state

2. The crystalline state

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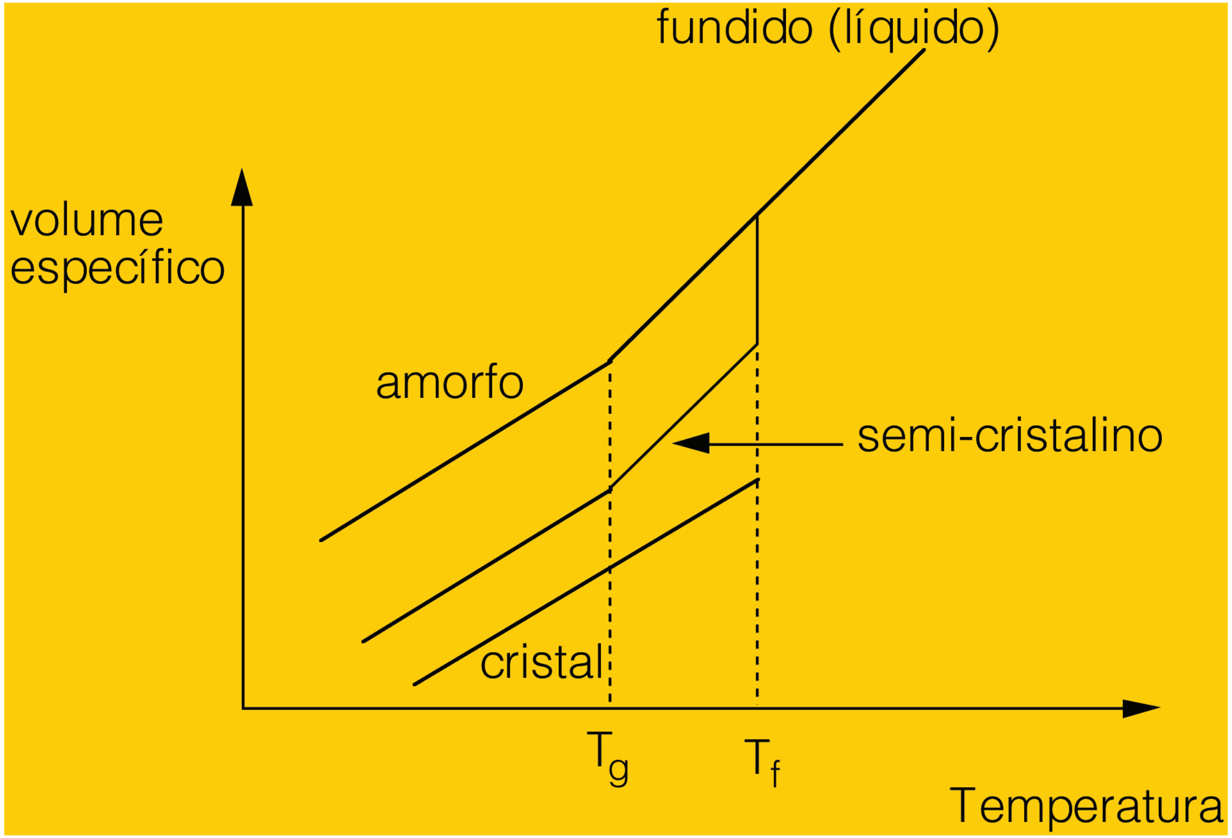
Crystalline state

Polymers in solid state: amorphous, crystalline or semi-crystalline.
Many "crystalline" polymers have 20-50% amorphous fraction.
Amorphous fraction: glass, melt, rubber = *f*(temperature, time scale of testing, cross-links)



Crystalline state

Polímeros cristalinos exibem:

i) maior resistência mecânica

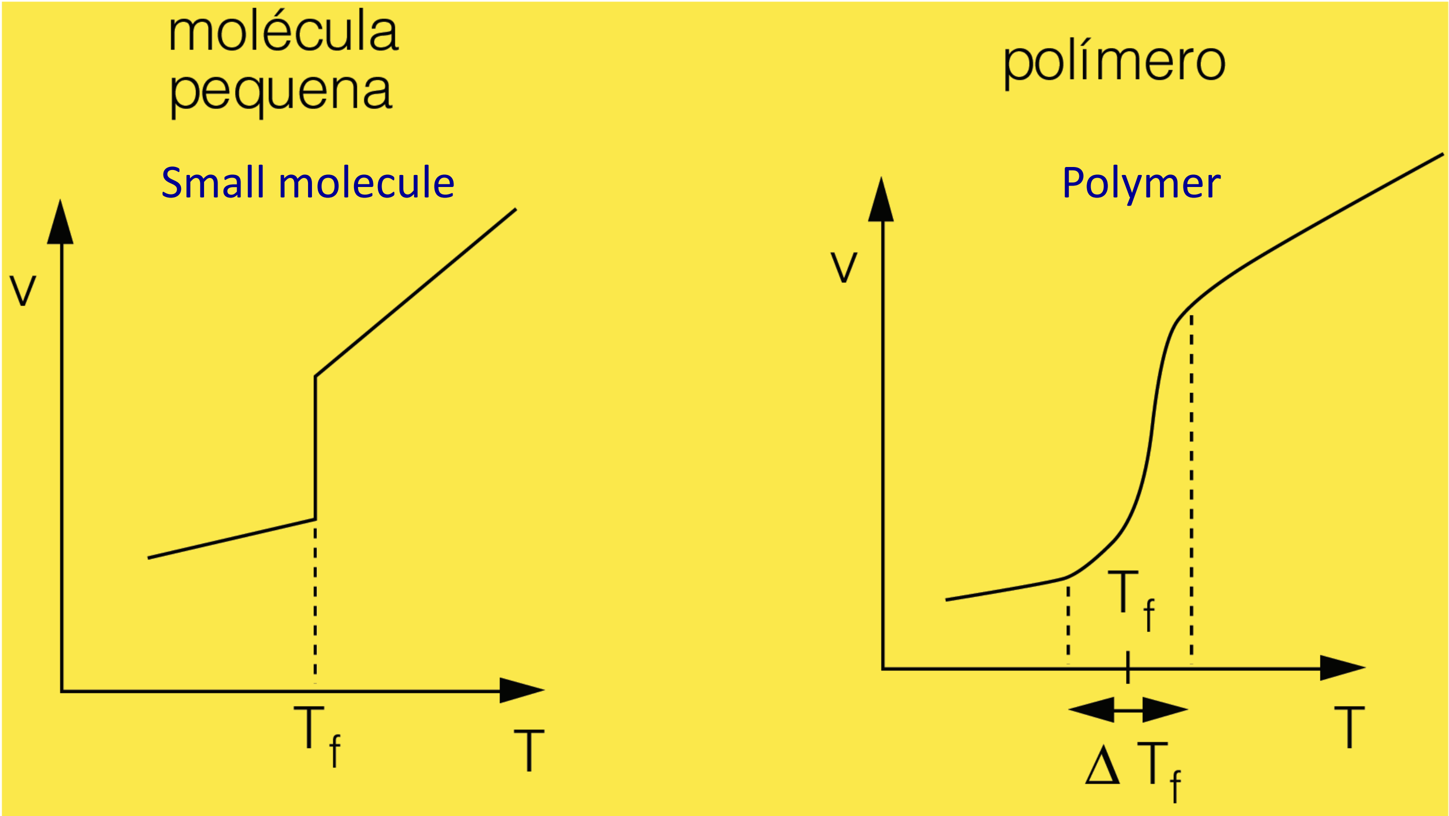
ii) maior opacidade

iii) maior resistência a solventes

iv) maior densidade

1.Crystallization thermodynamics

Melting temperature → Melting range



Crystallization thermodynamics

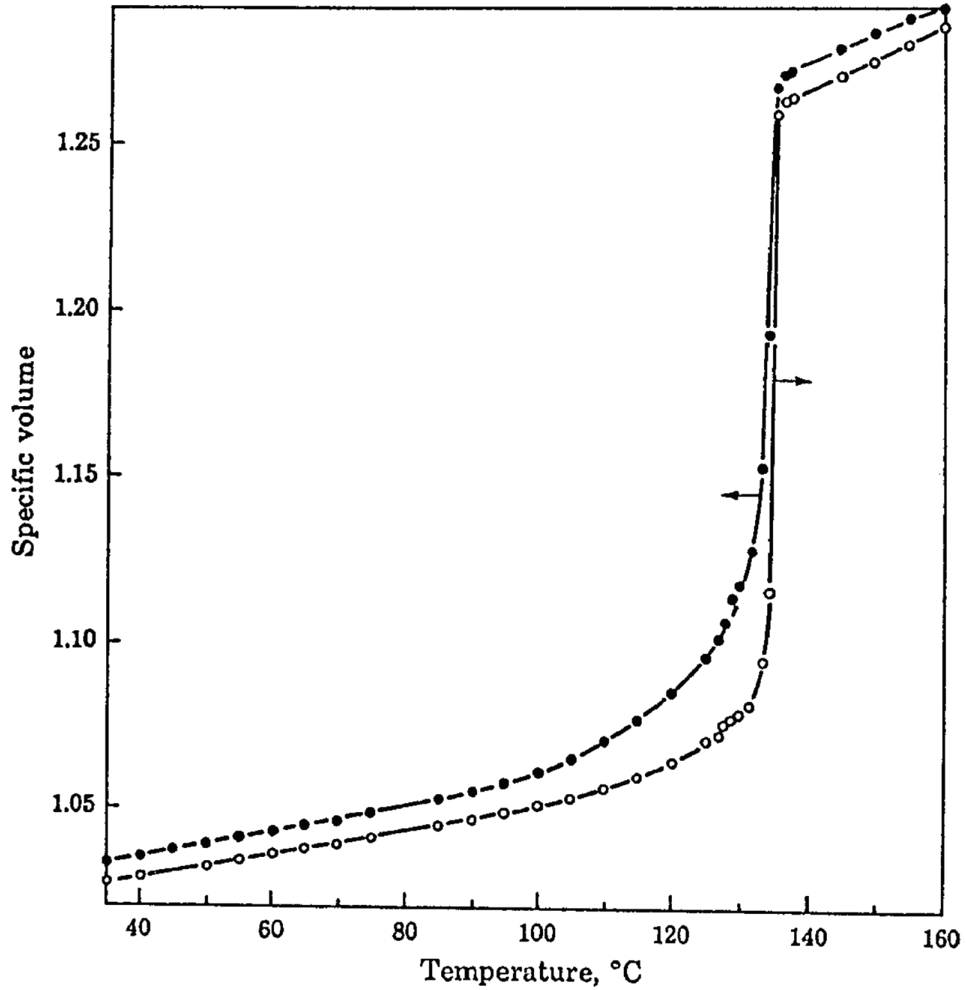


FIGURE 2. Specific volume versus temperature for the melting of linear polyethylenes. Key: ●, unfractionated polymer, and ○, fraction with a molecular weight of 32 000. (Reproduced from reference 1. Copyright 1961 American Chemical Society.)

Crystallization thermodynamics

Crystallization: *nucleation and growth*

1. *Chain regularity*

   Side chains/branching

   Statistical copolymers

2. *Polarity facilitates crystallization*

Crystallization Kinetics

Methodology:

- Study of the crystallization global process by dilatometry, calorimetry or spectroscopy.

- Determination of the spherulitic growth rate by direct microscope observation.

Crystallization Kinetics

Crystallization from the melt

The extent of crystallization, T(t)=1-λ(t), can be expressed as

$$T(t) = 1 - e^{-kt^n}$$

where t is time, k is the rate constant and n an integer that depends on the specifics of nucleation and growth processes. When two growing centers impinge upon one another their growth ceases.

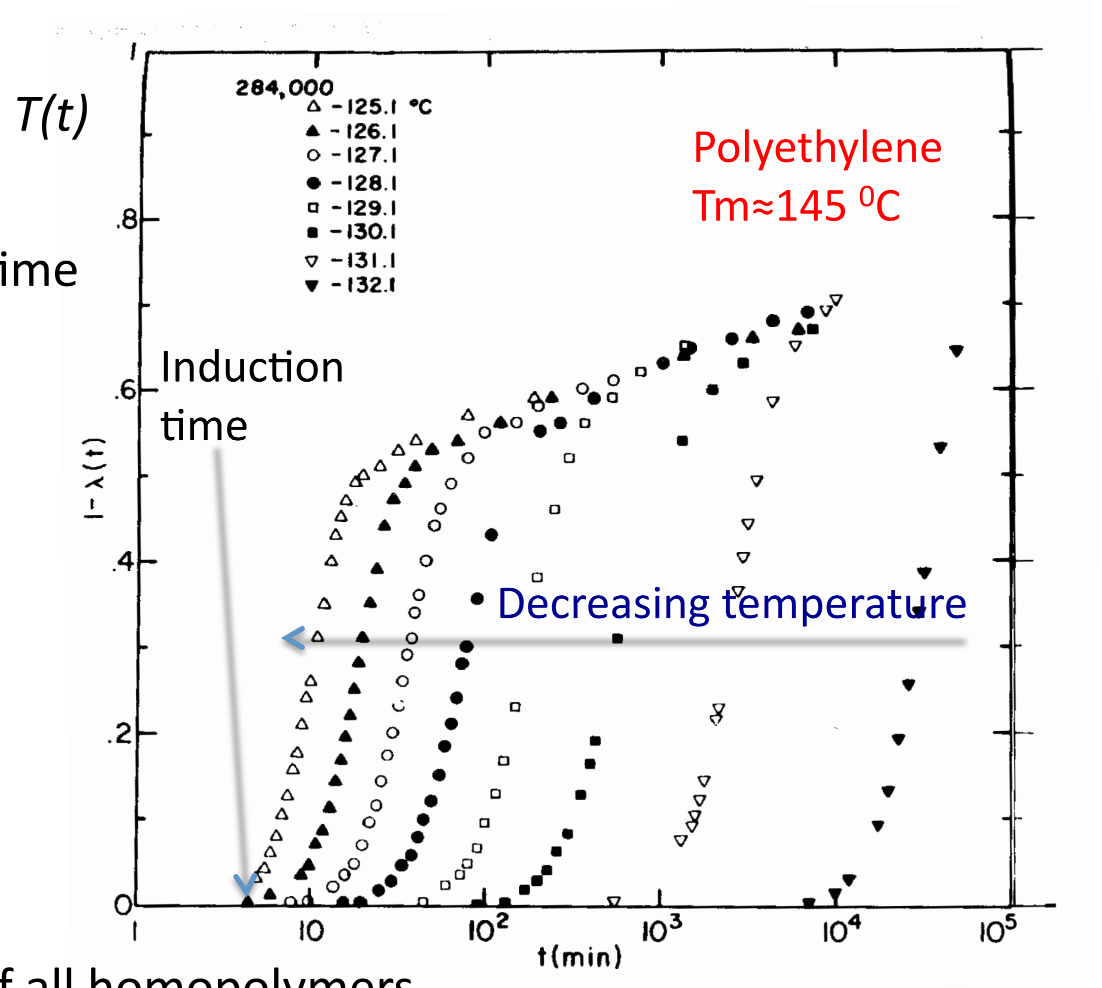
At small extent of transformation, the above equation is reduced to the “free growth” approximation

