Universidad
Carlos III de Madrid
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MATERIALS SCIENCE AND ENGINEERING

TOPIC 7. Polymeric materials

1. Introduction
   - Definition
   - General characteristics
   - Historic introduction
   - Polymers: Examples
2. Classification
3. Properties: Structural aspects
4. Solid state
   - Crystallinity
   - Thermal transitions
   - Mechanical behaviour

1. INTRODUCTION: DEFINITION

POLYMER

"Organic compound, natural or synthetic, with high molecular weight made of repetitive structural units "

Large size chains formed from the covalent union of various monomer units (macromolecule)

PLASTIC

1. Polymer whose fundamental property is plasticity (thermoplastic). It is deformed plastically under the action of pressure andor heat .

2. Mixture (of a polymer with additives) that can be transformed by flowing or moulding in liquid or molten state.

1. INTRODUCTION: GENERAL CARACTERISTICS

	Advantages	Applications
$\downarrow T_f$	Easy processing	Products of elevated consumption
$\uparrow \varepsilon$	High ductility	Neumatics. Plastics for packaging
$\downarrow \rho$	Light products	Automobiles , aeronautics and aerospace
$\downarrow \sigma_t$	Thermal insulators	Construction
$\downarrow \sigma_e$	Electic insulators	Coatings for wires
$\uparrow R_{chemic.}$	High $R_{corrosion}$	Tubes, bins, boxes, Coatings

1. INTRODUCTION: HISTORIC INTRODUCTION

Polymers: synthetic and natural materials:

Cellulose, starch, proteins, leather , wool , cotton , synthetic fibres of polyesters and polyamides, plastics, rubbers, adhesives etc

Production 1995: 110 millions of tons (Spain: 2,6)
2000: 180 millions of tons (Spain : 2,7)

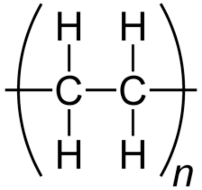
HISTORIC BACKGROUND

Origins of Humanity ⇒ natural products: leather , wool, cellulose….

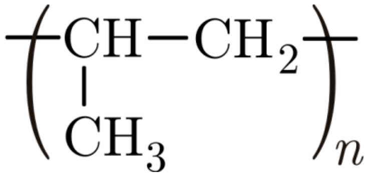
- 1838: Vulcanizing of natural rubber
- 1846 Cellulose nitrate
- 1870 Celluloid
- 1907 Bakelite
- 1920 Macromolecular Hypothesis (Staudinger)
- 1926 Polyvinyl chloride (PVC)
- 1933 Poly ethylene (PE)
- 1938-39 Nylon (fibers) y Polystyrene (PS)
- 1954 Polypropylene (PP)
- 1960 Applications of Epoxy Resins
- 198- Polymers of high specifications

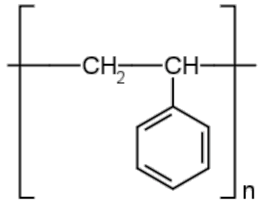
1. INTRODUCTION: EXAMPLES

Poly ethylene PE: Most popular plastic



Polypropylene PP: used as plastic and as fibre

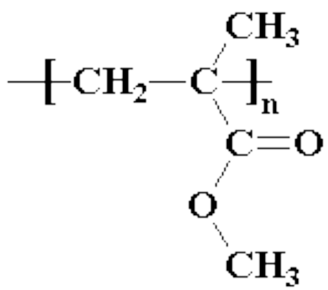




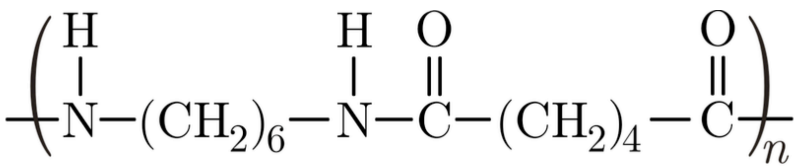
Polystyrene PS: economic and resistant. Styrofoam™: foam of PS

Polyvinylidene fluoride PVDF: high electric and fire resistance

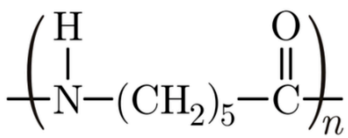
Polymethyl methacrylate PMMA: transparent plastic. Substitute of crystal



Nylon (polyamides): most common polymers used as fibers



Nylon 66



Nylon 6

2. CLASSIFICATION

CLASSIFICATION

According to origin
Natural, synthetic …

According to structure
Semicrystalline
and amorphous

According to chemical composition
Acrylics , vinyls…..

According to polymerization mechanism
Addition, condensation

According to applications
Elastomers, plastics, fibres, adhesives….

According to their behaviour with temperature
- Thermoplastic
- Thermosetting

2. CLASSIFICATION

According to applications

Elastomers. Are materials with very low modulus of elasticity and high extensibility

Plastics. Are the polymers in which, when a sufficiently intense force is applied, they irreversibly deform

Fibres Present a high modulus of elasticity and low extensibility

Coatings. Are substances, normally liquid, that adhere to the surface of other materials

Adhesives. Are substances that combine a high adhesion and a high cohesion,

According to their behaviour with temperature

Thermoplastic. Flow on heating and they become hard on cooling. Their molecular structure presents few (or none) crosslinks.

Thermosetting. They chemically decompose when heated, instead of flowing. This behaviour is due to a crosslinked structure

2. CLASSIFICATION

POLYMERS OF GENERAL USE (Commodity)

Polymers of high consumption: polyolefins, polyacrylates and methacrylates, polystyrene, PVC, resins ,phenols, urea and melamines, polyesters, polyurethanes, epoxy resins and diverse elastomers

TECHNICAL AND ENGINEERING POLYMERS

Good properties between 0-100 ºC: polyamides, polycarbonates, polyphenylene oxide (PPO), polysulfones, polyphenylene sulpphide (PPS), aliphatic-aromatic polyesters, Polyether ether ketone (PEEK)

SPECIAL POLYMERS

High price polymers with outstanding characteristics, liquid crystals of high modulus and advanced composite materials

Factors that determine their use : plastic, fibres or as rubber :

Flexibility in the chain , intermolecular interactions and grade of regularity in the polymer