$$T(t) = kt^n$$

Crystallization Kinetics

Crystallization from the pure melt

Degree of crystallinity versus time

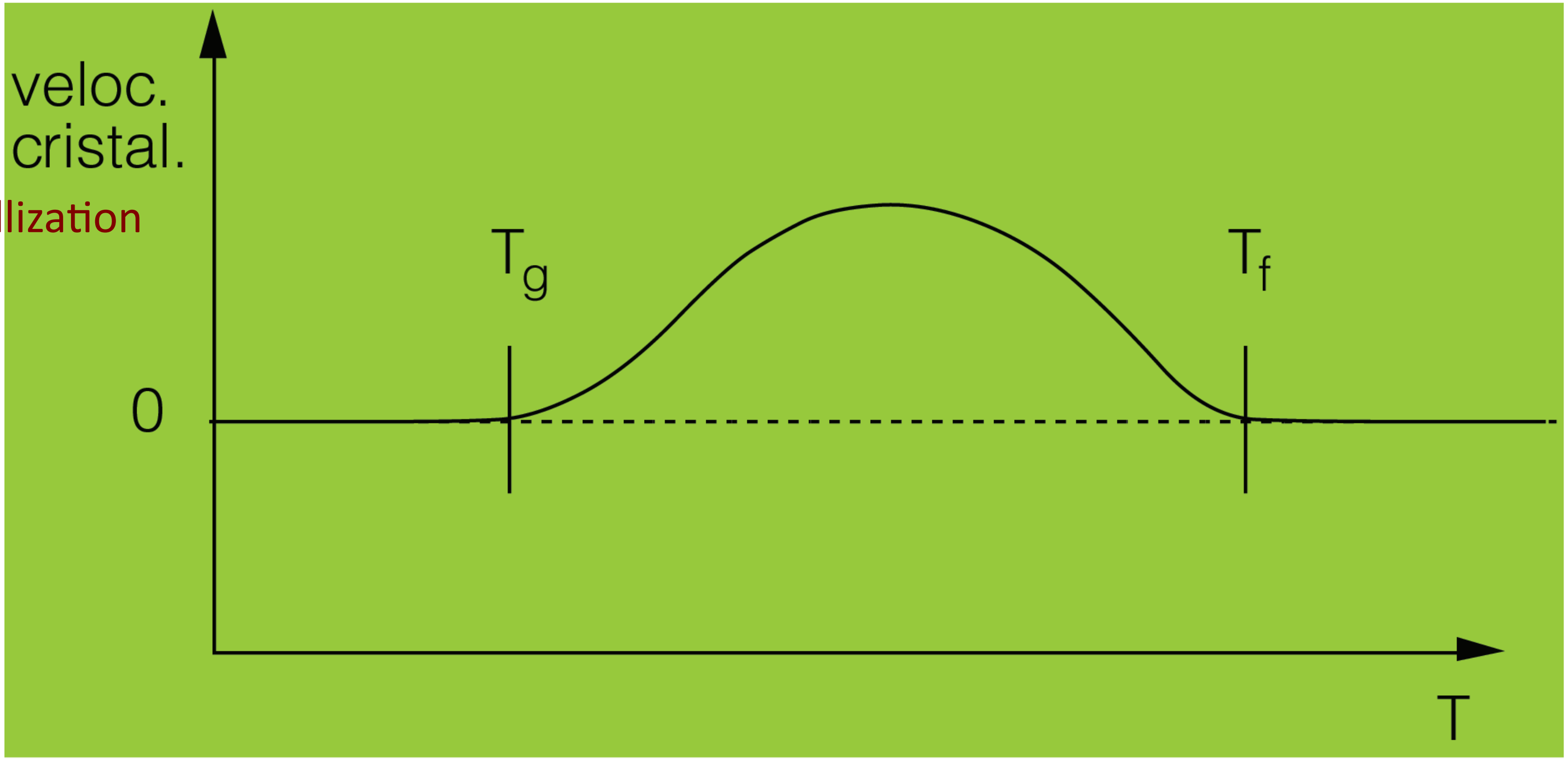


Sigmoidal isotherms_typical of all homopolymers

Crystallization Kinetics

Crystallization rate

Crystallization rate



Crystallization Kinetics

Spherulite growth rate

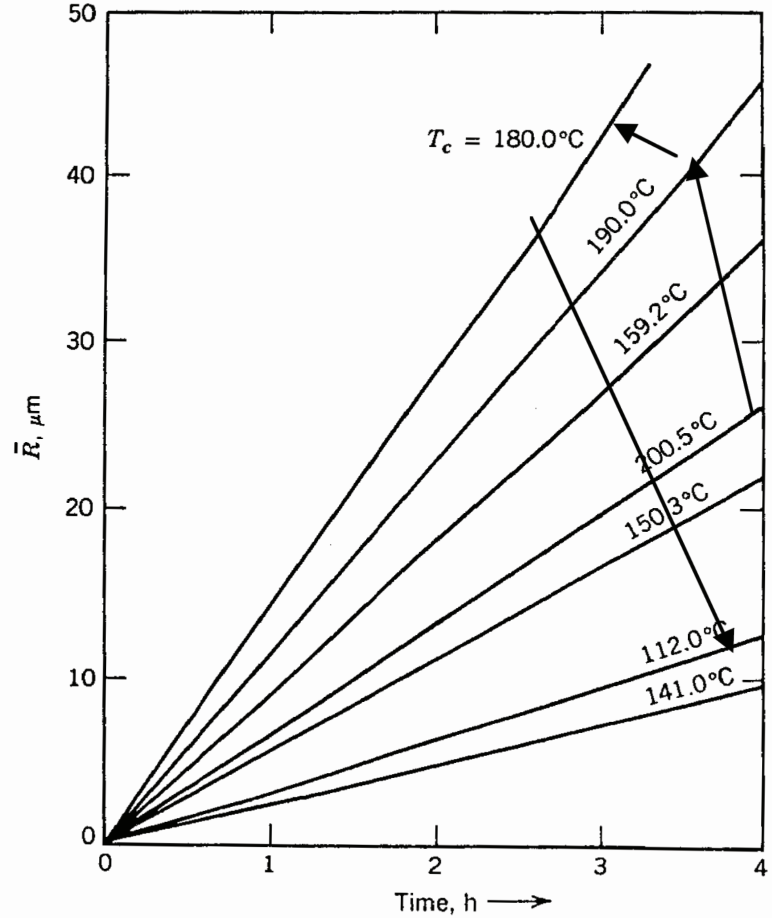


FIGURE 13. Plot of spherulite radius ($\bar{R}$) of isotactic polystyrene as a function of time. (Reproduced with permission from reference 15. Copyright 1970 Society of Polymer Science, Japan.)

At a given temperature, the growth rate is constant

Tm=243 °C

Crystallization Kinetics

Crystallization rate: effect of molecular weight

Molecular weight affects not only the level of crystallinity but also the time scale (crystallization rate)

Linear polyethylene fractions

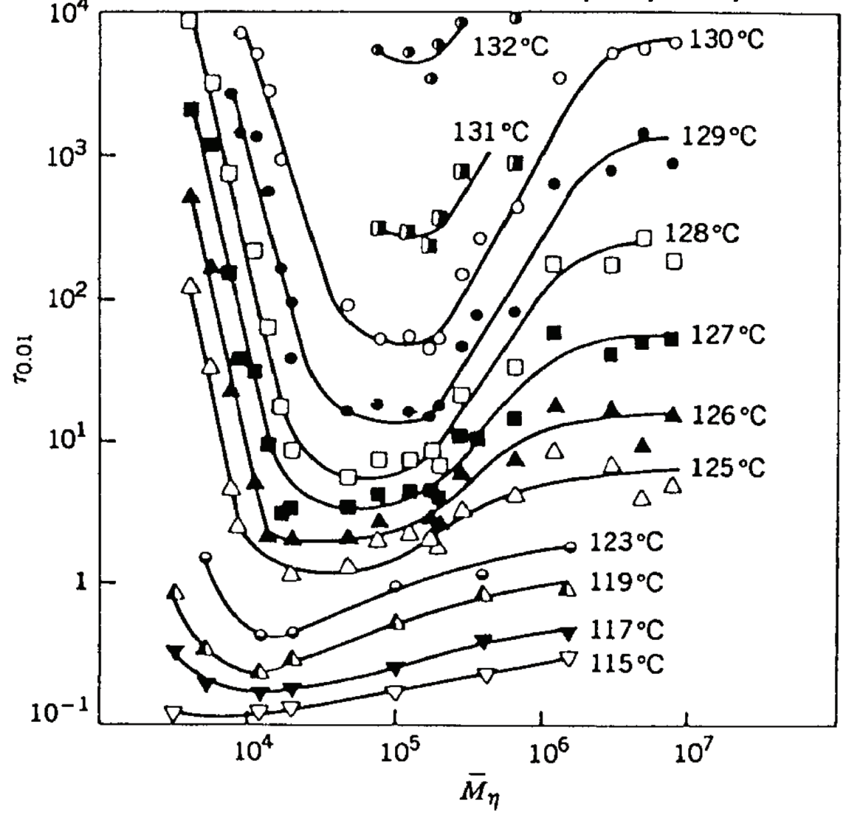