3. PROPERTIES

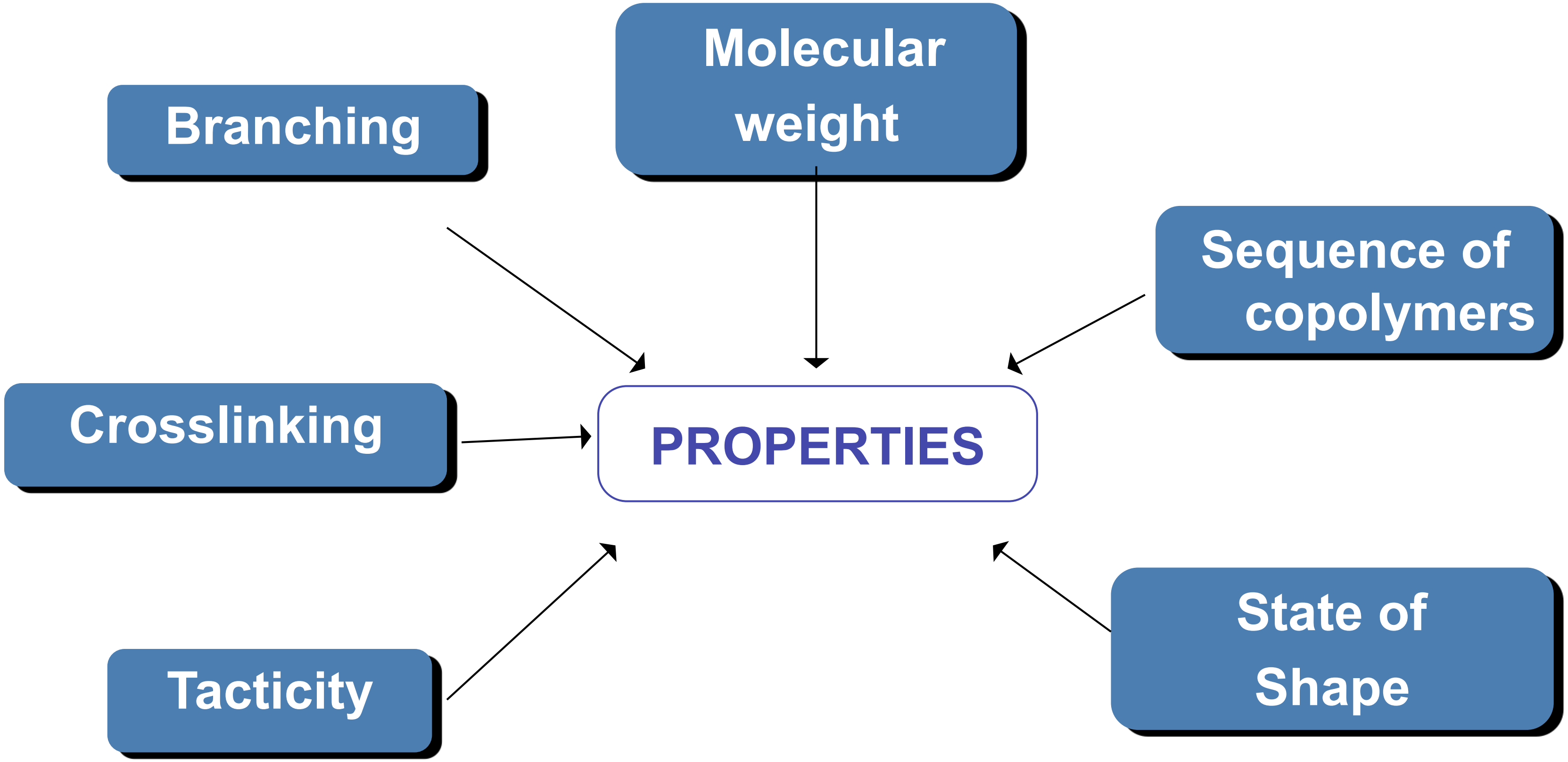
The properties of polymers depend on multiple factors:

- **Molecular Weight & its distribution**
- **Structural aspects**
- **Crystallinity**

- **Monomeric nature** (families of polymers)
- **Number of monomeric units** (molecular weight) and its distribution
- **Monomeric functionality** (branches and crosslinking)
- **Relative positions of the groups** (tacticity and changes in shape)
- **Ordering of the units** (sequences)
- **Ordering the positions of the chain branches** (crystallinity)

3. PROPERTIES

The factors that determine the application of the polymer



3. PROPERTIES: MOLECULAR WEIGHT

MOLECULAR WEIGHT

Macromolecular molecular weight : $M_n = M_0 X_n$

where:
M_n = number-average molecular weight
M_o = monomer molecular weight
X_n= degree of polymerization (average number of monomer units in a chain)

For a polymer ⇒ distribution of chain longitude or molecular weights :
MEAN MOLECULAR WEIGHT ⇒ Definition of the various molecular weights:

$$M_n = \Sigma M_i x_i$$

$$M_w = \Sigma M_i w_i$$

M_n = number-average molecular weight
M_w = weight-average molecular weight
M_i = mean molecular weight in size range *i*
x_i= fraction in number of molecules in range *i*
w_i= fraction in weight of molecules in range *i*

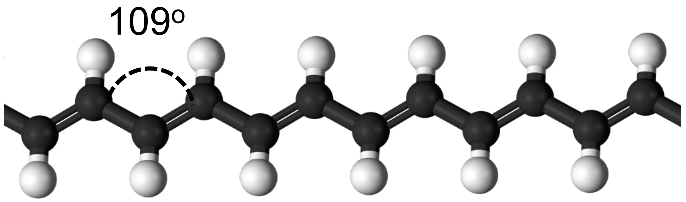
Index of polydispersion :