FIGURE 12. Double logarithmic plot of $\tau_{0.01}$ (time for 1% of the transformation) versus molecular weight for the indicated crystallization temperature. (Reproduced from reference 12. Copyright 1972 American Chemical Society.)

Structure and morphology

The molecular morphology (description of the arrangement of the polymer chains) is not directly observed. The structure of the unit cell is determined by X-ray diffraction.

The large scale morphology (gross morphology)-form and shape of the structures of interest-is directly observed by microscopic examination.

Structure and morphology

Crystallite structure

Lamellarlike crystallite habit is the characteristic gross morphological form developed by homopolymers during crystallization from the pure melt.

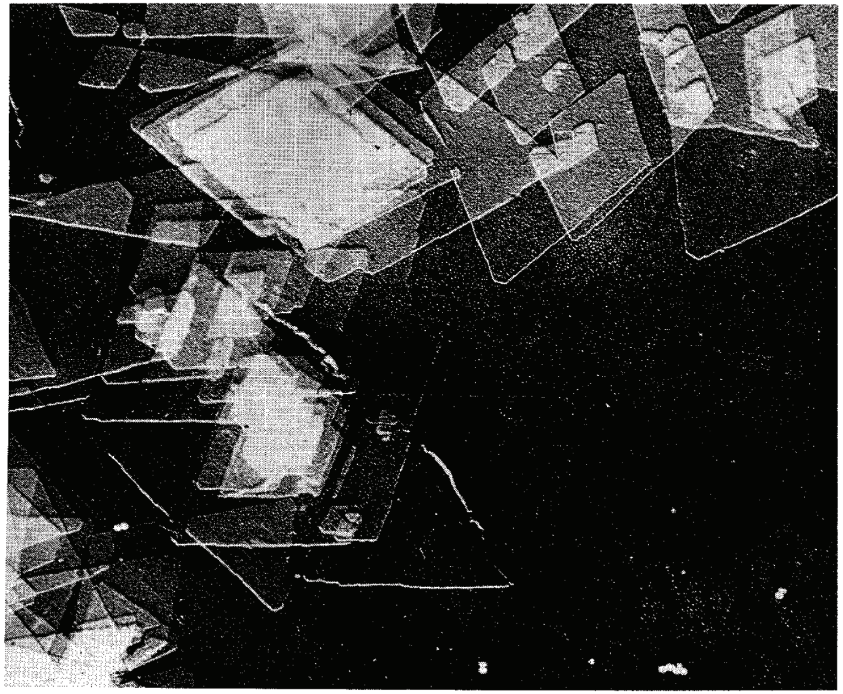
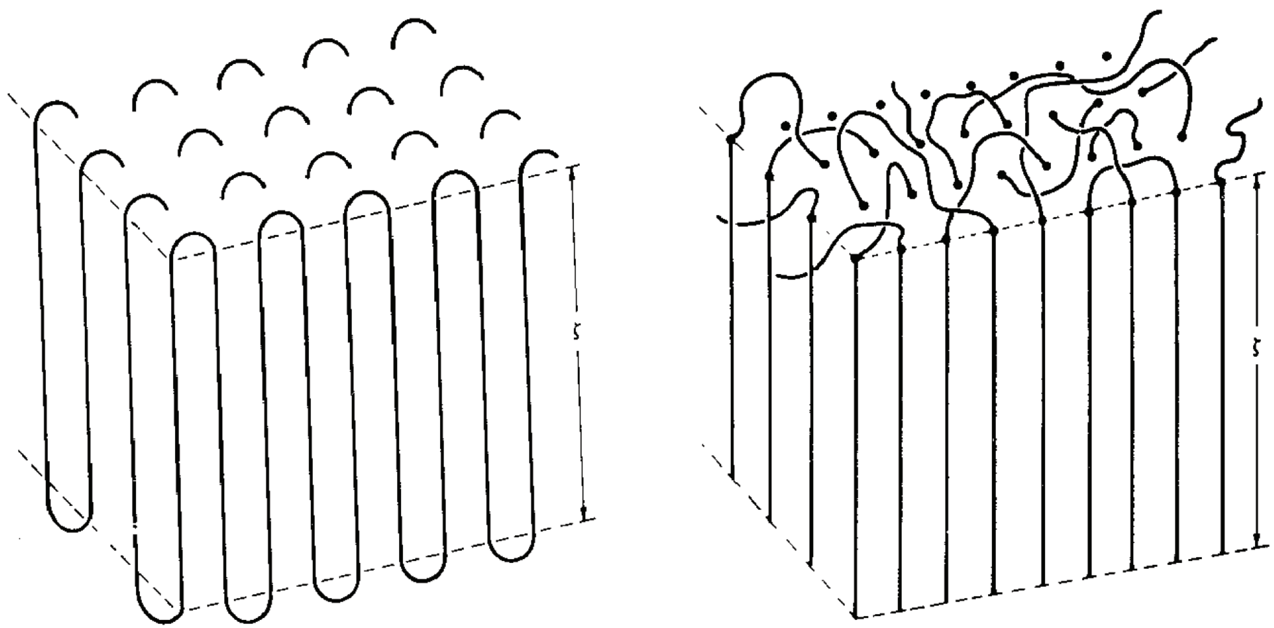