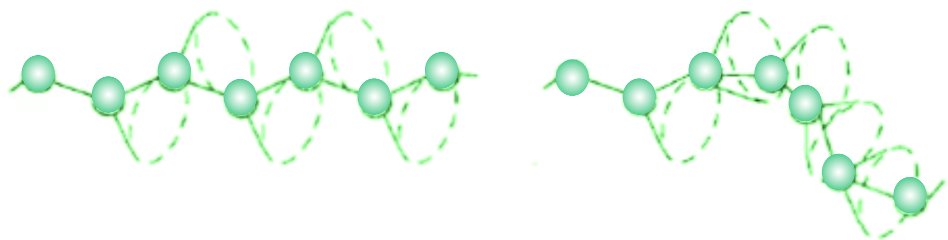
$$I = \frac{M_w}{M_n}$$

3. PROPERTIES: STRUCTURAL ASPECTS

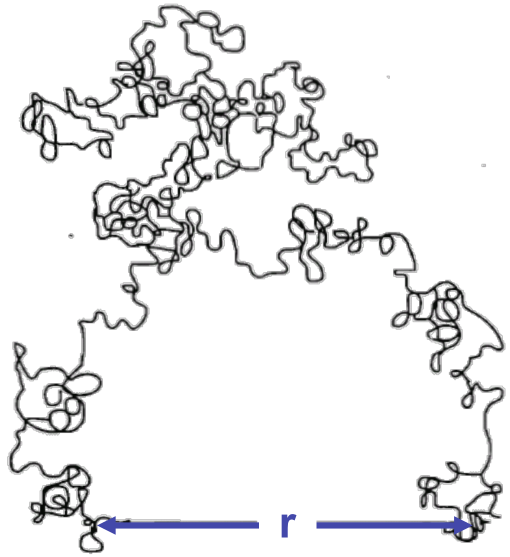
CONFIGURATION STATES

Polymeric molecular chains are NOT strictly straight:





Schematic representation of a molecular chain of a simple polymer with various fringes produced from bond rotation :



This behaviour provokes the entanglement between chains ⇒ high elasticity

<r> : distance between the extremes of the chain

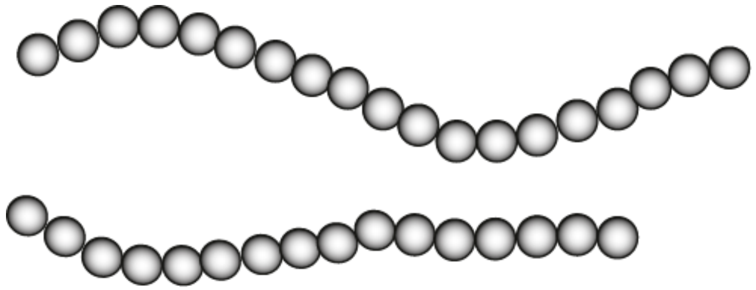
<s^2> : mean radius of rotation

Shape change → **Flexibility**

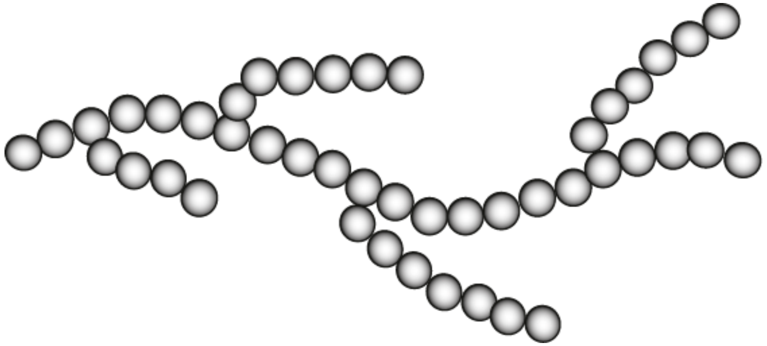
3. PROPERTIES: STRUCTURAL ASPECTS

MOLECULAR STRUCTURE

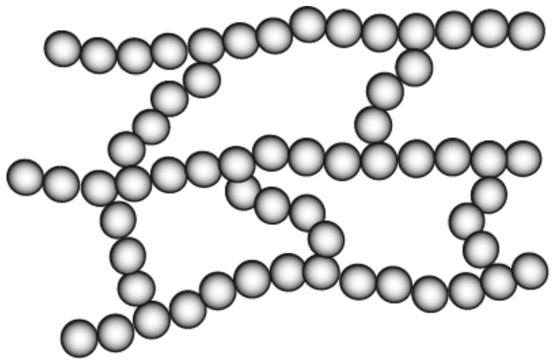
Linear



Branched



Crosslinked

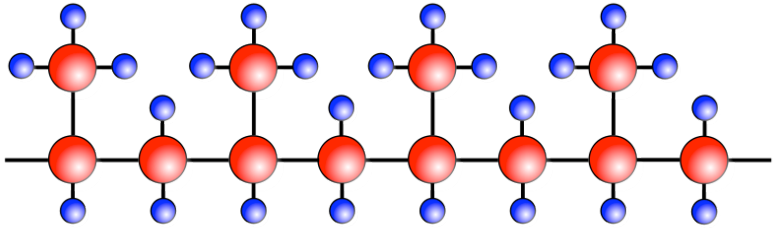


3. PROPERTIES: STRUCTURAL ASPECTS

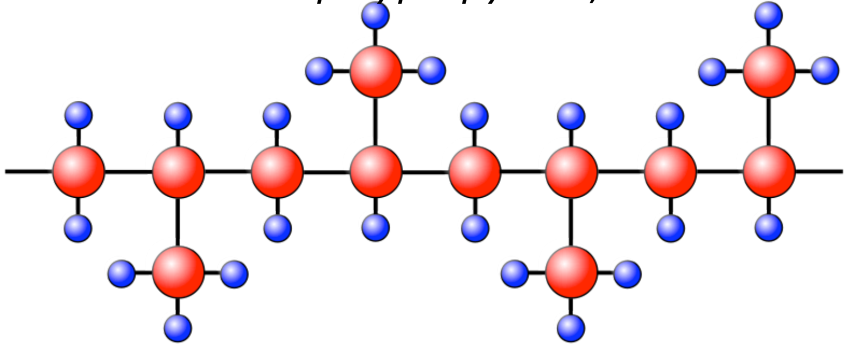
TACTICITY

The best example is polypropylene

PP isostatic

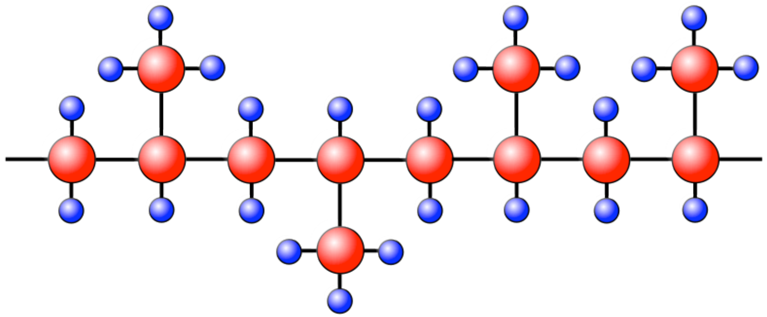


isotactic polypropylene, has excellent mechanical properties



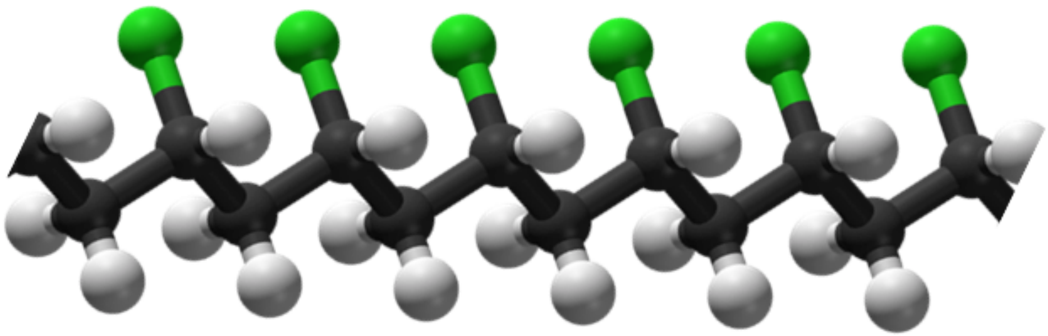
PP syndiotactic

PP atactic

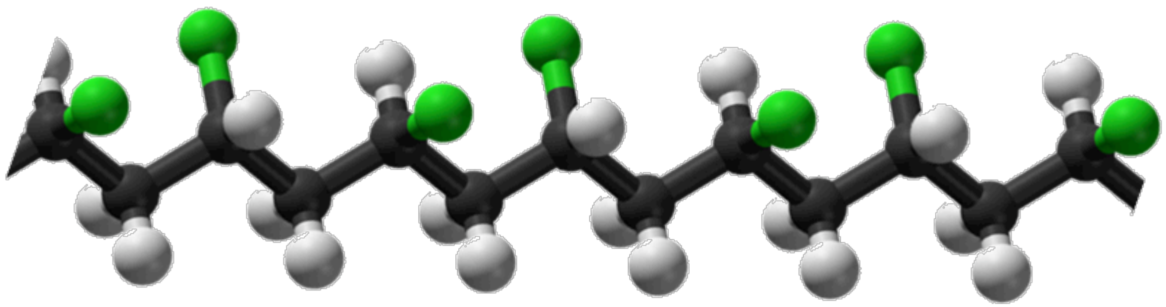


atactic polypropylene is a wax type material, with very bad mechanical properties