FIGURE 15. Electron micrograph of lamellae formed by linear polyethylene crystallized from dilute solution.

The lamellar thickness of the crystals formed from dilute solution is ≈ 100-200 Å. In bulk crystallized systems can be higher than 1000 Å.

Structure and morphology

Crystallite structure



(a) (b)

FIGURE 16. Schematic diagrams of possible chain structures within lamellar crystallite. (a) Regularly folded array and (b) nonregularly folded chains. Loop lengths are variable. (Reproduced from reference 20. Copyright 1962 American Chemical Society.)

Structure and morphology

Crystallite structure

The electron microscope provided the first observation of lamellar crystallites in bulk-crystallized systems.

FIGURE 17. Electron micrograph of surface films of linear polyethylene showing the lamellar structures of bulk-crystallized polymers. (Reproduced with permission from reference 21. Copyright 1959 John Wiley and Sons, Inc.)

Structure and morphology

Interlamellar structure

- The interlamellar region can be a significant portion of the total system.
- There is evidence for the existence of disordered chains: isotropic region.
- Properties are similar to those of melts or disordered states: observation of glass transition in crystalline systems.

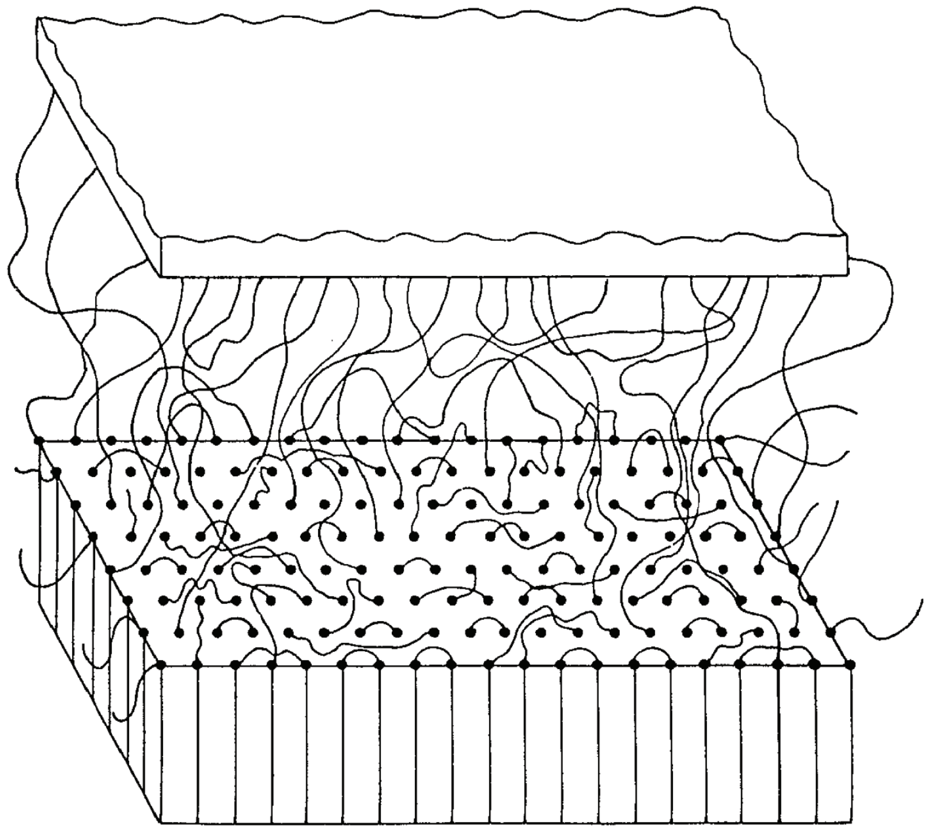


FIGURE 24. Schematic representation of chain structure in the interlamellar region.

Structure and morphology

Morphology of semicrystalline polymers

Existence of three regions with different chain conformations and crossed by many individual chains:

- Crystalline region
- Interfacial region
- Interlamellar or liquid-like region

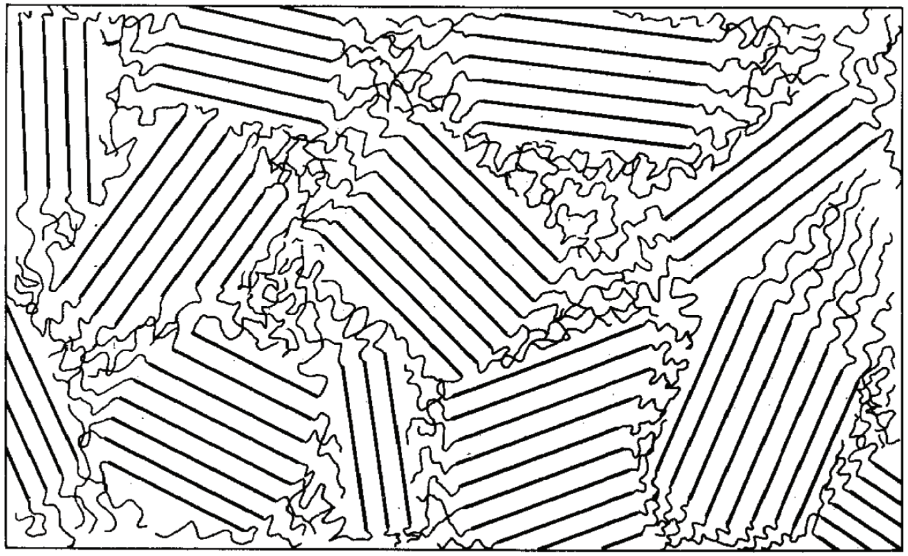
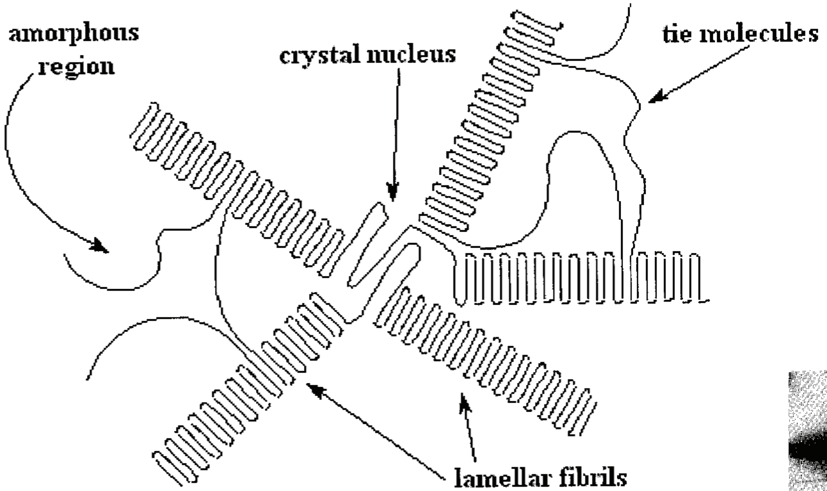


Fig. 1.4–1. Diagrama ilustrando a estrutura proposta da "micela em franja" de polímeros semi-cristalinos. [De P. J. Flory, *Principles of Polymer Chemistry* (Ithaca, N. Y.: Cornell University Press, 1953,) p. 49.]