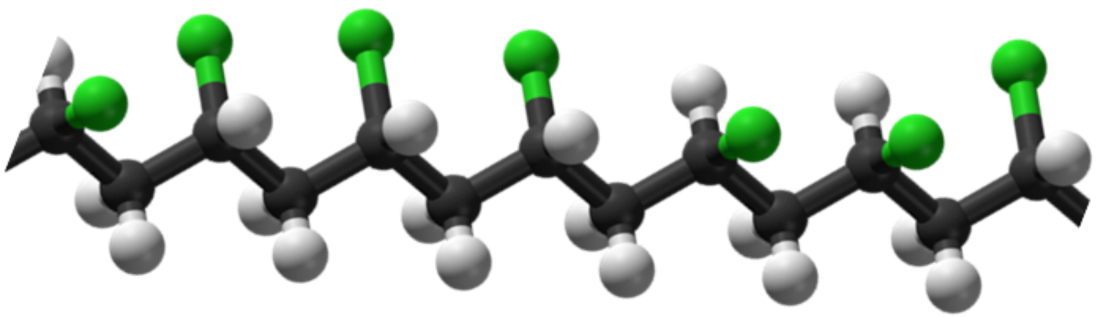
3. PROPERTIES: STRUCTURAL ASPECTS



ISOTACTIC



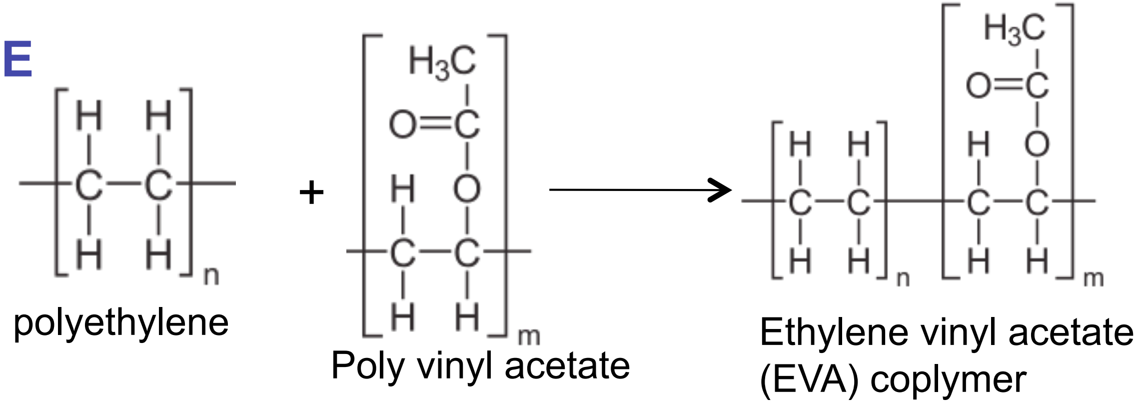
SYNDIOTACTIC

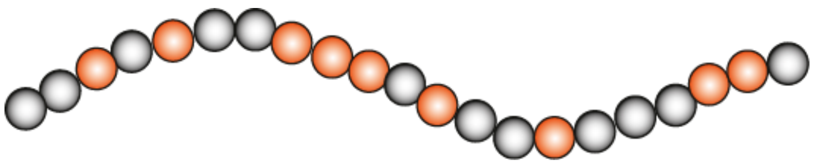


ATACTIC

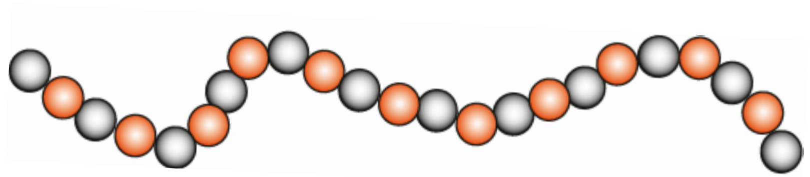
3. PROPERTIES: STRUCTURAL ASPECTS

COPOLYMERS IN SEQUENCE

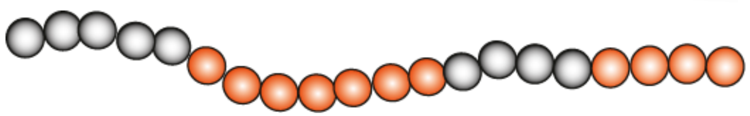




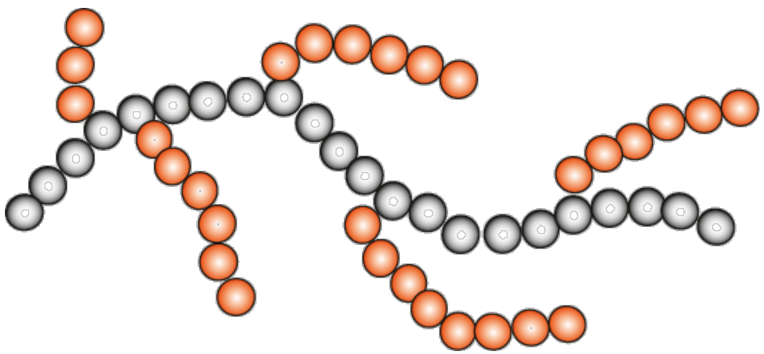
Copolymer with <u>random</u> units



Copolymer with <u>alternating</u> units



Copolymer with <u>block</u> units



<u>Graft</u> copolymers

3. PROPERTIES: CRYSTALLINITY

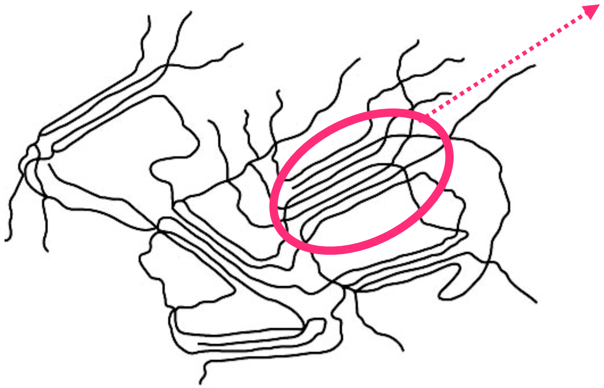
CRYSTALLINITY OF POLYMERS

Packing macromolecular chains in order to produce an atomic arrangement with periodic order .

POLYMER

Amorphous Regions (disordered)

Crystalline Regions (ordered)



Properties = depend on the amount of crystallinity

Crystallization ⇒ ↑ amount of packing

density$_{(\text{crystalline polymer})}$ > density $_{(\text{amorphous polymer})}$

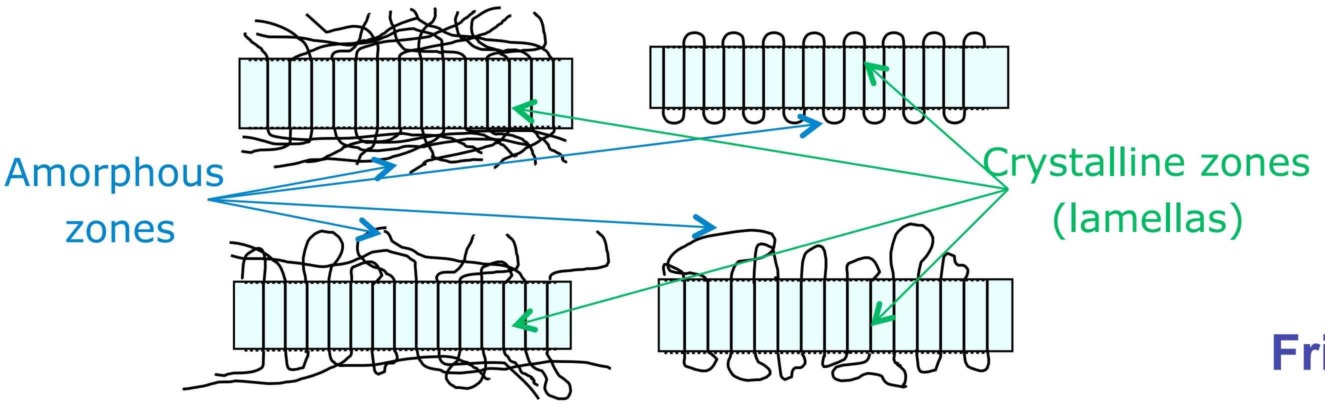
4. SOLID STATE: CRYSTALLINITY

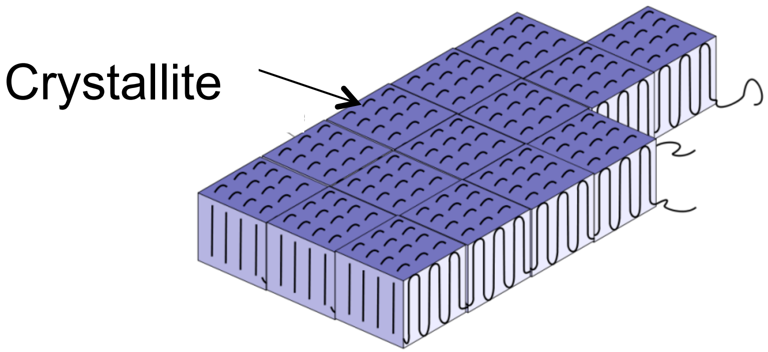
Morphology of the polymeric crystals

✓ **Polymeric monocrystals**

⇒ **Different type of bundles :**

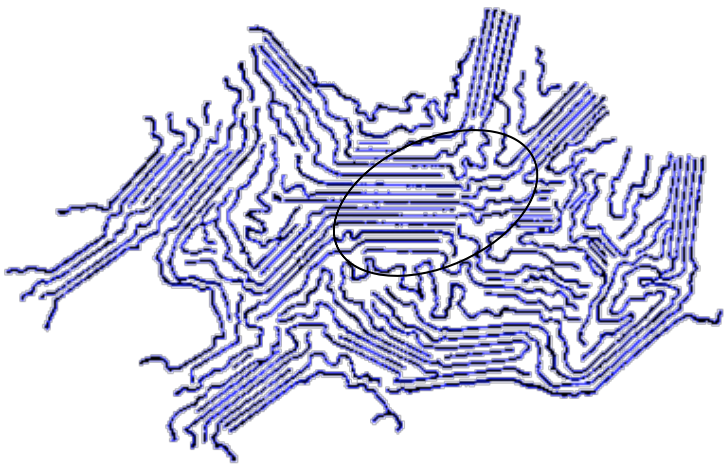
Chain-folded model





Structure of a chain-folded lamina

Fringed-micelle model:

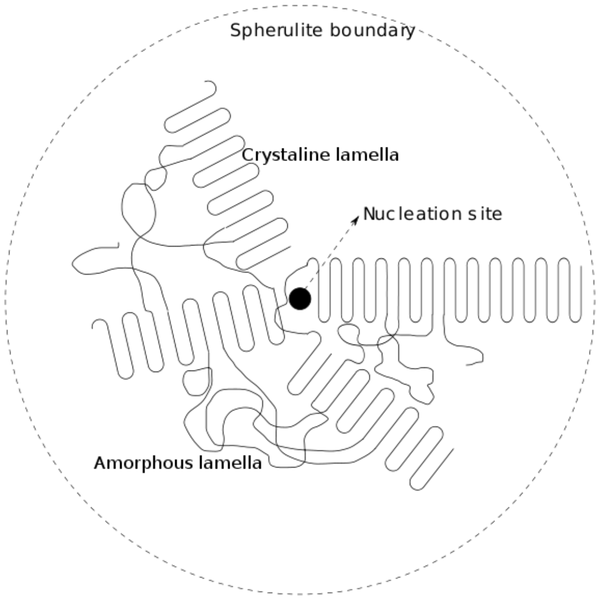


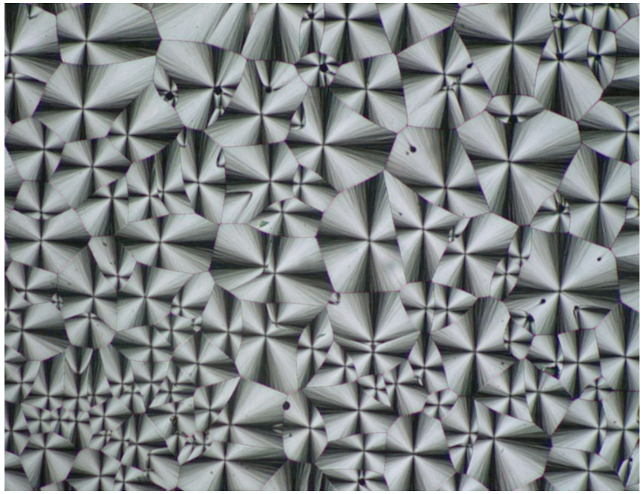
http://commons.wikimedia.org/wiki/File:Lamellenbildung_bei_der_Kristallisation_von_PolymerenEN.svg

4. SOLID STATE: CRYSTALLINITY

The majority of polymers that crystallize from liquids form:

SPHERULITES



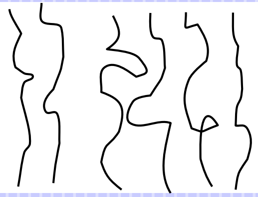


Transmitted polarized light photomicrograph of PE

William D. Callister, Jr., Materials Science and Engineering An Introduction: John Wiley & Sons, Inc.

$$\%\,\text{crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

Crystalline lamina



Crystalline lamina

Interlaminar connections condition the properties of the polymer

ρ_s = actual density of the polymer
ρ_c = density of totally crystalline polymer
ρ_a = density of totally amorphous polymer

4. SOLID STATE: CRYSTALLINITY

FACTORS THAT AFFECT CRYSTALLINITY

1. KINETIC FACTORS

Conditions for Crystallinity:

The number and size of crystals formed = depend on

$\Delta T = T_{melting} - T_{crystallization}$

⇒ Increasing ΔT the size of the crystal decreases and the number of crystals increases

The FLEXIBILITY of the chains depends on the structure:

- **Linear polymers have a greater amount of crystallinity compared to branched polymers**
- **Complex monomeric structures ⇒ decreases the amount of crystallinity**

In order for a polymer to crystallize, its molecules must have sufficient elasticity in order to be able to move and be accurately placed.

4. SOLID STATE: CRYSTALLINITY

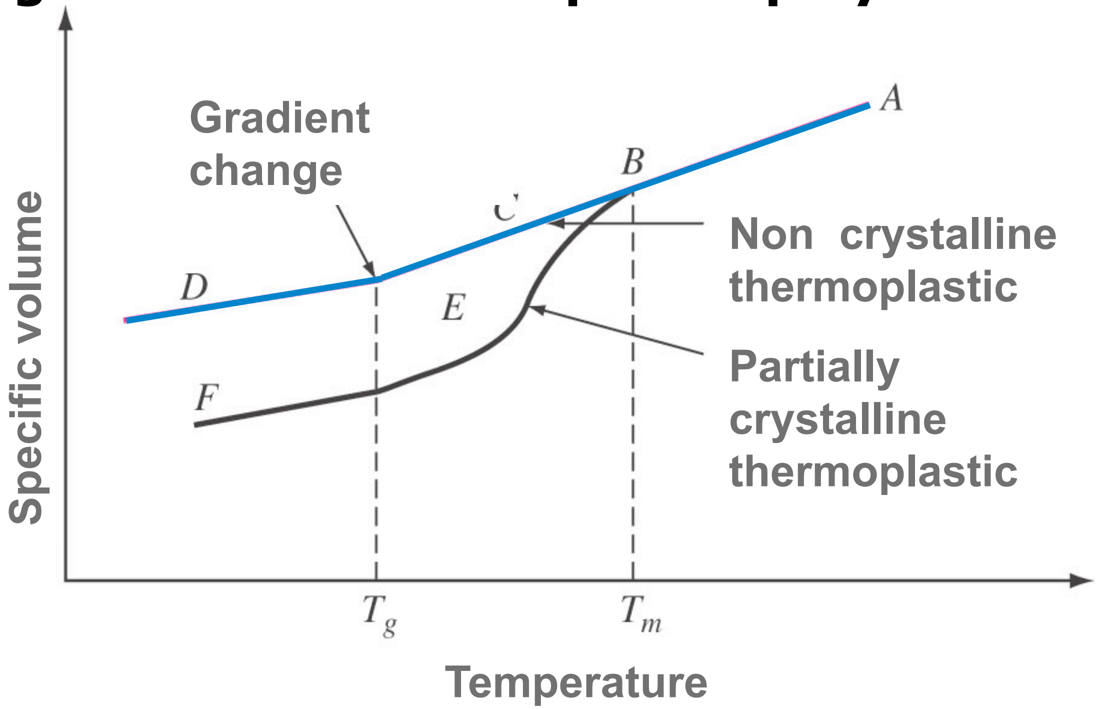
2. STRUCTURAL FACTORS THAT AFFECT CRYSTALLINITY