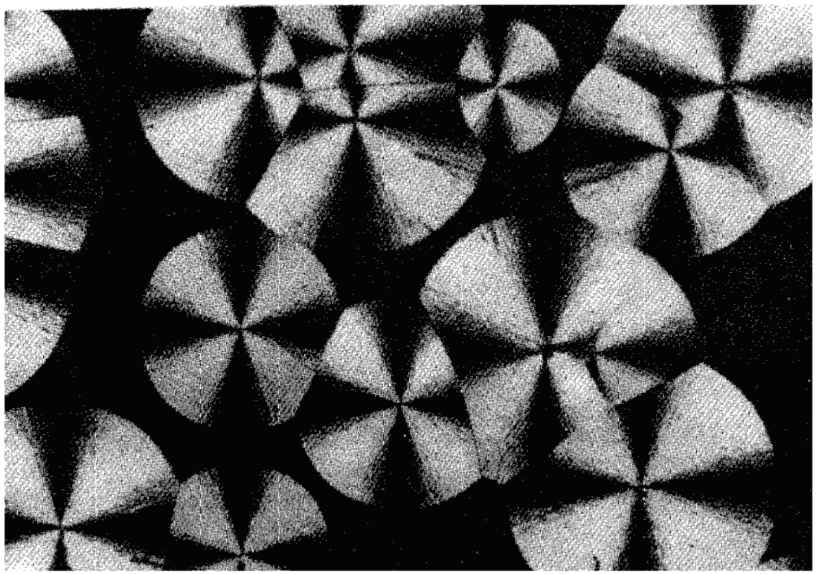
Structure and morphology

Supramolecular arrangements of crystallites: spherulites



a polymer crystalline spherulite

Growing spherulites



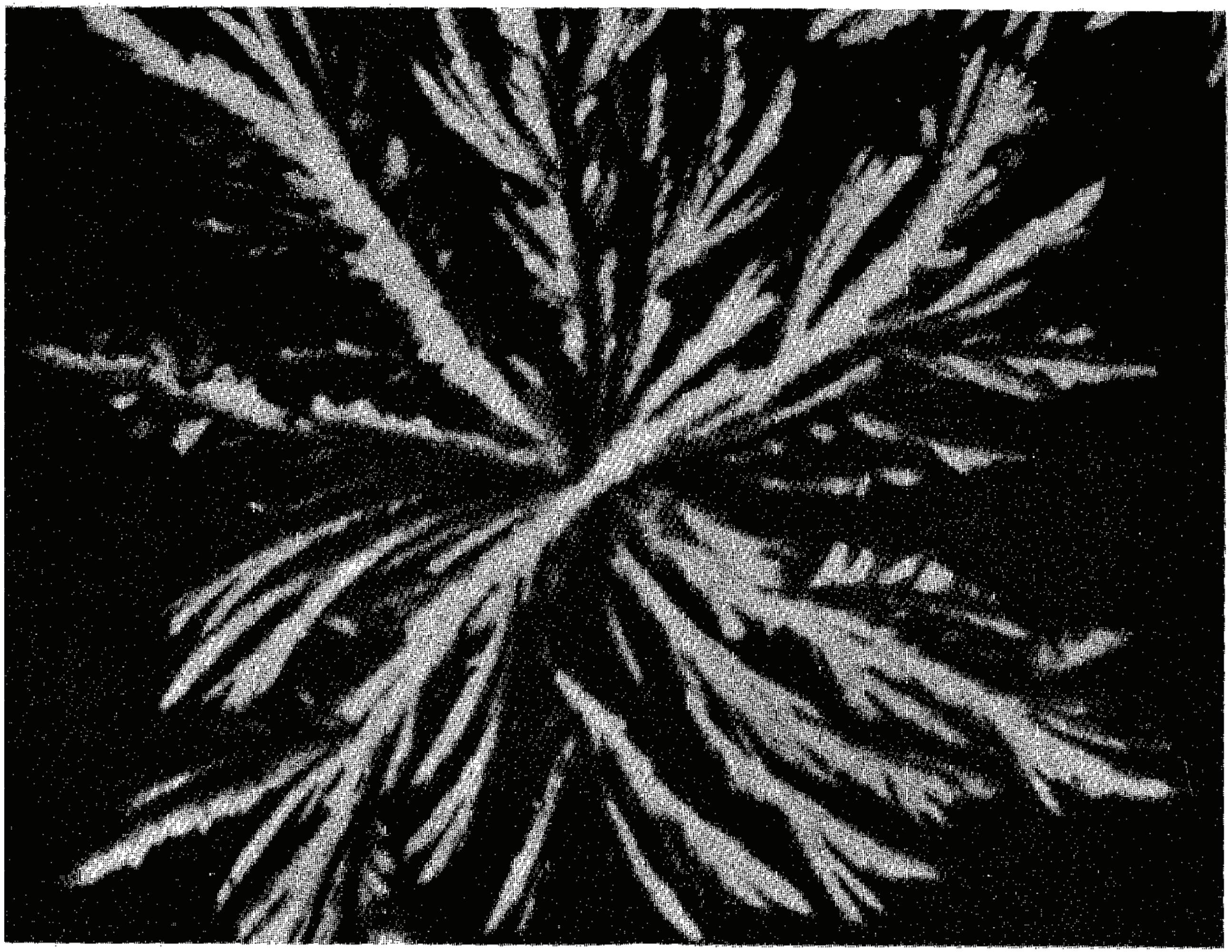
Structure and morphology

Supramolecular arrangements of crystallites: spherulites

Nylon

Structure and morphology

Supramolecular arrangements of crystallites: spherulites



Polypropylene

Tm and Tg for homopolymers

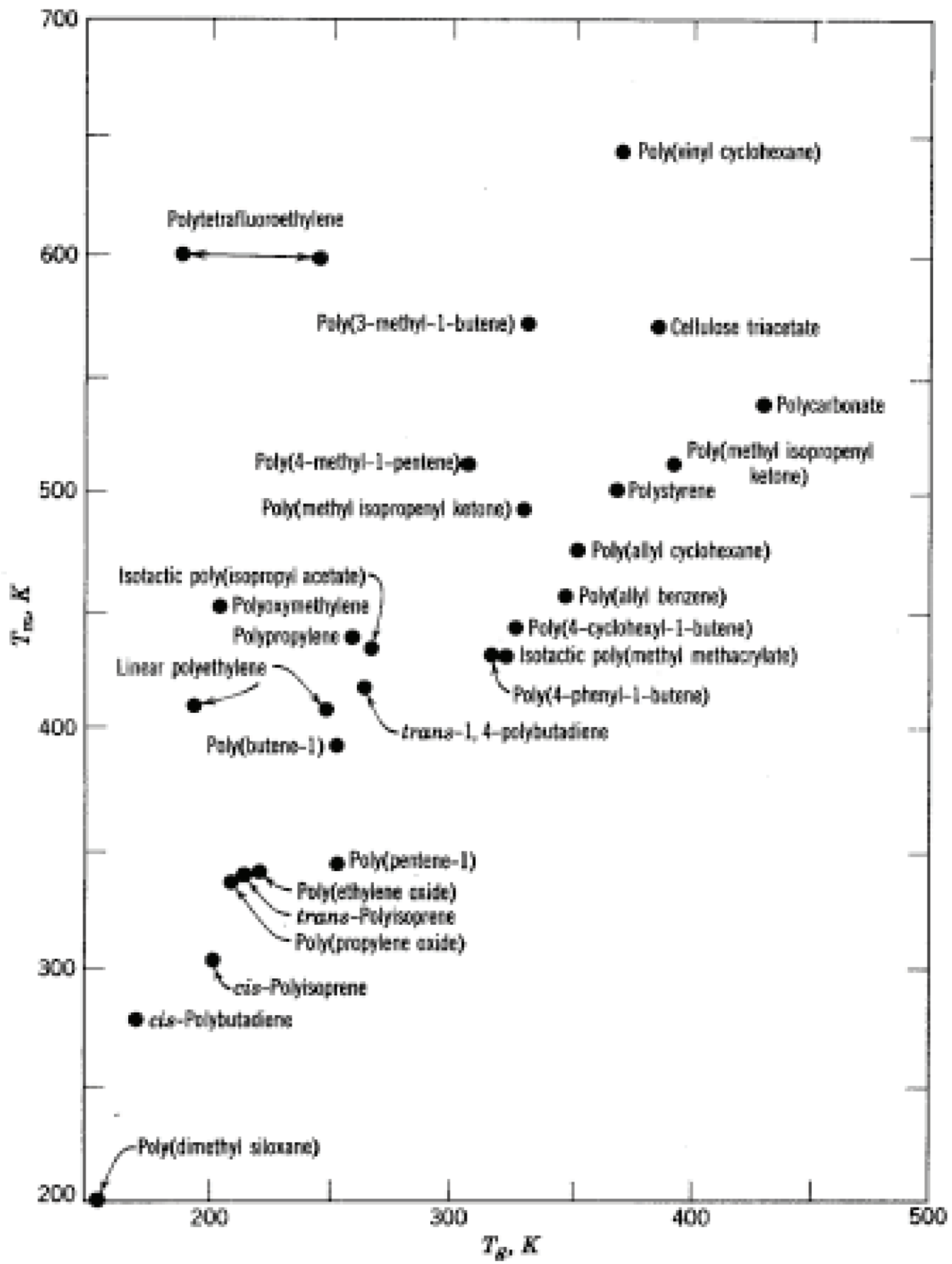


FIG. 12-4. Relation between T_m and T_g for various polymers (Boyer 1963).

Degree of crystallinity

The degree of crystallinity depends on the molecular weight and the structural regularity of the chain.

An increase of molecular weight leads to a reduction of crystallinity: chain entanglements restrict the crystallization process

$$\%C = \frac{\rho - \rho_{amorphous}}{\rho_{crystal} - \rho_{amorphous}} \times 100$$

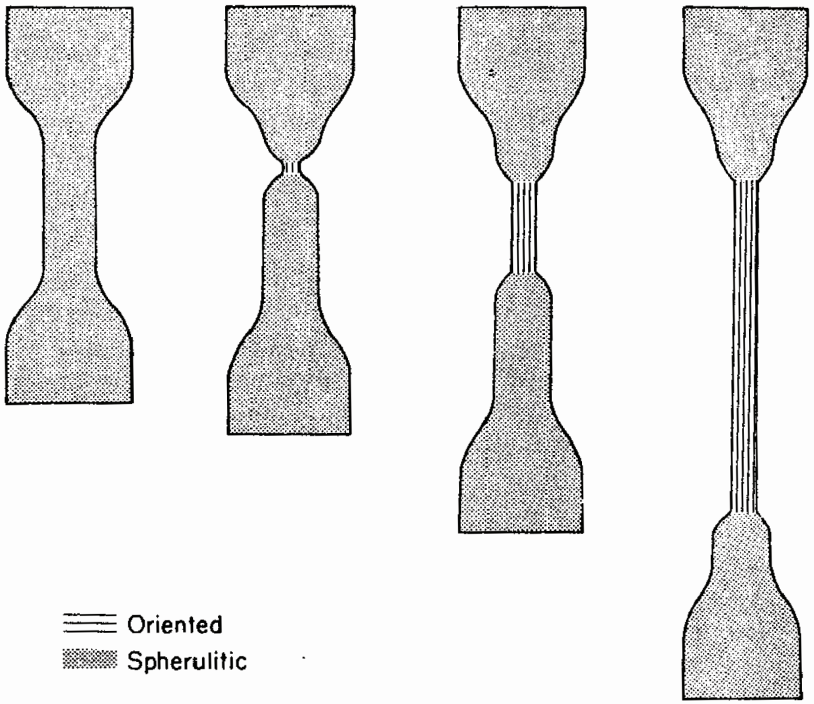
Spherulites and drawing. Fibers.

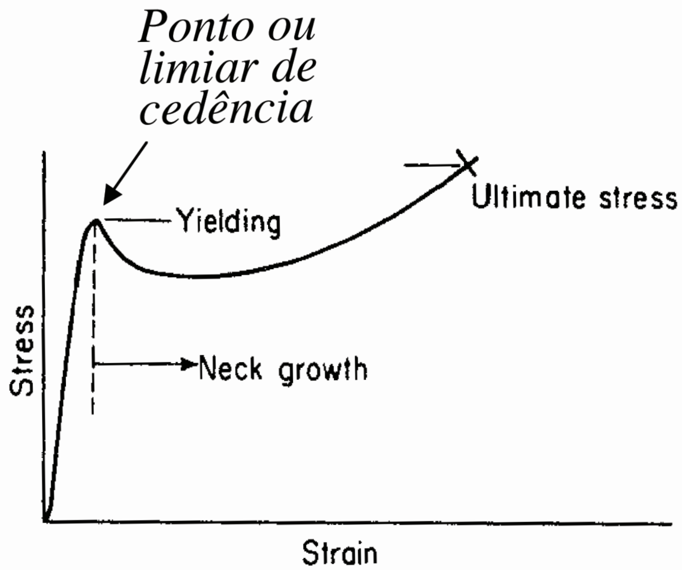
The crystallization of a polymer from its melt leads in general to spherulitic structures (crystallites growing from a nucleation center).

When a crystalline polymer undergoes an elongation process, at a temperature between Tg and Tm, there is:

i. A plastic deformation_reorientation of the polymer chains in the amorphous region
ii. Above the elastic limit there may be a reorganization of the polymer chains in the crystalline regions_orientation of the crystallites.

Drawing (*estiramento*) of a spherulitic polymer





Textile fibers

Most synthetic fibers are highly crystalline, with the crystallites essentially oriented along the fiber axis.

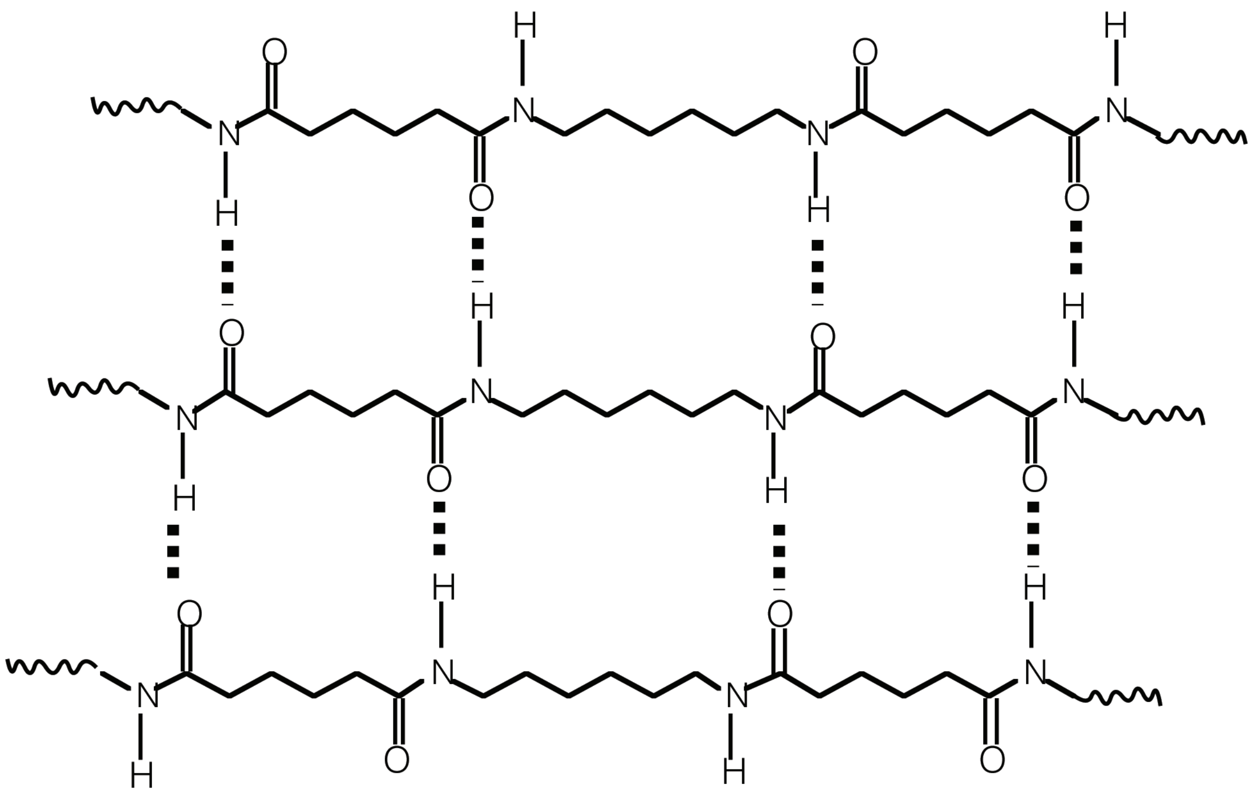
1.The polymer is firstly "spun" into filaments; by extruding the polymer melt/solution through pores of a spinneret.

2.These filaments are drawn to align the fibers further, at a temperature between Tg and Tm

Consequences:

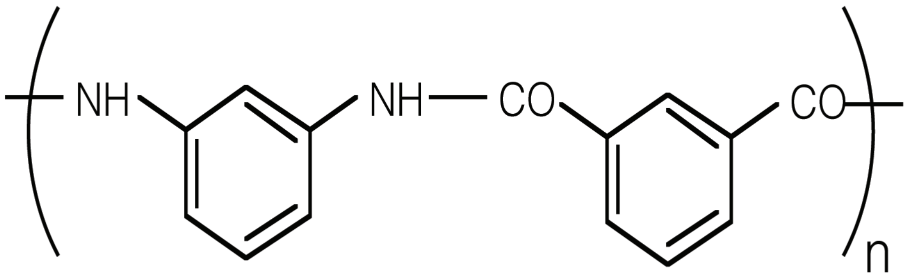
1. Increasing crystallinity, tensile strength and stiffness
2. Lower deformation at rupture

Textile fibers

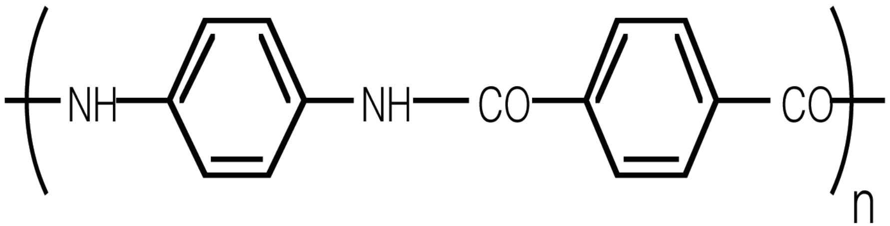


Nylon 6,6

Textile fibers



Nomex



Kevlar

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