Greater crystallinity ⇒ greater T_m

- **Symmetry**
- **Tacticity:**
  - **Atactic ⇒ amorphous**
  - **Isotactic, syndiotactic ⇒ crystalline**
- **Branched**
- **Configuration CIS against TRANS**
- **Nº of C pairs in between heteroatoms**
- **Molecular weight**
- **Copolymerization**
- **Plasticisers**
- **Polarity: favours ordering**

4. SOLID STATE: THERMAL TRANSITIONS

Cooling curves for thermoplastic polymers



T_g=Glass transition temperature

T_m=Melting temperature

Non crystalline thermoplastics cool throughout the line ABCD

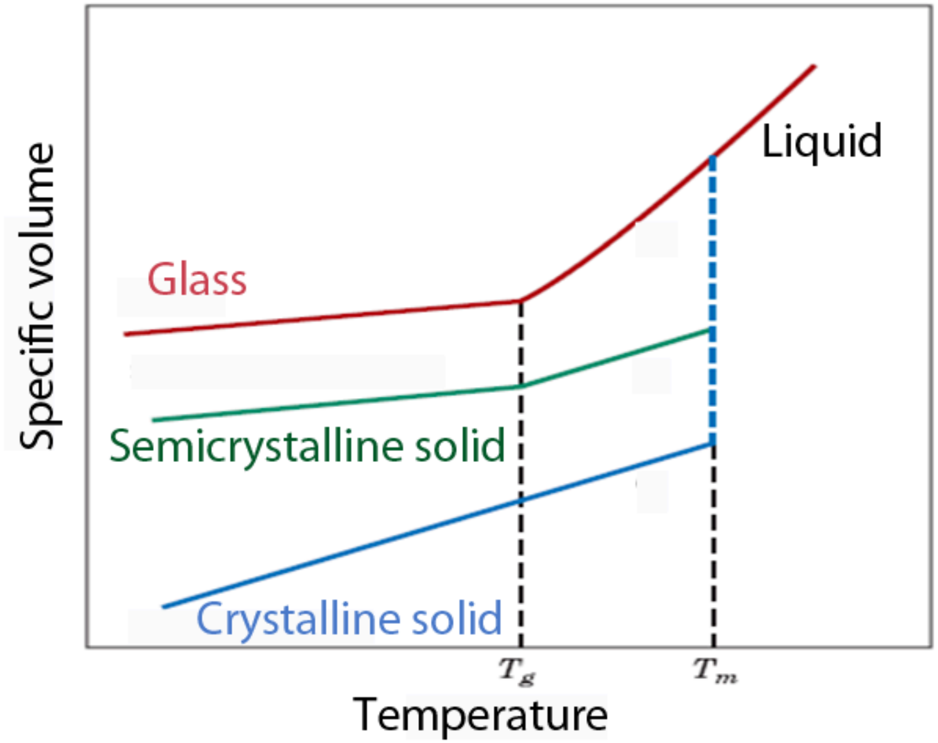
Partially crystalline thermoplastics cool throughout the line ABEF

A= liquid, B=liquid of high viscosity C= undercooled liquid (rubbery)
D= glassy solid

E= solid crystalline regions in matrix of supercooled liquid
F= solid crystalline regions in glassy matrix

4. SOLID STATE: THERMAL TRANSITIONS

Cooling curves for thermoplastic polymers



Specific volume versus temperature upon cooling from the liquid melt for polymers with different structure

4. SOLID STATE: THERMAL TRANSITIONS

Thermal transitions : T_m and T_g

T_m : Melting temperature → crystalline regions

T_g : Glass transition temperature → amorphous regions

Glass transition → changes in the specific heat and the dilatation coefficient

4. SOLID STATE: THERMAL TRANSITIONS

Factors that influence in the T_g

MOLECULAR WEIGHT

Increasing the molecular weight we decrease the mobility of the chains $\Rightarrow \uparrow$ Tg

INTERMOLECULAR INTERACTIONS

Increasing the interactions $\Rightarrow \uparrow$ Kinetic Energy $\Rightarrow \uparrow$ Tg

CHAIN FLEXIBILITY

Greater mobility $\Rightarrow$ Decreases the rotational energy and increases the entropy and decreases Tg

SYMMETRY

Symmetric Molecules present a low dipolar moment and therefore low Tg

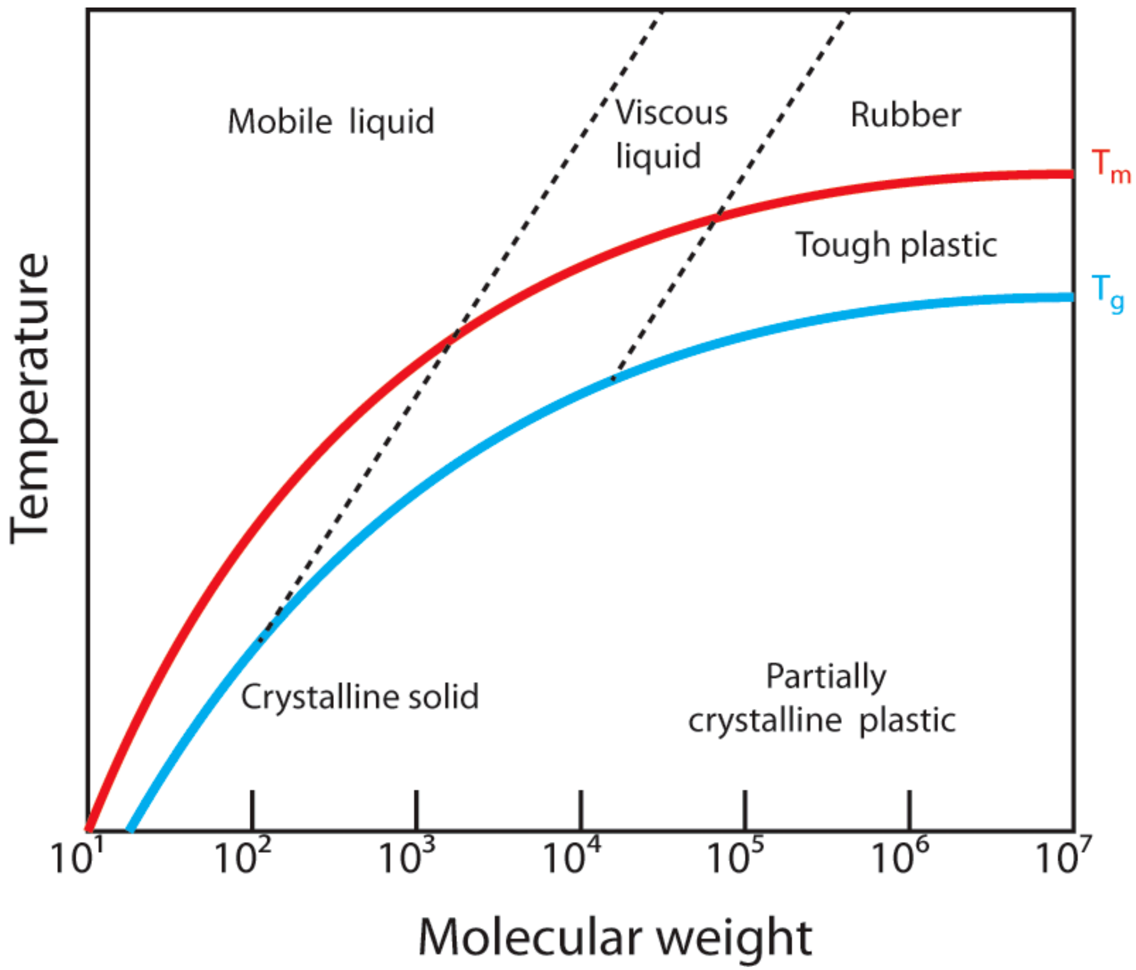
$[-CH_2\text{-}CHX\text{-}]_n$ with X	T_g (ºC)
-H (PE)	-110
$-CH_3$ (PP)	-20
-Cl (PVC)	81
-C≡N (AN)	97
$-C_6H_5$ (PS)	100

4. SOLID STATE: THERMAL TRANSITIONS

Melting and Glass Transition Temperatures for Some of the More Common Polymeric Materials		
Material	**Glass transition temperature (ºC)**	**Melting temperature (ºC)**
Polyethelene (low density)	-110	115
polytetrafluoroethylene	-97	327
Polyethelene (high density)	-90	137
Polypropylene	-18	175
Nylon 6,6	57	265
Polyester (PET)	69	265
Poly(vinyl chlloride)	87	212
Polystyrene	100	240
Polycarbonate	150	265

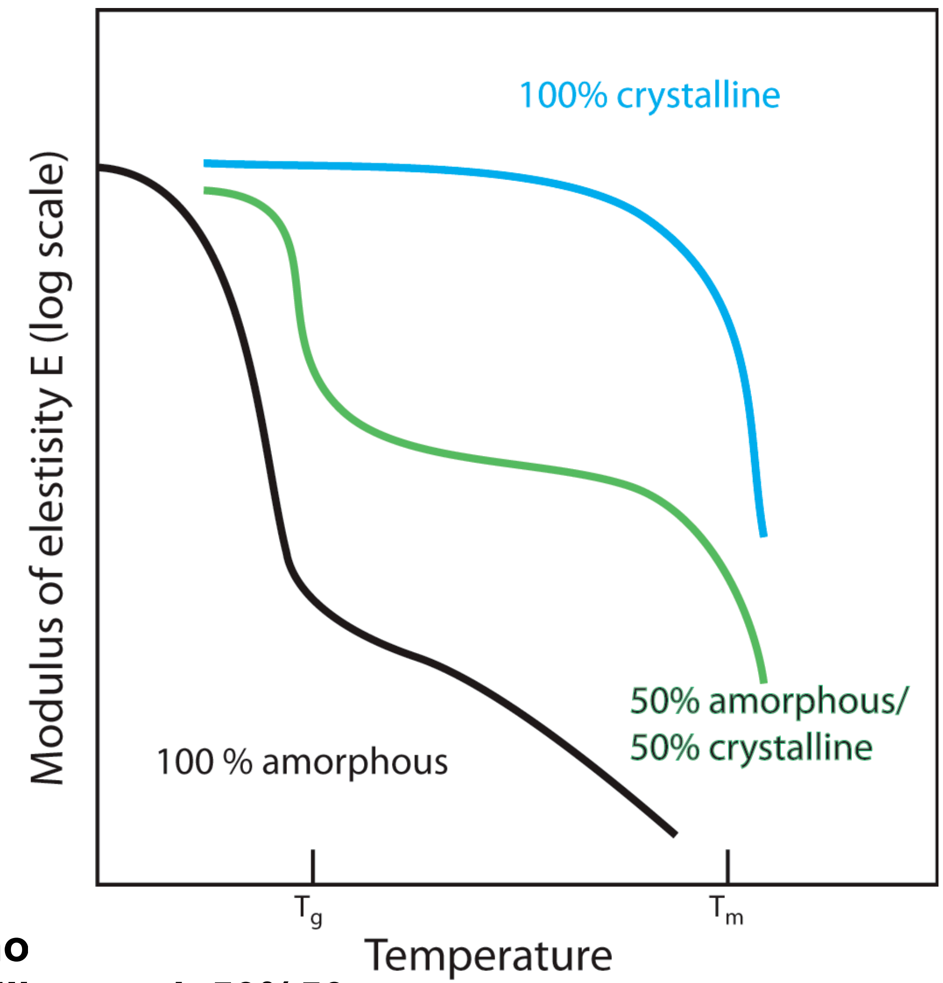
4. SOLID STATE: THERMAL TRANSITIONS

Influence of Molecular Weight



4. SOLID STATE: MECHANICAL BEHAVIOUR

MECHANICAL BEHAVIOUR : Thermoplastic polymers



Behaviour of thermo amorphous, crystalline and 50%50 amorphous/crystalline

4. SOLID STATE: MECHANICAL BEHAVIOUR

MECHANICAL BEHAVIOUR: Thermoplastic polymers

Effect of the crystallinity in the modulus of elasticity: