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Mascara

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معسكر

Faculty of Science and Technology
Mechanical engineering department

Physical-Chemical and Mechanical Properties of Polymers: Course Handout

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For use by Master's and Bachelor's students
in Materials Engineering and Mechanical Construction.

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Preface

Polymers, these materials with myriad applications, are ubiquitous in our daily lives, from food packaging to medical prosthetics, as well as automotive parts and textile fibers. Their significance in numerous industrial sectors cannot be overstated.

This course aims to delve deep into the fundamental characteristics that define polymers, with a particular emphasis on their physical, chemical, and mechanical properties. Understanding these properties is essential for designing materials tailored to specific applications and for developing new innovations in the field of polymers.

We will begin by examining the basics of polymer chemistry, exploring the molecular structure of polymers, the different types of chemical bonds involved, as well as methods of polymer synthesis. We will then focus on the mechanical properties of polymer materials, discussing factors that influence these properties, such as molecular structure, crystallinity, and processing conditions. Additionally, we will cover linear viscoelasticity and rheological models specific to polymer materials. Finally, we will conclude this work by presenting the electrical and dielectric behavior of polymers.

This course is intended for anyone interested in materials science, chemistry, or engineering, as well as those working in sectors where polymers are ubiquitous. Whether you are a student, researcher, or industry professional, we hope this course will provide you with a solid foundation for understanding and manipulating the physico-chemical and mechanical properties of polymers in your future projects.

CONTENTS

Historical

Polymer history spans centuries, but its modern development began in the 19th century with the discovery of synthetic polymers. Here's a brief overview of key milestones:

Early Discoveries: The concept of polymers, long-chain molecules composed of repeated subunits, was observed in natural materials like rubber and proteins. Rubber, derived from the latex of certain plants, was used by ancient civilizations.

- Vulcanization of Rubber (1839): Charles Goodyear accidentally discovered vulcanization, a process that strengthens rubber by heating it with sulfur. This made rubber more durable and opened up new applications.
- Celluloid (1869): John Wesley Hyatt invented celluloid, the first synthetic polymer, as a substitute for ivory in billiard balls. Celluloid is made from cellulose nitrate and camphor.
- Bakelite (1907): Leo Baekeland invented Bakelite, the first synthetic polymer derived from petrochemicals. Bakelite was a versatile material used in electrical insulators, telephones, and various consumer goods.
- Nylon (1935): Wallace Carothers and his team at DuPont developed nylon, the first synthetic fiber, which revolutionized textiles and materials. Nylon stockings became especially popular after their introduction.
- Polyethylene (1933): Reginald Gibson and Eric Fawcett at Imperial Chemical Industries (ICI) discovered polyethylene, a versatile plastic used in packaging, containers, and various applications.
- Polyester (1941): British chemists John Rex Whinfield and James Tennant Dickson invented polyester, a synthetic polymer used in textiles, packaging, and fibers.
- Silicone Polymers (1940s): Eugene Rochow and Richard Müller developed silicone polymers, which have applications in sealants, adhesives, lubricants, and medical devices.
- Discovery of High-Density Polyethylene (HDPE) and Polypropylene (PP): In the 1950s, Karl Ziegler and Giulio Natta independently discovered catalysts for the polymerization of HDPE and PP, respectively. These materials have a wide range of applications in industries such as packaging, automotive, and construction.
- Polycarbonate (1953): Hermann Schnell and Dr. Daniel Fox invented polycarbonate, a transparent and impact-resistant plastic used in eyewear, CDs, DVDs, and automotive parts.
- Discovery of Teflon (1938): Roy Plunkett accidentally discovered polytetrafluoroethylene (PTFE), commonly known as Teflon, while working for DuPont. Teflon has non-stick properties and is used in cookware, industrial applications, and as a lubricant.

Polymer Chemistry Advancements: Throughout the 20th century and into the 21st century, significant advancements were made in polymer chemistry, leading to the development of new materials with enhanced properties, such as biodegradable polymers, conductive polymers, and polymers with specific functionalities for various applications. These milestones illustrate the evolution and significance of polymers in modern society, impacting industries ranging from textiles and consumer goods to electronics and healthcare.

Part-I: Structures of polymers and their classifications

I.1 Major classes of materials

I.1.1 Classification according to atomic order

Materials can be divided into two classes, depending on their crystalline or amorphous state:

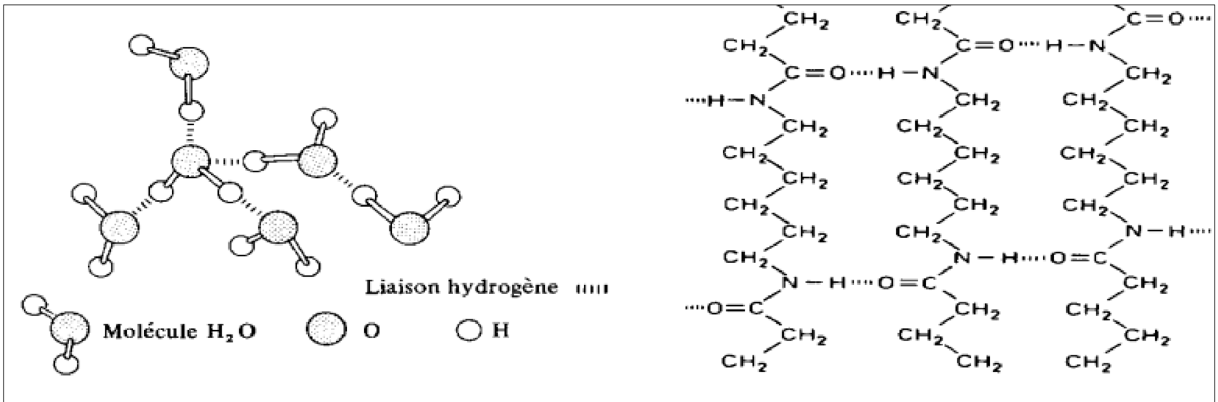
1. **Crystalline materials:** Atoms are regularly arranged in a three-dimensional lattice (14 distinct lattice types, braver lattice).
2. **Amorphous state:** the atoms are placed irregularly with respect to each other, so that it is possible to build no network at a great distance.

I.1.2 Classification according to type of atomic bond

1. **Ionic bonding**: example, sodium chloride ($Na^+ cl^-$), these two ions having an opposite charge that attracts, this interaction between these two charged particles is called ionic bonding. The energy of the ionic bond varies between 600 and 1500 kg/mol, hence the ionic materials are hard and brittle materials, their melting temperature is very high, these materials are bad as current and temperature conductor.
2. **Covalent bond:** Let's take the example of carbon, this atom has four electrons on its Valence layer. When crystallized in diamond form, each atom is surrounded by four close neighbors, so that it is surrounded by eight electrons, four of which are ready for it. This type of bond is called covalent bonds. Covalent bond: Let's take the example of carbon, this atom has four electrons on its Valence layer. When crystallized in diamond form, each atom is surrounded by four close neighbors, so that it is surrounded by eight electrons, four of which are ready for it. This type of

bond is called covalent bonds. The main characteristics of the covalent bond are as follows:

- It is only done in fixed directions of space.
- Its binding energy can be very high, as in the case of diamond which has a melting temperature close to 355°c. It is possible that it is very weak, like bismuth.
- These covalent materials are very poor conductors of current and heat.



rappel : liaisons Van der Waals

liaisons VdW entre des chaînes de polyamide 6-6 (nylon)

3. **Metal bonding:** In this type of bonding, called metal bonding, the external electrons are shared by all the atoms so that they can no longer be associated with a single atom. Metal bonding: In this type of bonding, called metal bonding, the external electrons are shared by all the atoms so that they can no longer be associated with a single atom. The main characteristics of the metal bond are as follows:

- It applies in all directions of space;
- A high quality of thermal conductivity due to free electrons.

4. **Secondary binding:** Low energy, less than 45 kg /mol. These are two molecules which, although generally neutral.

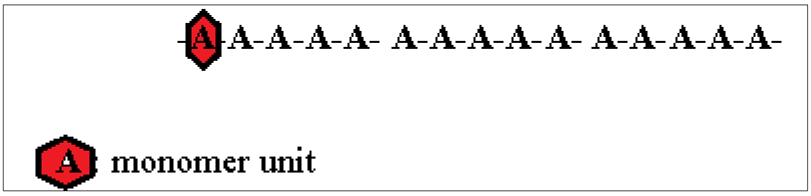
I.1.3 Classification according to behaviour

- Metals and their alloys ;
- Ceramics ;
- Organic polymers.

I.2 Macromolecule concepts

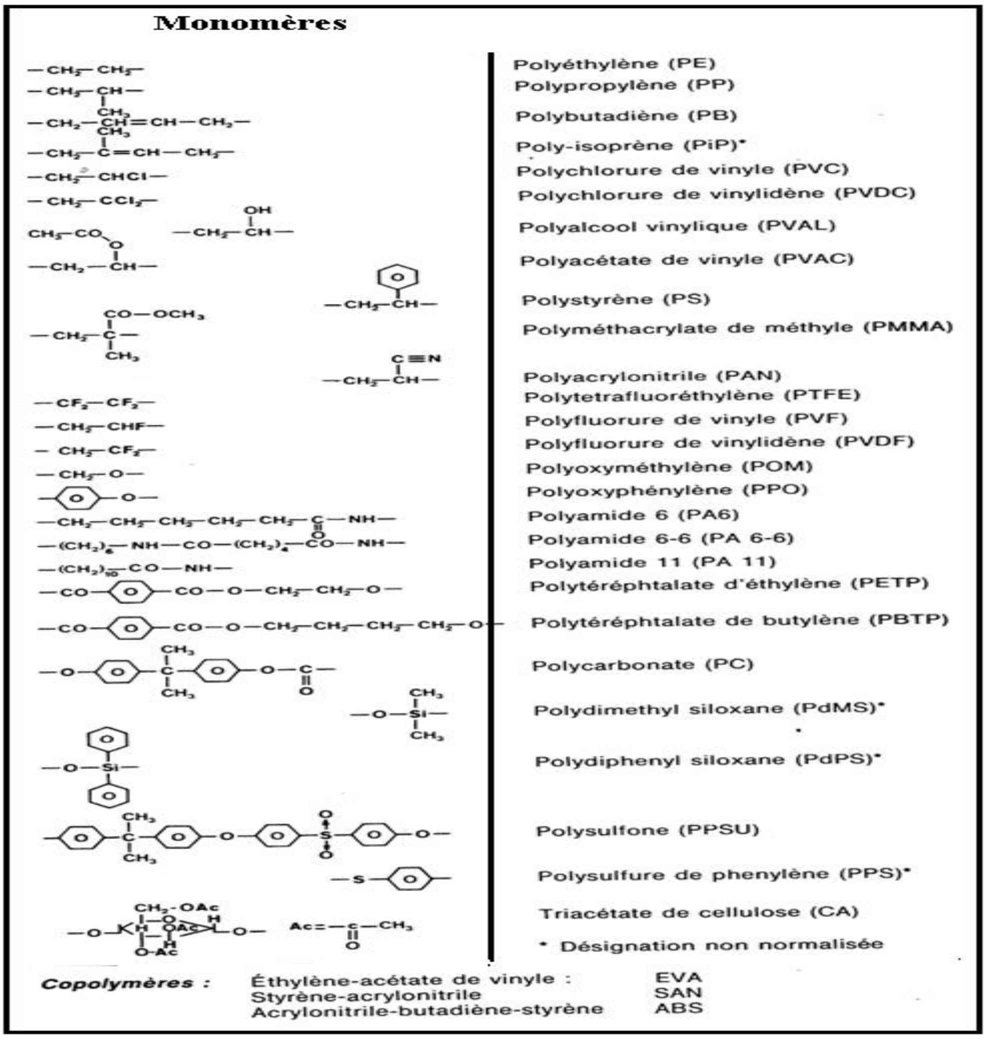
I.2.1 Definition

A polymer is a material composed of long molecular chains called macromolecules. A macromolecule is a molecule resulting from the covalent linking of monomer units.



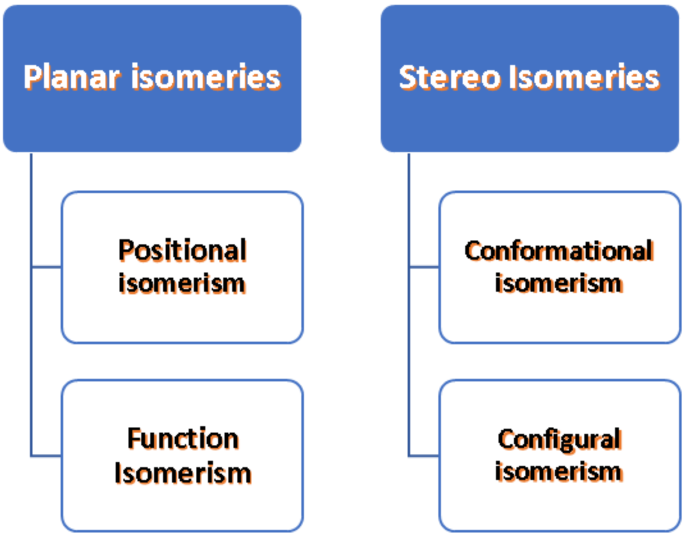
By convention, the molar mass of a macromolecule is greater than 5000 g. Organic polymers are made from monomer units composed of elements specific to organic chemistry (C, H, O, N, Cl, F, S, etc.). A homopolymer is a polymer containing only one type of monomer; in cases where there are several, it is called a copolymer.

I.2.2 Different types of macromolecules



I.3 Reminders on isomerism

Two molecules are isomers when there is the same composition with different properties.

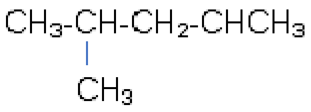


I.3.1 Position Isomerism

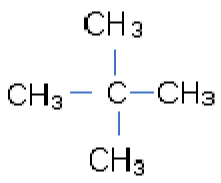
C_5H_{12}

These three molecules have the same composition and different properties.

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$ **(1)**


$$\underset{\displaystyle CH_3}{CH_3\text{-}\underset{|}{CH}}\text{-}CH_2\text{-}CHCH_3$$

(2)


$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$$

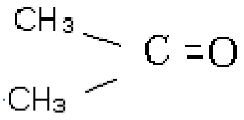
(3)

I.3.2 Function Isomerism

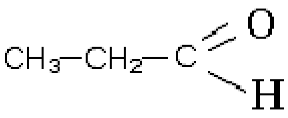
C_3H_6O

These molecules have different behaviors associated with dissimilar functions.

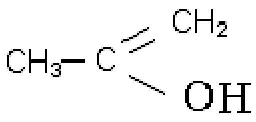
Acétone



Propanol

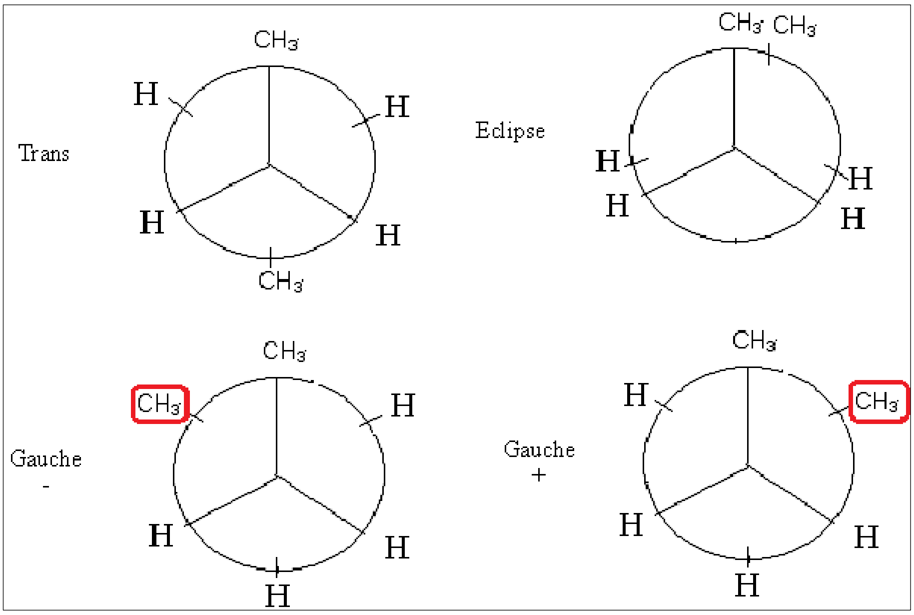


Propénal- 2



I.3.3 Conformational isomerism

The term conformation refers to all special arrangements caused by rotation around the sigma link alone.



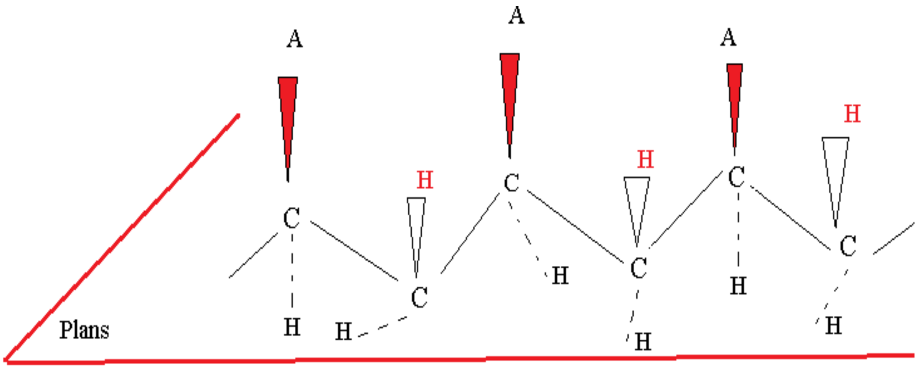
Newman representation of different conformations of the molecule.

In the case where there is a small difference in potential energy between the different conformations, the chain is said to have a statistical conformation. Otherwise, the conformation is said to be regular. A planar Trans-conformation: the skeleton of the macromolecule is in a plane, following a straight line.

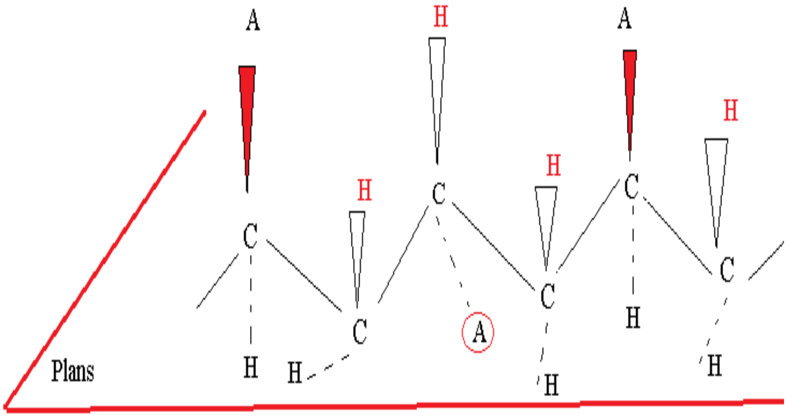
I.3.4 Configural isomerism

Configurational means that the different spatial arrangements that a molecule can have.

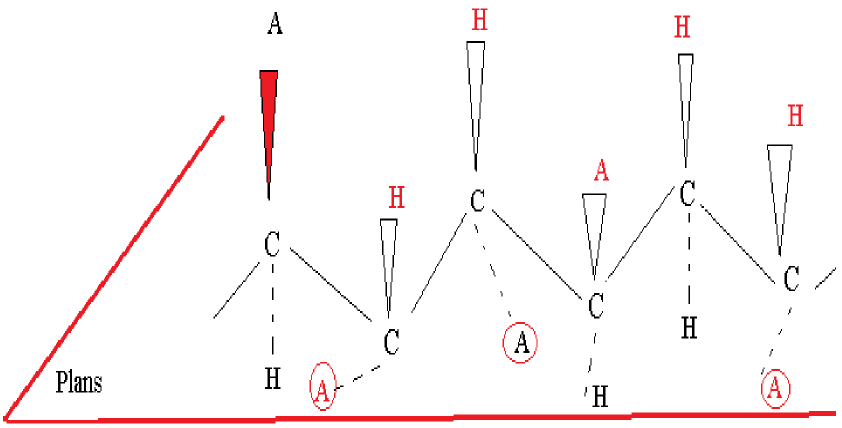
- A polymer is said to be isotactic when all substitutions are on the same side of the plane formed by the carbon skeleton.



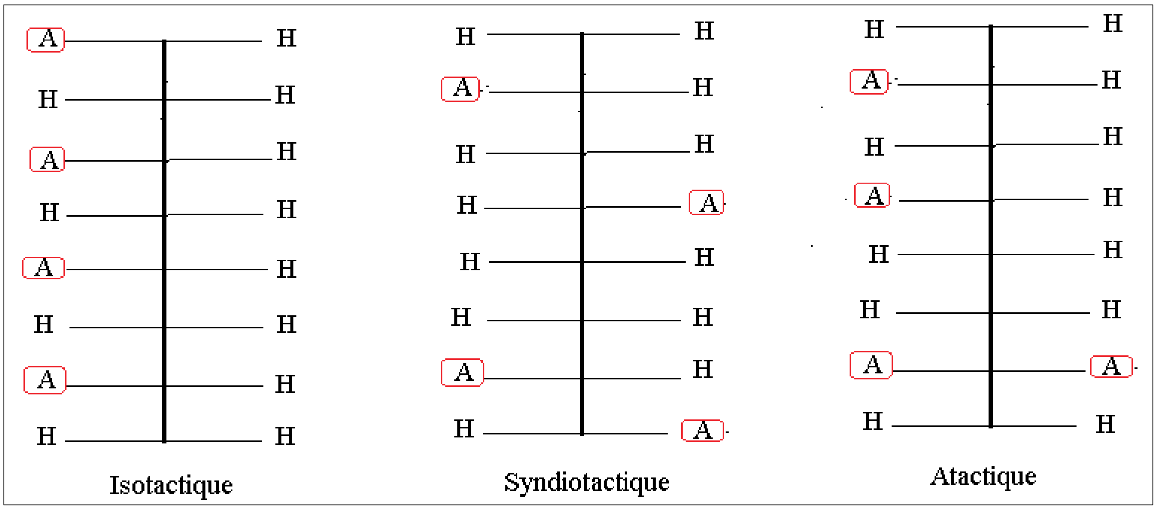
- A polymer is said to be syndiotactic when all substituents are alternated.



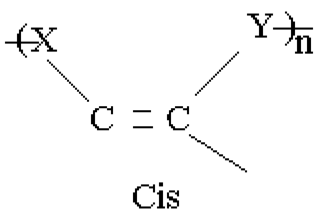
- A polymer is said to be atactic when the distribution of side groups along the chain is random.

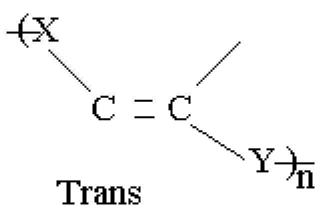


Another way to illustrate the configurational isomerism can be proposed:



I.3.5 Cis-Trans Isomerism

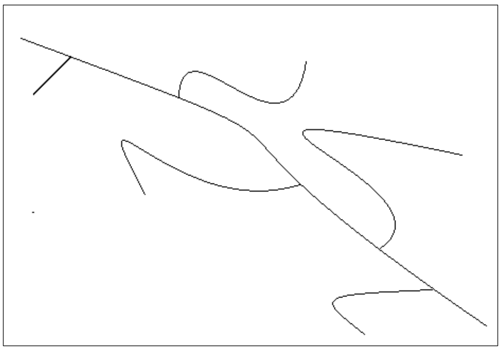




I.4 Special architects

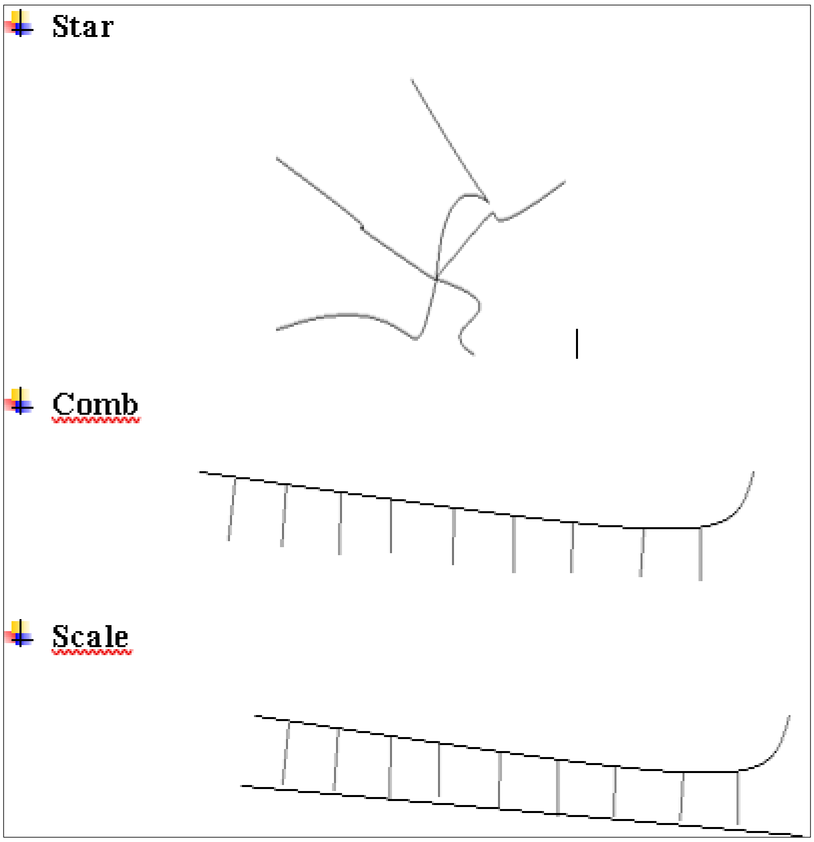
I.4.1 Ramified Polymers

It can be said that branched polymers have different characteristics than perfectly linear polymers, so branching decreases crystallinity and lowers melting points.



Example: starch and polyethylene.

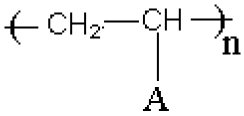
It should be noted that branched polymers can take several forms.



I.5 Sequencing of units

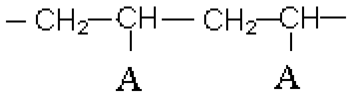
I.5.1 Homopolymers

Example: Vinyl



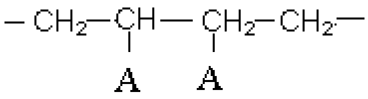
$$\left(CH_2-\underset{A}{\underset{|}{CH}} \right)_n$$

There are several types of linking in polymers, namely head to tail (a), head-to-head (b), and tail to tail (c), as illustrated in the figures below.



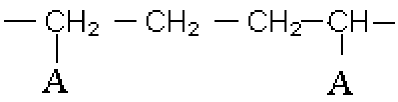
$$-CH_2-\underset{A}{\underset{|}{CH}}-CH_2-\underset{A}{\underset{|}{CH}}-$$

(a)



$$-CH_2-\underset{A}{\underset{|}{CH}}-\underset{A}{\underset{|}{CH_2}}-CH_2-$$

(b)

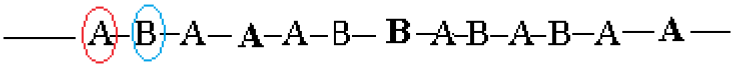


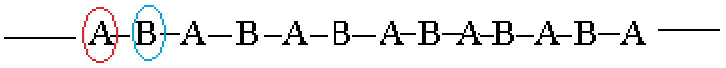
$$-\underset{A}{\underset{|}{CH_2}}-CH_2-CH_2-\underset{A}{\underset{|}{CH}}-$$

(c)

I.5.2 Copolymers

The copolymers are polymers resulting from the polymerization of two monomers. The most common copolymers are random copolymers (A and B are statistically distributed along the chain).





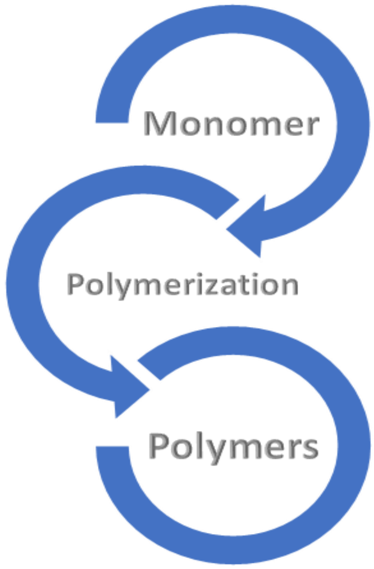
Alternating Copolymers

_ AA......AA-BB.....AA........AA-BB.........BB-

Linear copolymers

I.6 Synthesis of polymers

The synthesis of polymers involves polymerization reactions, which consist of associating the repeating units with covalent bonds.



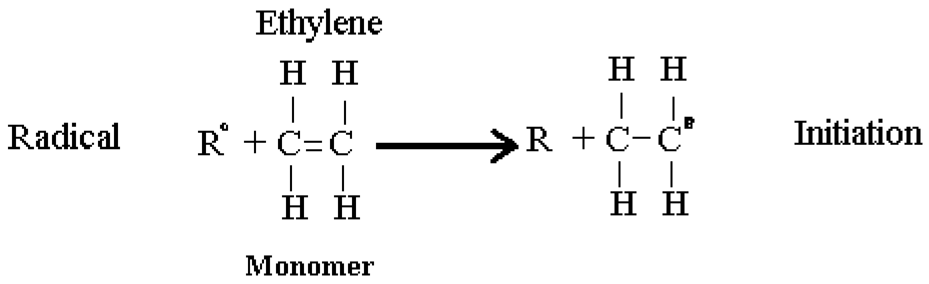
I.7 Synthesis method

There are three ways:

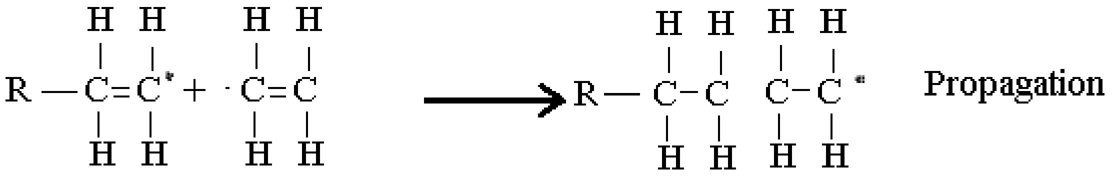
- Polymerase Chain Reaction (PCR),
- Step polymerization reaction (Polycondensation),
- By chemical modification of another polymer.

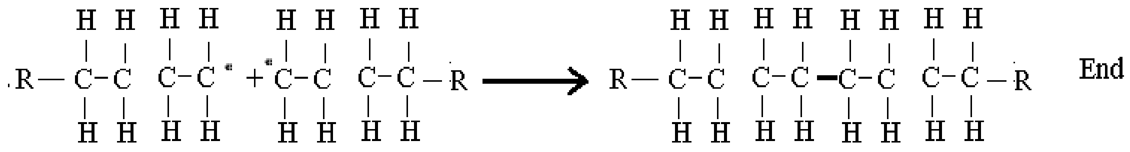
I.7.1 Chain polymerization reaction (Polyaddition)

- **Radical Polymerization**



$$R^{\bullet} + \underset{H\quad H}{\overset{H\quad H}{C=C}} \longrightarrow R + \underset{H\quad H}{\overset{H\quad H}{C-C^{\bullet}}}$$


$$R-\underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}}{}^{\bullet}+{}^{\cdot}\underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}}\longrightarrow R-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}\;\;\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}{}^{\bullet}$$


$$.R-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}\;\;\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}{}^{\bullet}+{}^{\bullet}\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}\;\;\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\dot{R}\longrightarrow R-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}\;\;\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}\;\;\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\dot{R}$$

So, the general form of addition polymerization is:

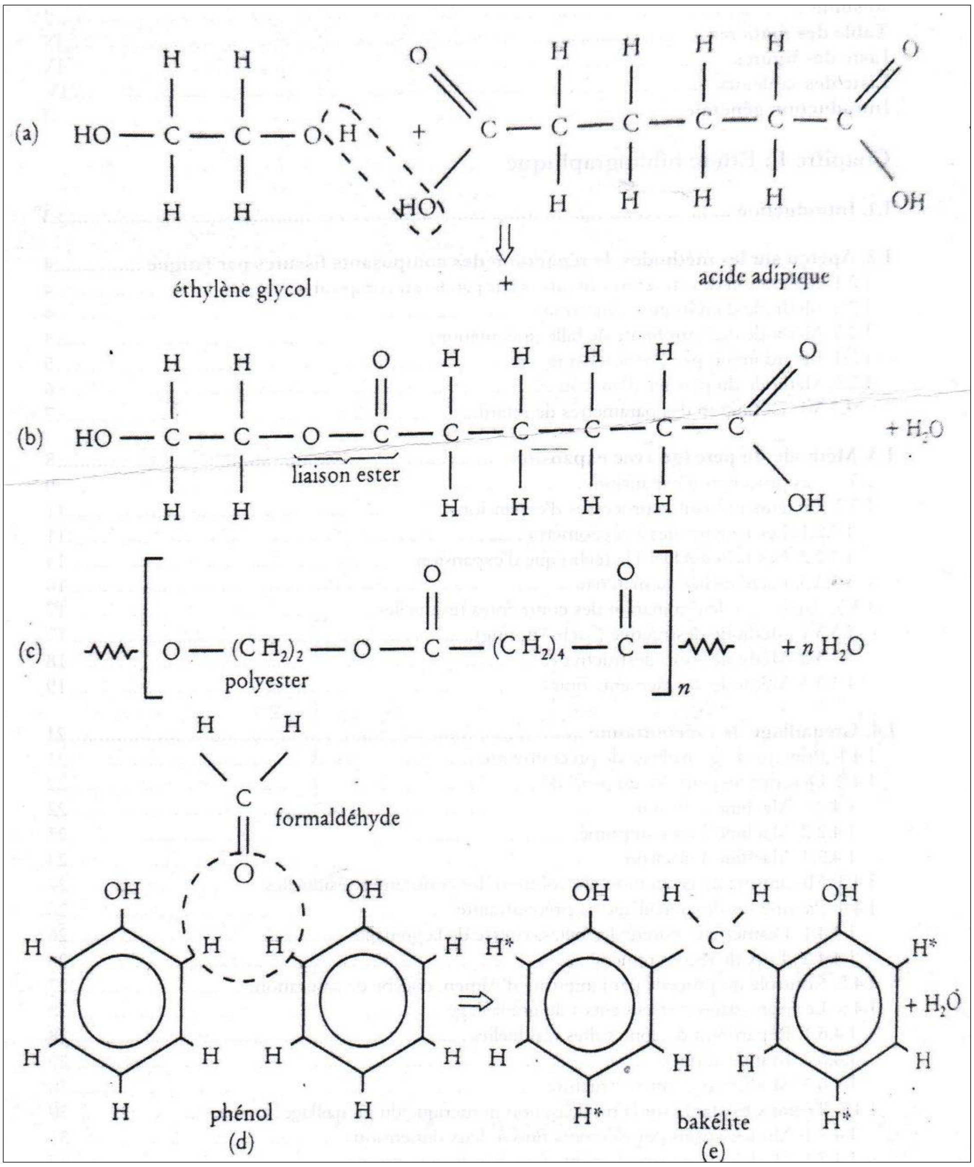
$$nCH_2=CH_2 \longrightarrow -\!\left(CH_2-CH_2\right)_{n}\!-$$

I.7.2 Stepwise polymerization reactions (Polycondensation)

A stepwise synthesis is the reaction of two different products to form a third one, accompanied by a by-product. The general form of this reaction is of the following form:

$$A+B \longrightarrow \text{Polymer} + \text{By-Product}$$

Example of condensation polymerization reactions: a), b), and c) condensation polymerization of polyester; d) and e) condensation polymerization of bakelite.



I.8 Macromolecular arrangement

Cohesion of macromolecular systems

There are three types of intermolecular interaction:

- Van der Waal interaction ;
- Hydrogen interaction or no hydrogen bridges;
- Ionic interaction.

a) **Van der Waal interaction: These** are weak bonds whose energy is always proportional to (r $^{-}$6) (r is an inter-dipole distance).

b) **Hydrogen or hydrogen bridge interaction: These** are bonds of electrostatic origin. They are established between a hydrogen atom linked to a strongly electronegative atom (F, O, N...), and a second electronegative atom is joined to another carbon atom.

c) **Ionic Interaction:** These interactions are due to electrostatic attraction and repulsion between ions.

I.9 Polymer classifications

There are several ways to classify polymers:

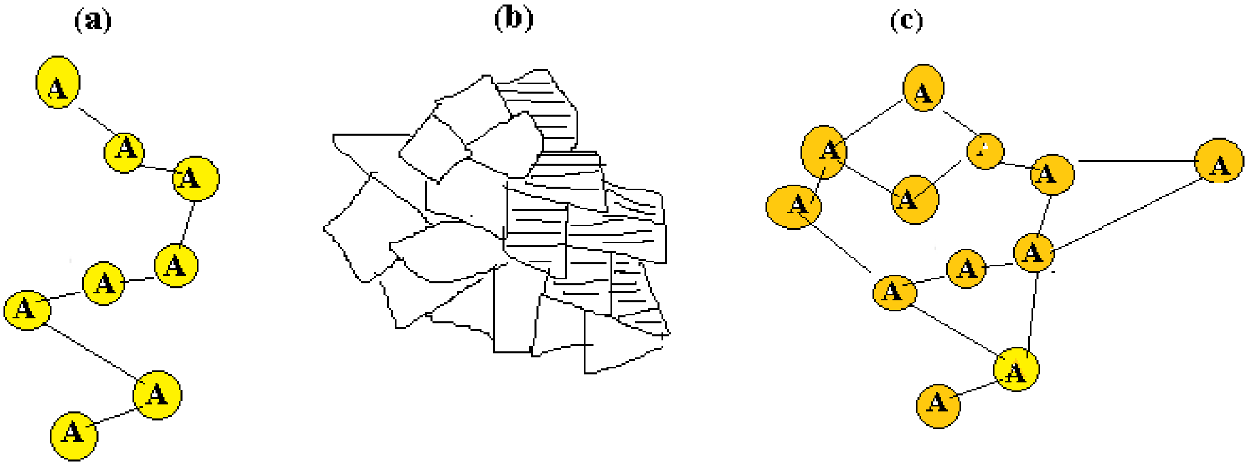
I.9.1 classification according to origin

- Natural polymers ;
- Artificial polymers,
- Synthetic polymers.

I.9.2 Classification according to the architect

we find three types of compounds

- Linear (sequence in one direction,
- Two-dimensional (sequence in two directions),
- Three-dimensional (it is possible to transform linear molecules into 3D molecules by bridging).



I.9.3 Classification according to properties

This classification is the most used because the physico-chemical and mechanical properties of materials are directly related to the macromolecular structure of polymers and because of the choice of an industrial application.

I.10 Polymer families

The three families of polymers are:

- Thermoplastic polymers ;
- thermosetting polymers ;
- Elastomers.

I.10.1 Thermoplastic polymers

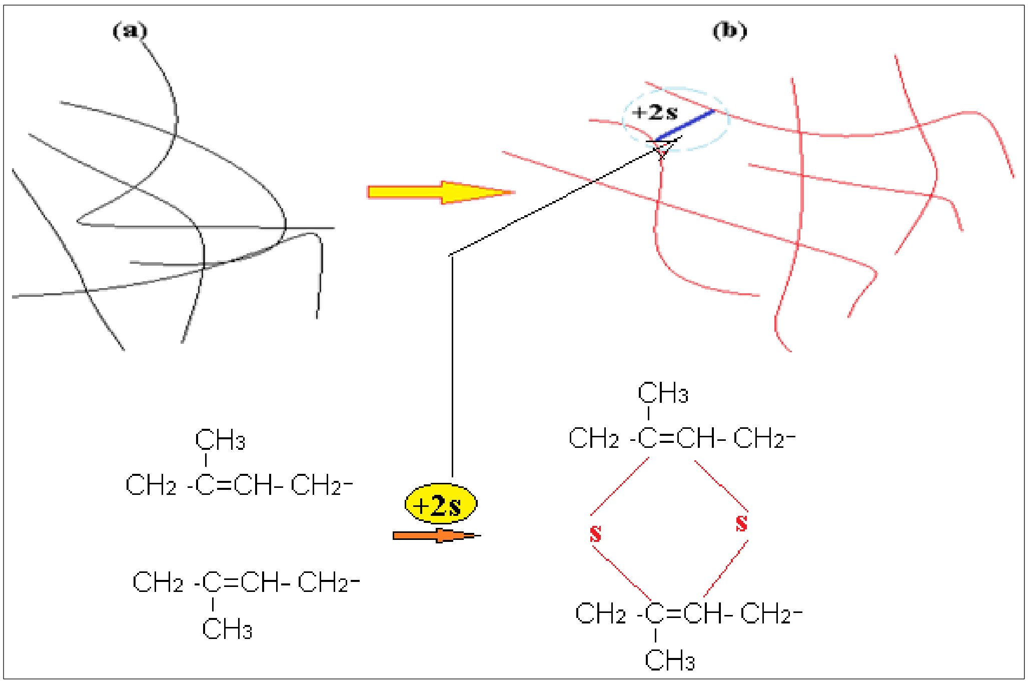
They consist of macromolecules of limited linear or branched size. The term thermoplastic refers to all polymers whose lateral cohesion is only provided by secondary bonds (Van Der Waal, hydrogen, etc.).

I.10.2 Thermosetting

They are highly crosslinked; the rate of crosslinking is 10 to 100 times higher than in elastomers.

I.10.3 Elastomer

They are initially formed by linear polymers with weak secondary bonds; they are extremely viscous. They are carried out by bridging between the chains to have a very dimensional structure, which is known as an extension operation.



Diagrams of the extension operations before and after bridging.

Exercises

Exercises I-1

Indicate whether the following statements are true or false.

1. Bulky side groups along linear macromolecule chains increase polymer rigidity.
2. For a degree of polydispersity of 1, the number-average and mass-average molar masses are equal.
3. A linear polymer chain's skeleton contains double bonds (C=C), making it more flexible.
4. Vulcanization involves creating covalent bonds between linear chains.
5. Polymers provide good electrical insulation.
6. Linear chains crystallize more easily with an atactic arrangement of side groups.

Exercise I-2

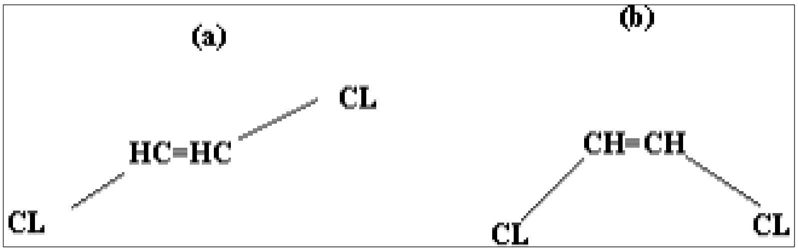
Either a sample of polymer having the following sequence:

………….-CF2-CF2-CF2- CF2-CF2-CF2- CF2-…………………

1. Identify the Teflon pattern?
2. What is Teflon's synthesis equation?

Exercise I-3

The empirical formula for this monomer is « $C_2H_2CL_2$ ».



- What do the two monomers (a, b) represent?

Exercise I-4

A polymer with an average molar mass of 51.8 g/mol has a polymerization index of $1.85x10^{-3}$.

- Deduct the molar mass of its monomer.

Exercise I-5

Either a polymer with an average molecular mass of 63,000 g/mol or a monomer with a molar mass of 42 g/mol.

- Determine its polymerization index ?

Exercise I-6

Some laboratory staff use a woven polypropylene gown.

1. Is it a natural, artificial or synthetic fibre?
2. What is the pattern of the following macromolecule?
3. Deduct the formula and name of the monomer?
4. Write the equation of the polymer formation reaction?
5. What is the type of reaction?
6. What does your "n" call?
7. The average molar mass of this polymer is 84g/mol, deduce the degree of

I.11 Polymer structure

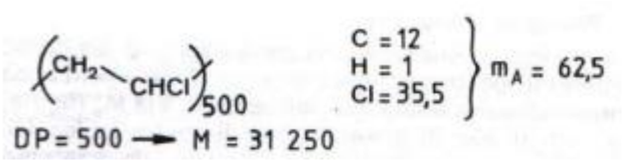
I.11.1 Statistical tools for characterizing a polymer sample

I.11.1.1 Dimensions of macromolecules

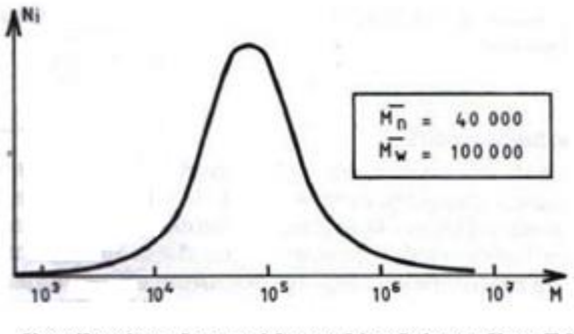
After studying regular or irregular chains and their linking modes, we will consider whole chains and study the characteristics that justify the name macromolecule. The mechanical properties, the characteristic transitions of the amorphous state, the melting of the crystalline zones, the rheological properties in the molten state for example, are to varying degrees influenced by the length of the chains.

I.11.1.2 Definition of a macromolecular chain

Either a macromolecular chain comprising **i** monomers **A** of molecular mass **mA**. Its degree of polymerization is DP_i. Its molecular weight is **$M = i \times m_A$** (see figure below. In fact, industrial polymerizations lead to a mixture of species of different molecular weights, so we must talk about average molecular weight and molecular weight distribution.



In fact, industrial polymerizations lead to a mixture of species of different molecular weights, we must then speak of average molecular weight and molecular weight distribution (fig. 1).



distribution des poids moléculaires d'un PS

For a sample of 1 g, "N_i" is the number of macromolecules of mass $\mathbf{M_i = i \times m_A}$. A certain number of average magnitudes are defined:

$\overline{DPn}$: Average degree of polymerization by number.
$\overline{Mn}$: Average molecular weight by number.
$\overline{DP_w}$: Average degree of polymerization by weight.
$\overline{M_w}$: Average molecular weight by weight.

I.11.2 Molar and weight fraction

"Ni" defined the number of macromolecules of molecular mass "M_i", the total number of macromolecules in the sample is determined by the following relationship:

$$N = \sum_{i=1}^{\infty} N_i \tag{1}$$

Xi fraction in number of macromolecular chains

$$\chi_i = \frac{N_i}{N} = \frac{N_i}{\sum N_i} \tag{2}$$

- *Mass "W_i" of macromolecular chains*

$$W_i = N_i \times M_i \tag{3}$$

- *Total mass "W" of macromolecular chains*

$$W = \sum_{1}^{\infty} w_i = \sum_{1}^{\infty} N_i \times M_i \tag{4}$$

- *Mass fraction of mass chains Mi*

$$\vec{W} = \frac{wi}{W} = \frac{wi}{\sum_{1}^{\infty} N_i \times M_i} \tag{5}$$

I.11.3 Number and weight average molecular weight

- **number average molecular weight**

The number average molecular weight Mn is the total mass of all macromolecules in a sample divided by the total number of macromolecules in the sample.

$$\bar{M}_n = \frac{W}{N} = \frac{\sum_1^\infty wi}{N} = \frac{\sum_1^\infty N_i \times M_i}{\sum_1^\infty N_i} \tag{6}$$

$$\bar{M}_n = \sum_1^\infty \chi_i \times M_i \tag{7}$$

- **weight-average molecular weight**

$$M_w = \frac{\sum_1^\infty w_i \times M_i}{W} = \frac{\sum_1^\infty N_i \times M^2{}_i}{\sum_1^\infty N_i \times M_i} \tag{8}$$

I.11.4 The average degree of polymerization

The number-average degree of polymerization is equal to the ratio of the total number of monomers that the macromolecules belong to.

$$DP_n = \sum_1^\infty i \times \chi_i = \frac{\sum_1^\infty i \times N_i}{\sum_1^\infty N_i} \tag{9}$$

I.11.5 Number and weight average molecular mass

- By number : $\bar{M}_n = M_0 \times DP_n$ (10)

- By weight: $\bar{M}_w = M_0 \times DP_w$ (11)

A sample is characterized by a more or less wide distribution of molecular weights and is more or less polydisperse. Polymers with an infinitely narrow distribution (homodisperses) exist in biology but not in the field of industrial polymers. The polydispersity can be characterized by the following ratio:

$$P = \frac{\bar{M}_w}{\bar{M}_n} \tag{12}$$

When the sample is homodisperse, we have P = 1. P, depends on the synthesis conditions. In anionic polymerization, we can have $1 < P < 1.1$. Radical polymerization of PVC generally leads to P= 2, as does polycondensation. On the other hand, the polymerization of ethylene can lead to P> 10, that is to say to a distribution covering several decades of molecular weight.

Exercises

Exercise I-7

We consider a polymer sample consisting of two monodisperse families composed respectively of eight chains with a mass of 1000 g/mol and two chains with a mass of 10^5 g/mol.

1. Calculate the number and mass fractions of the two families?
2. To give feedback

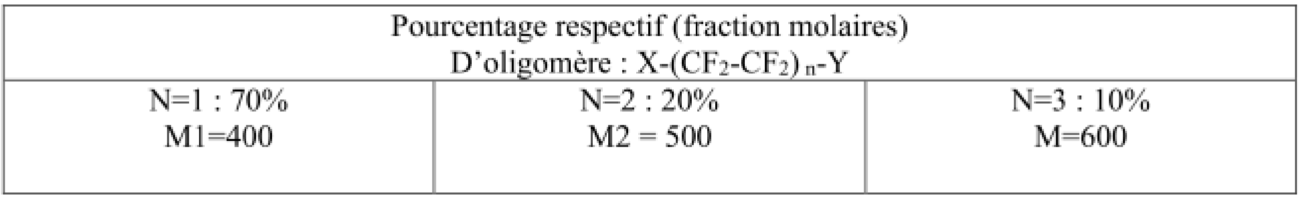
Exercise I-8

Two monodisperse polymers of mass 10^3 g/mol and 10^5 g/mol are considered, which are mixed in an equimolar and equilibrium manner.

1. Calculate the number and mass fractions of the two cases?
2. Calculate the number and mass average molar mass of the mixture?

Exercise I-9

An experimental study carried out at 175°C provides the following molar fraction distribution for different oligomeric short chain polymers.

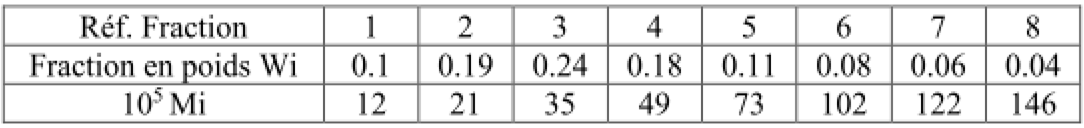


Pourcentage respectif (fraction molaires) D'oligomère : X-$(CF_2\text{-}CF_2)_n$-Y		
N=1 : 70% M1=400	N=2 : 20% M2 = 500	N=3 : 10% M=600

1. Define and give the numerical expression of the number and weight average molar mass of the polymer obtained?
2. Determine the polymerization index of the polymer obtained?

Exercise I-10

A polystyrene sample is subjected to fractional precipitation. The eight recovered fractions are assumed to be monodispersed. The characteristics of each fraction are reported in the following table:



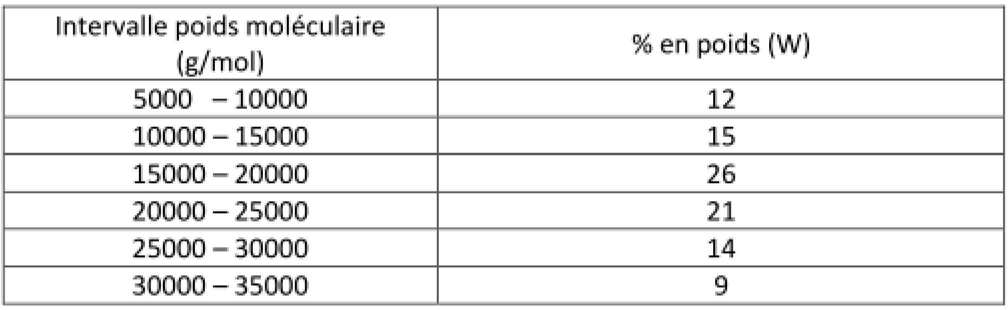
Réf. Fraction	1	2	3	4	5	6	7	8
Fraction en poids Wi	0.1	0.19	0.24	0.18	0.11	0.08	0.06	0.04
10^5 Mi	12	21	35	49	73	102	122	146

1. Calculate the number and mass average molar mass of the sample?

Exercise I-11

A sample of polyvinyl chloride (PVC) analyzed by chromatography; the results obtained are presented in the following table:

We give M_0 =62.5 g/mol



Intervalle poids moléculaire (g/mol)	% en poids (W)
5000 – 10000	12
10000 – 15000	15
15000 – 20000	26
20000 – 25000	21
25000 – 30000	14
30000 – 35000	9

1. Calculate the number and mass average molar mass of the sample?
2. Determine the polydispersity of this sample?

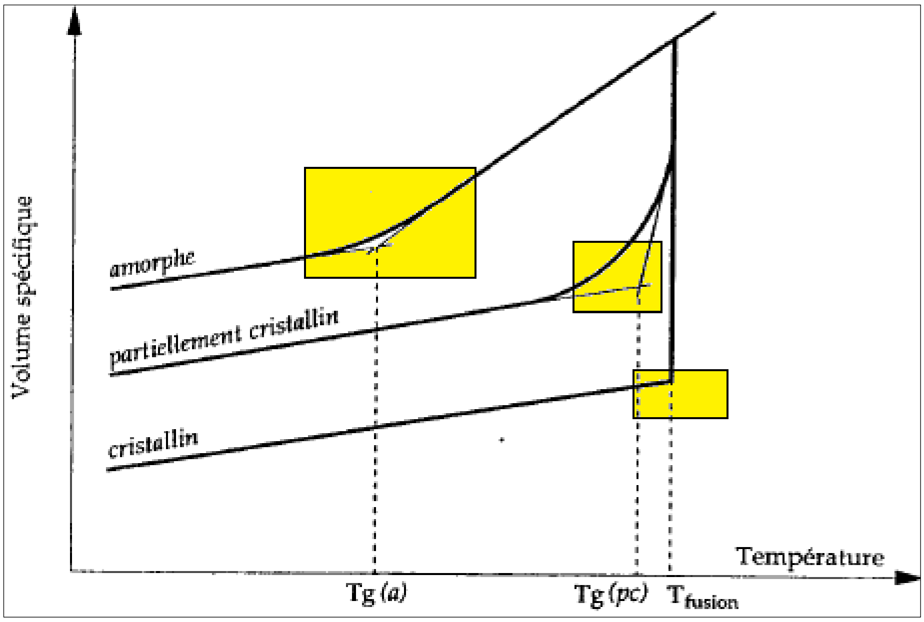
I.12 Glass Transition Temperature

For polymers in general, there is a temperature (T_g) that delineates a boundary between two fundamental states.

- A rubbery state refers to a soft, viscous liquid at high temperatures.
- A glassy state is hard and brittle at low temperatures.

The influence of temperature on the physical properties of polymers is typically studied from high to low temperatures. The glass transition temperature is a boundary phenomenon that was first observed in elastomers, such as natural rubber. Subsequently, it was identified in thermoplastic polymers. The transition is more noticeable when the material is amorphous; in a partially crystalline polymer, only the amorphous part is affected by the glass transition temperature. This temperature can be illustrated by the variation of specific volume as a function of temperature, as shown in the figure below

(Variation of specific volume as a function of temperature for an amorphous, partially crystalline, and crystalline polymer).



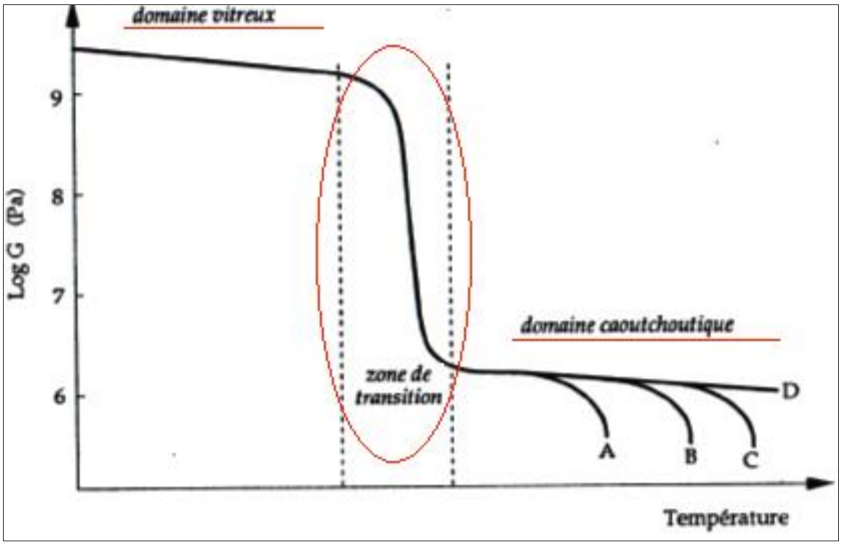
For a completely amorphous polymer, there is a clear change in slope. By convention, the glass transition temperature corresponds to the intersection of the two slopes. However, when the polymer is completely crystalline, there is no marked change in slope until the melting point. Therefore, there is no glass transition temperature for a crystalline polymer. For partially crystalline polymers, there is a variation that falls between the characteristics of amorphous and crystalline polymers. The glass transition marks a sudden change in many physical properties of the material, such as mechanical, optical, dielectric, and thermal properties. The glass transition is not clearly defined and depends on the measurement kinetics. Due to the physical variations, it causes, the glass transition phenomenon is of interest both from a fundamental perspective (improved structural modeling of polymers) and from an industrial standpoint (softening of the material and feasibility of processing).

I.12.1 Mechanical aspect

The area surrounded by a red circle in the figure below represents a transition marking a passage from the solid state to the viscous liquid state for an amorphous polymer. These two states correspond respectively to the glassy domain and the rubbery domain. The glassy domain is characterized by a plateau corresponding to a high value of the shear modulus. In this temperature range, the rates of deformation at rupture are relatively low because molecular movements have low amplitude. On the other hand, the plateau corresponding to the rubbery domain is characterized by a low shear modulus, where the rates of deformation at rupture are considerably larger. This high extensibility is related to molecular movements of large amplitude, allowing for the complete extension of macromolecular chains.

The rubbery plateau strongly depends on the polymer network structure.

- Domain (A): The polymer has a low average mass, with a flow temperature close to Tg.
- Domain (B): The polymer has an average mass of about 30,000, exhibiting a rubbery plateau before chain flow.
- Domain (C): For polymers with an average mass greater than 100,000, the plateau becomes very apparent before flow. This phenomenon is due to a dense polymer network with a high rate of chain entanglement. The nodes between the macromolecular chains only untangle at a high temperature.
- Domain (D): Cross-linked polymer. In this situation, there can be no flow. The material remains stable until it undergoes thermal degradation.

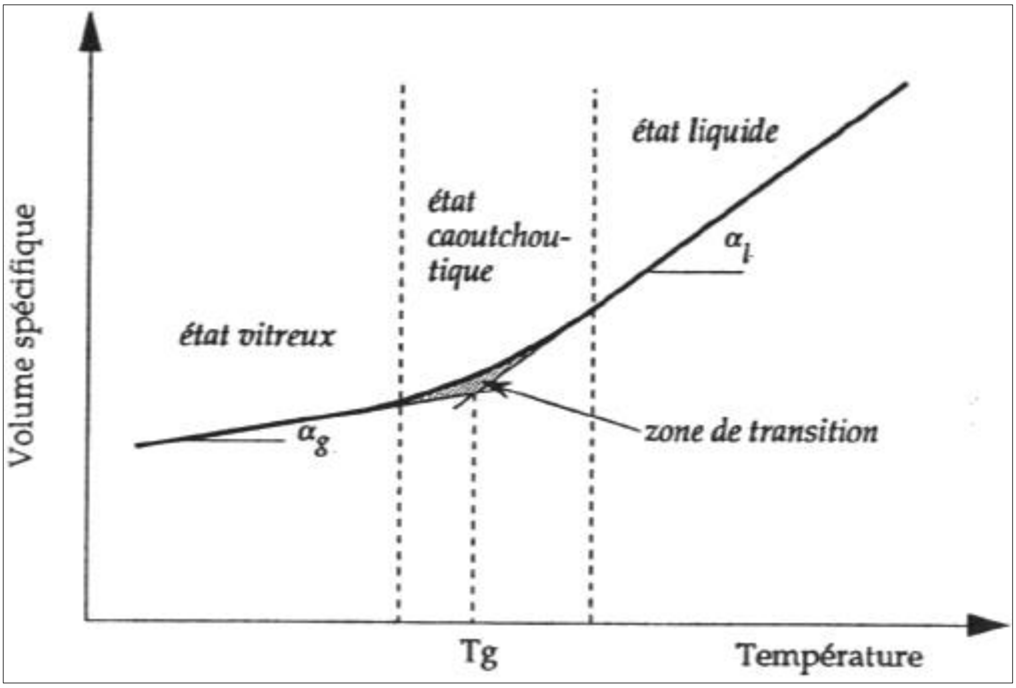


I.12.2 Volumetric aspect

The only method for determining the glass transition temperature was to measure the variations in specific volume of a sample as a function of temperature. This is expressed in m^3/kg, cm^3/g, or ml/g. The transition zone depends on kinetics, with the specific volume varying linearly with temperature as shown in the figure below. From this, the two coefficients of volumetric expansion can be deduced: α_1 for $T > Tg$ and α_g for $T < Tg$. The coefficient of volumetric expansion is defined by the following relationship:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{13}$$

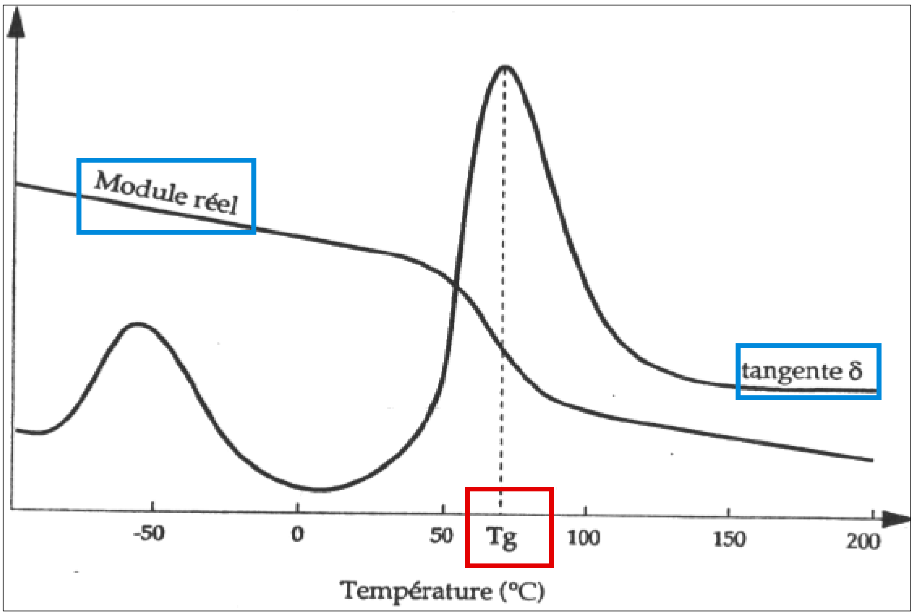
The dimension of this coefficient is equal to the inverse of a temperature; it is generally expressed in K-1. For polymers, the average values of these coefficients are: (α_1 = 6,25 x $10^{-4}K^{-1}$ et α_g = 2,9 x $10^{-4}K^{-}$)^1.



I.12.3 Dynamic Aspect

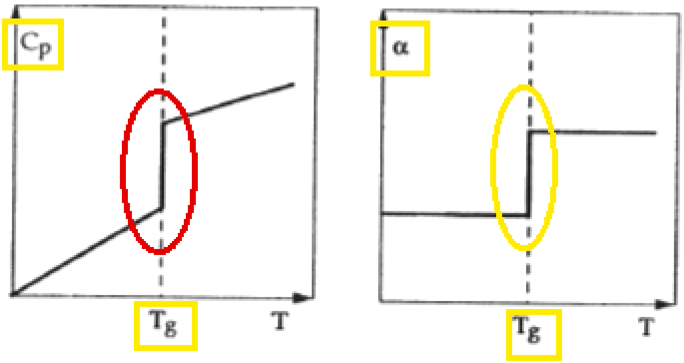
The glass transition corresponds to an energy absorption that enables a shift from low-amplitude local molecular agitation to a significant agitation extending throughout the macromolecular chains. This energy absorption can be observed during dynamic measurements. The torsion pendulum is a simple way to conduct this type of measurement. Dynamic Mechanical Analysis (DMA) involves subjecting a sample to torsion, then releasing it to measure the material's behavior over time in the low deformation domain. Each test is conducted under isothermal conditions. This process is repeated at different temperatures within a range typically varying from -200°C to +200°C. This device enables us to obtain two parameters related to temperature, as illustrated in the figure below (variation of the real modulus and the tangent of the loss angle as a function of temperature).

- G' represents the real (or storage) modulus.
- Tangent (δ) = tangent of the loss angle.



In the figure above, which illustrates an example of a polymer material, two peaks can be observed in the plot of tan δ as a function of temperature. The number of peaks typically depends on the nature of the material and can range up to four peaks. Each of these peaks is linked to a transition. These transitions are associated with varying degrees of molecular movements, which can include possibilities such as:

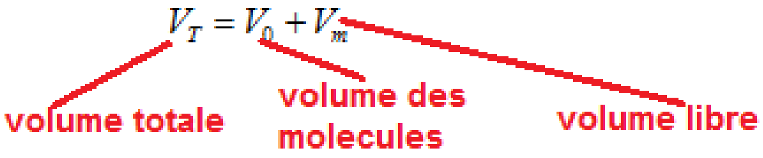
- The α-transition represents the initial phase transition observed when the temperature is lowered. This peak is consistently more pronounced compared to other transitions and signifies the shift from a rubbery state to a glassy state, indicating a transition from high molecular mobility to low molecular motion amplitude. The peak maximum of the α-transition is denoted as T_g.
- The transitions denoted as Transition-β, γ, and δ correspond to temperature-induced transitions. These peaks are less prominent because they are associated with movements of specific small molecular groups.



I.12.4 Thermodynamic aspect

In thermodynamics, a transition is defined as any abrupt change from one physical state to another. There are two types of transitions:

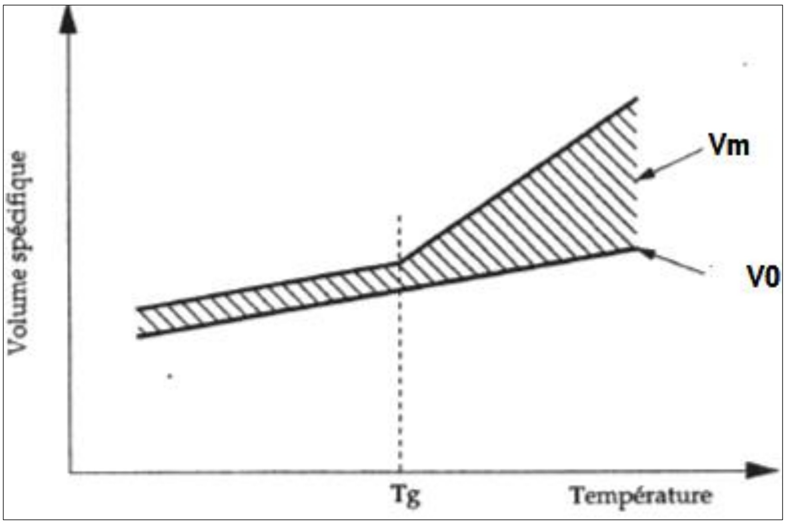
- A first-order transition is characterized by a sudden change in fundamental thermodynamic properties, such as volume or enthalpy. Crystalline fusion is an example of a first-order transition because it results in a sudden change in volume.
- A second-order transition is defined by a sudden change in the first derivatives of these fundamental quantities. The glass transition is an example of a second-order transition, as illustrated in the figure below (Effect of the glass transition on the values of molar heat capacity and volumetric expansion in an amorphous polymer), due to its abrupt impact on the volumetric expansion coefficient and molar heat capacity Cp.
-



$$V_T = V_0 + V_m$$

I.13 Theoretical approach (Fox and Flory theory)

This theory was developed in 1950 and is based on the concept of free volume, which represents the unoccupied space between macromolecules (resulting from incomplete compaction of chains due to their statistical conformation in amorphous polymers). The presence of this free volume can be demonstrated through the dissolution of a polymer in a solvent. As depicted in the figure below, this theory suggests that in an amorphous polymer, the free volume decreases steadily with temperature until a certain limit (T_g) is reached. Below this limit, the free volume remains constant.



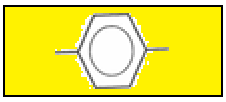
Representation of the two components of the specific volume v_o represents the volume occupied by the molecules, while v_m indicates the free volume (shaded area).

I.14 Factors influencing the value of T_g

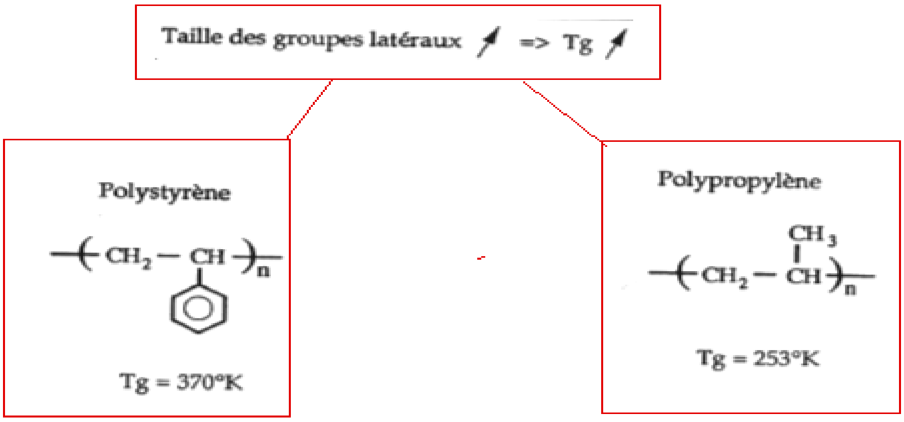
Factors that influence the value of the glass transition temperature include the flexibility of chains, the size and polarity of side groups, molecular weight, crystallinity, and tacticity.

I.14.1 flexibility of macromolecular chains

The flexibility of macromolecular chains is defined by the ease with which rotation can occur around a single bond within the main backbone. The flexibility of a macromolecule is influenced by the atomic groups that make up its main skeleton. One of the most well-known chain "stiffeners" is the:

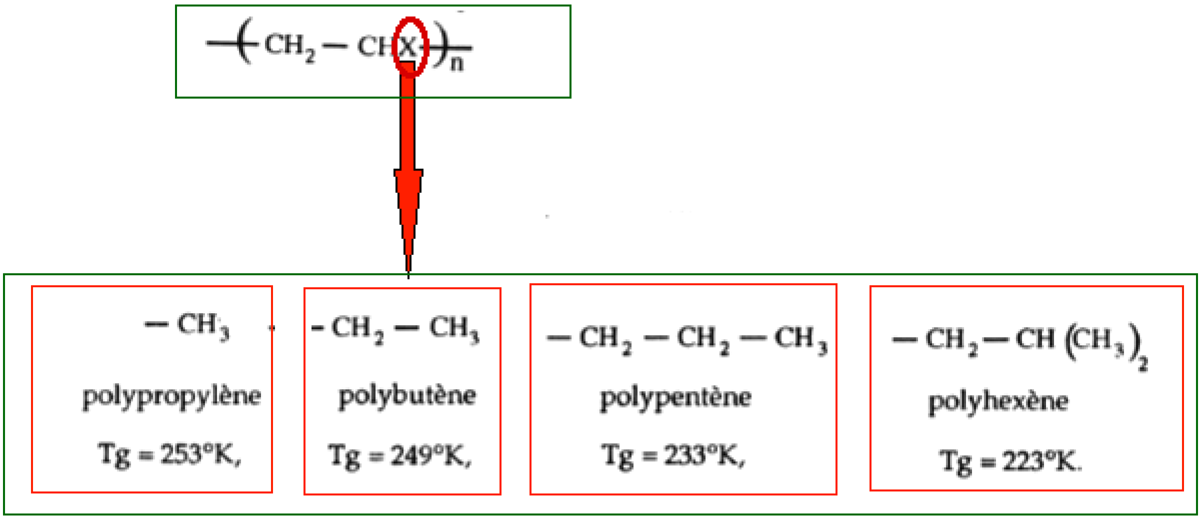


groupe para-phénylène



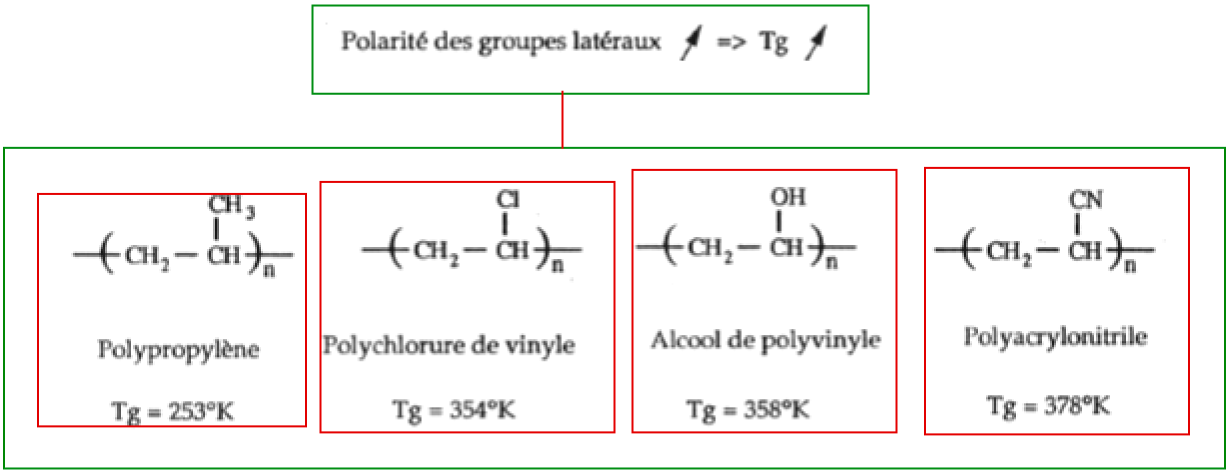
I.14.2 Size of the lateral groups

The larger the size of the side groups, the higher the glass transition temperature. The rule is only followed when the side groups are rigid. For flexible groups, the mobility of the lateral sequences adds extra free volume, which becomes more significant as the sequence length increases. This phenomenon is known as internal plasticization. In this scenario, a decrease in glass transition temperature (T_g) is observed as the size of the side groups increases, as illustrated in the figure below.



I.14.3 Polarity of lateral groups

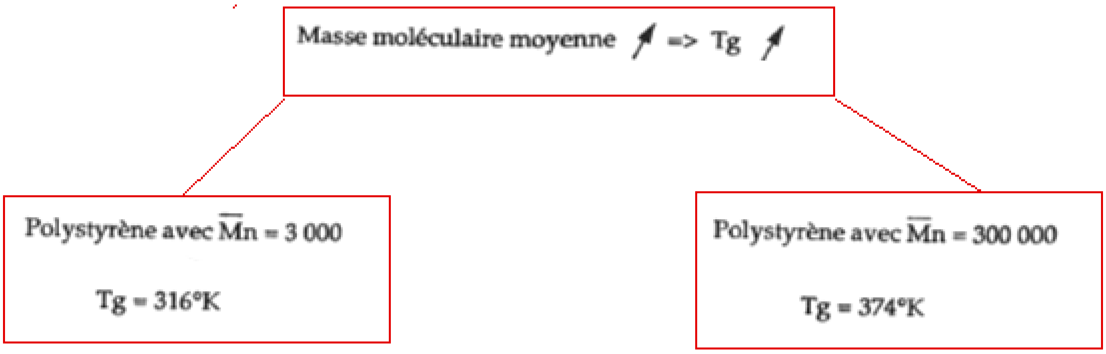
The higher the polarity of the lateral groups, the higher the glass transition temperature. Therefore, a highly polar group will result in a higher Tg compared to an equally sized but less polar group. Example :



A symmetrical distribution of lateral groups along the chain will result in a decreasing glass transition temperature (Tg) since the influence of polarity will be weaker.

I.14.4 Molecular Weight

For linear polymers, the glass transition temperature increases with the average molecular weight. The phenomenon is related to the concentration of chain ends. The greater the number of chain ends (resulting in lower average mass), the larger the free volume, which leads to a lower glass transition temperature (Tg).



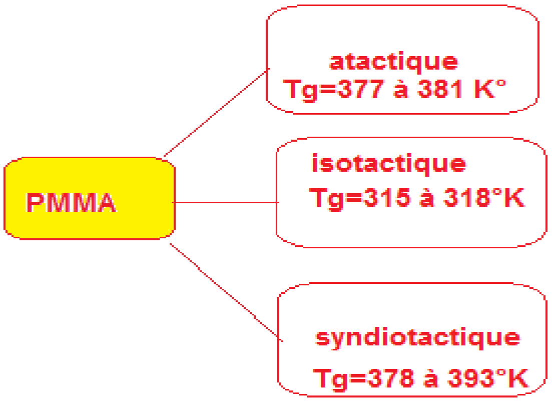
I.14.5 Tacticity

Example 1: In this type of polymers, tacticity has no influence:

$-\!\left(CH_2 - CHX \right)_n\!-$

For these polymers, tacticity has an influence: $-\!\left(CH_2 - CXY \right)_n\!-$

Example 2:



I.14.6 Crystallinity

In most cases, Tg increases with crystallinity due to the stiffening of the sample's structure.

Exercises

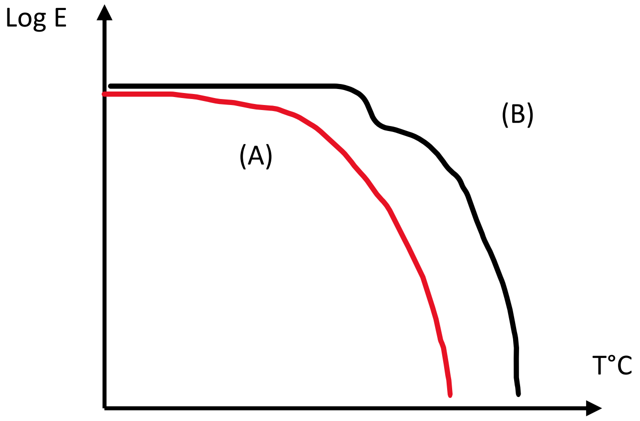
Exercise I-12

1. Describe the physical states of crystalline, semi-crystalline, and amorphous polymers as a function of temperature.
2. In each case, represent the evolution of the Young's modulus as a function of temperature."

Exercise I-13

curves (A) and (B) below represent the variation of temperature as a function of Young's modulus for two polyesters of different tactics, Atactic and synthiotactic.

1. Assign curves A and B.
2. Provide a representation of each polyester chain. What are the characteristics of these polymers?



Exercise I-14

Consider the following three polymers:

1. Polyethylene (PE)
2. Atactic polystyrene (PS)
3. Phenol-formaldehyde (PF) Bakelite

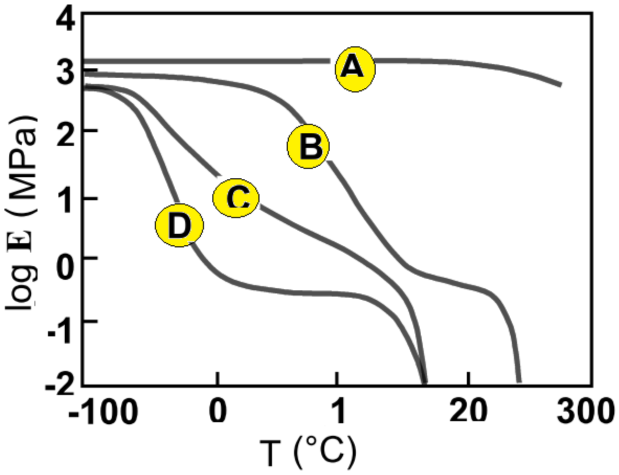
a) Complete this table by indicating which are:

1. Polymers with linear chains;
2. Thermosetting polymers;
3. Crystallizable polymers.

b) Associate one of the log E = f(T) curves presented below with each of these three polymers.

c) What is the difference in microstructure of the polymer between curves C and D?

Polymers	Linear Chain	Thermosetting	Crystallizable	Curve E=f(T)
PE				
PS				
PF				



Exercise I-15

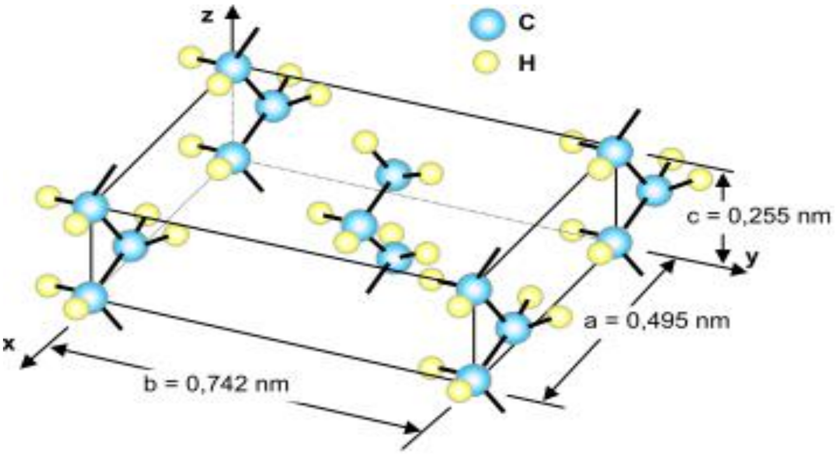
For each of these polymer classes, associate the statements that apply to them.

Class: **Thermoplastics** **Thermosetting**

1. are typically amorphous.
2. exhibit a rubbery state when temperature increases.
3. have a cross-linked structure.
4. can partially crystallize under certain conditions.
5. are recyclable multiple times.
6. are formed of linear or branched chains.
7. decompose without melting during a temperature increase.
8. have a Young's modulus that depends on the duration of the applied load.
9. are obtained solely through addition polymerization without condensation.

Exercise I-16

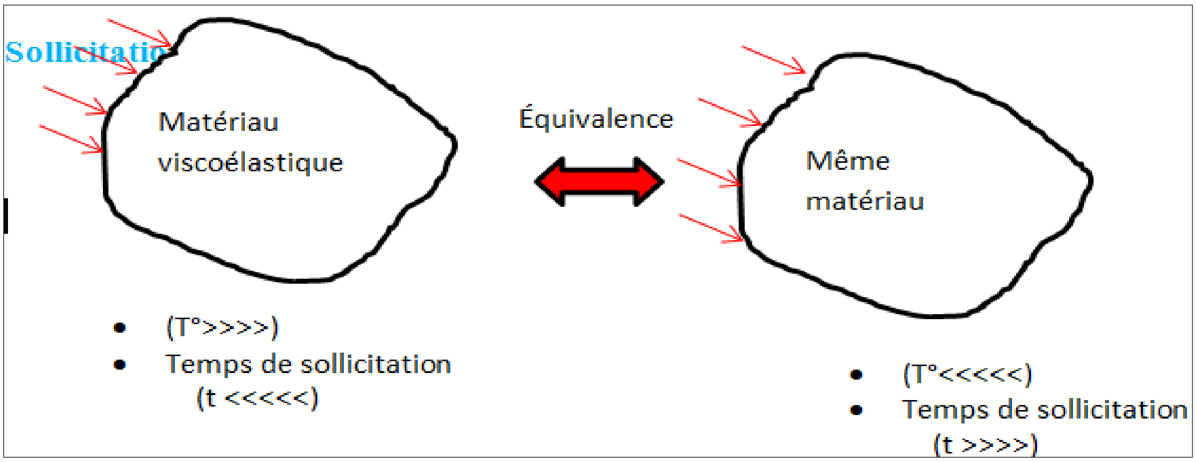
Derived from the ethylene monomer C_2H_4, polyethylene (PE) can crystallize. In the fully amorphous state, its density is 0.880 g/cm^3, while it is 0.995 g/cm^3 in the fully crystallized state. The centered orthorhombic crystalline lattice of crystalline polyethylene is shown below.



1. What is the functionality value of the monomer?
2. How many carbon (C) and hydrogen (H) atoms make up the unit of crystalline polyethylene?
3. What is the number of carbon atoms and hydrogen atoms that belong specifically to the unit cell of crystalline polyethylene?
4. What is the degree of crystallinity (in %) of a high-density polyethylene (HDPE) with a density equal to 0.955 g/cm^3?

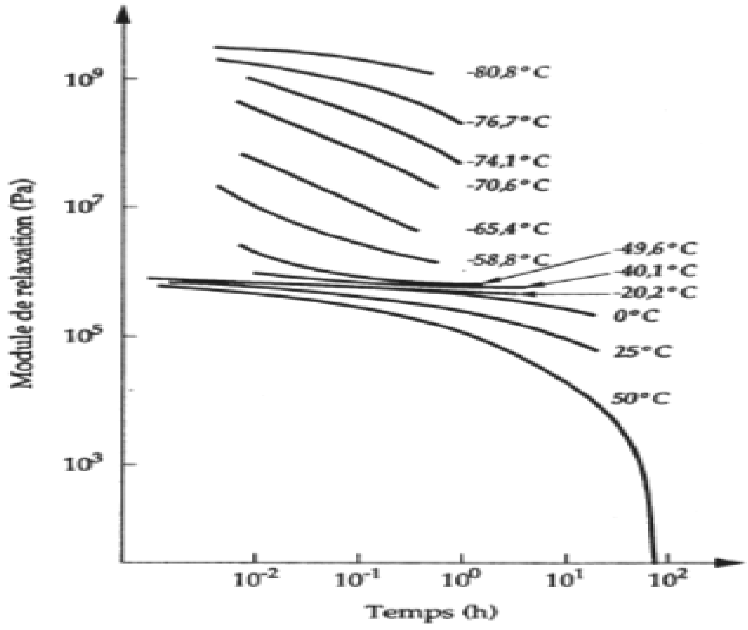
I.15 Time-Temperature Equivalence

In 1941, H. Leaderman was the first to suggest that in a viscoelastic material, there is an equivalence between stress and temperature over time.



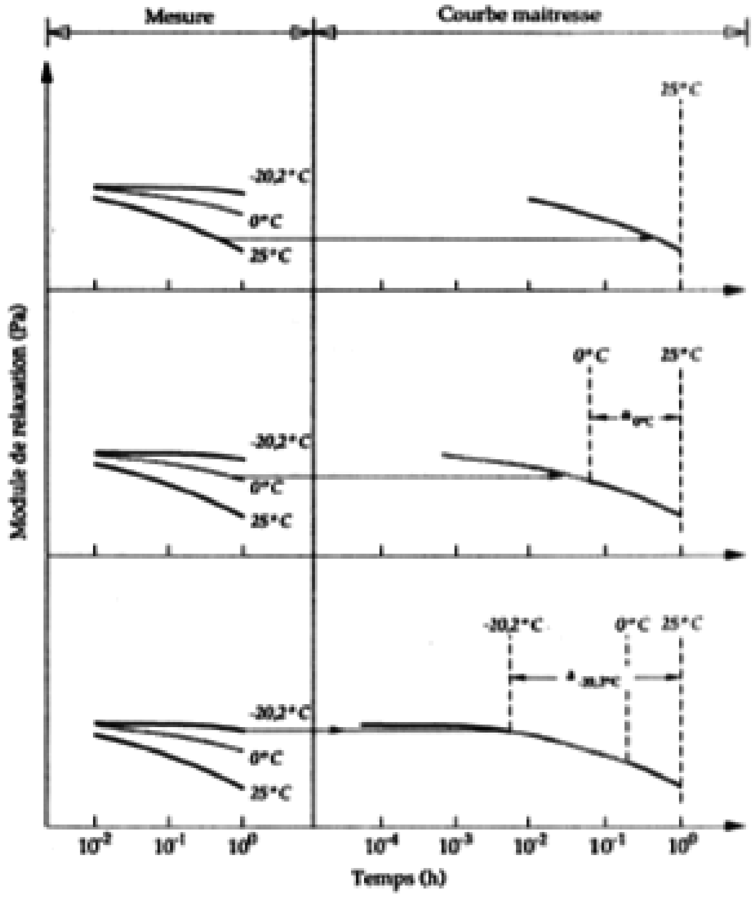
I.15.1 Principle of Time-Temperature Equivalence

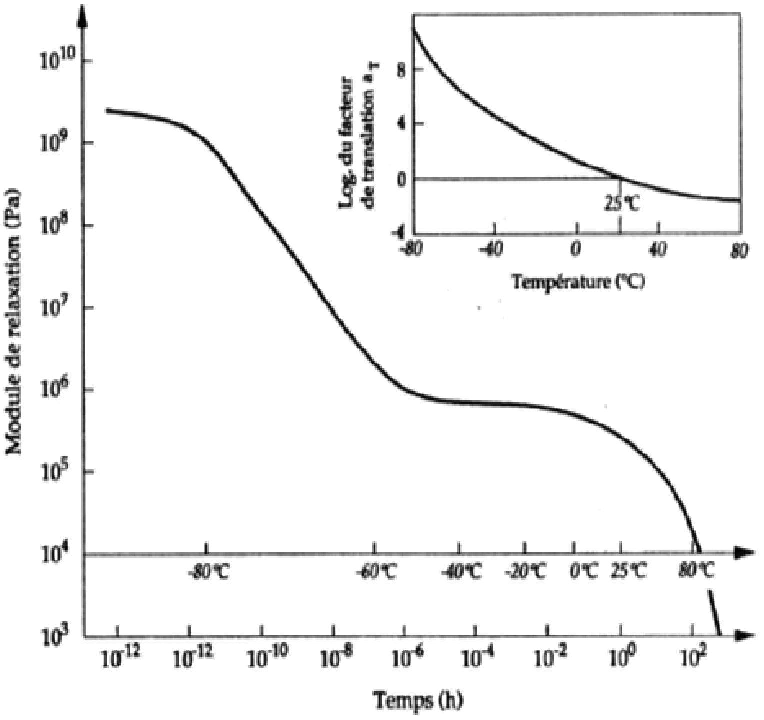
The simplest way to demonstrate the principle of equivalence between time and temperature is by measuring the relaxation modulus E(t) under isothermal conditions. One can plot the evolution of the relaxation modulus over time for various temperatures, as depicted in the figure below: (Variation, in log-log scale, of the relaxation modulus E(t) over time at different temperatures).



According to the figure, we can see that at low temperatures, extremely long measurement times would be needed to obtain a complete curve. However, at high temperatures, only very short measurement times are necessary to achieve this complete curve. Unfortunately. (Example of constructing a master curve from the data in the previous figure for a reference temperature of T_{ref}). The temperature is 25°C, constrained between 10^{-2} h and 10^{0} h.

To plot a complete curve from a single temperature, one arbitrarily chooses a reference temperature, for example, T_r = 25°C. Then, a complete curve can be constructed by translating and overlaying all curve segments obtained at different temperatures, as shown in the figure above. The curve obtained in this manner is referred to as the "master curve," as illustrated in the figure below.





For each translation along the time axis of a curve segment, one can measure the time difference for a given temperature T relative to the reference temperature Tr. This value is called the translation factor (a_T). Through the relaxation modulus E(t), we can express the principle of time-temperature equivalence in the following mathematical form:

$$E(T,t) = E\left(T, \frac{t}{a_T}\right) \tag{14}$$

With **(t)** and **(T)** representing respectively a given time and temperature.

The module E (Tr, t) measured at temperature Tref and time t is equal to the module E (Tr, t/a_T) measured at temperature T and time t/aT. The effect of a temperature change is thus equivalent to applying a multiplicative factor to the time scale; this is known as the principle of time-temperature equivalence. The provided relation is not entirely accurate, as one needs to consider variations in the sample's volume with temperature and the impact of temperature on the system's free enthalpy. We obtain then :

$$E(T,t) = \frac{\rho(T_r)}{\rho(T)} \frac{T_r}{T} E\left(T, \frac{t}{a_T}\right) \tag{15}$$

$\rho(T)$, $\rho(T_r)$ représentent respectivement les densités en fonction des deux températures, Tr et T. Même sous une contrainte imposée, on peut établir une relation en introduisant la conformité de fluage D(t).

$$D(T,t)=\frac{\rho(T_r)}{\rho(T)}\frac{T_r}{T}D\left(T,\frac{t}{a_T}\right) \tag{16}$$

The same logic applies to dynamic measurements as a function of frequency. Consequently, we derive the storage modulus E' as :

$$E^{'}(T,\omega)=\frac{\rho(T_r)}{\rho(T)}\frac{T_r}{T}E^{'}\left(T,\omega a_T\right) \tag{17}$$

Under an imposed constraint, we can have the real compliance.

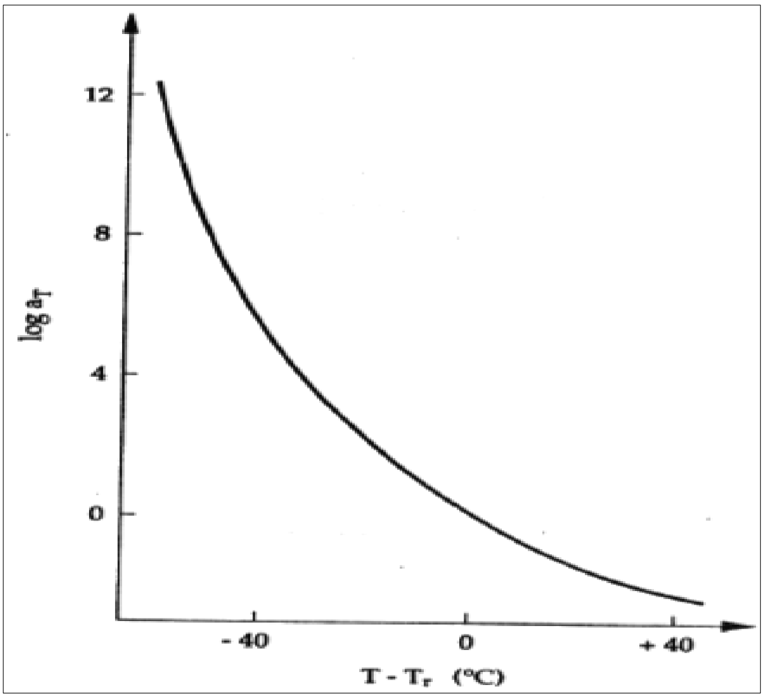
$$D^{'}(T,\omega)=\frac{\rho(T_r)}{\rho(T)}\frac{T_r}{T}D^{'}\left(T,\omega a_T\right) \tag{18}$$

ω : Represents the frequency

By utilizing these relationships, we can create a master curve that illustrates the polymer properties at temperature T_r across a broad spectrum of frequencies. Amorphous polymers generally adhere to the principle of time-temperature equivalence. However, it is truly applicable only within a limited range of time and temperature. The best way to verify the validity of the time-temperature equivalence principle is to measure (a_T) as a function of the relaxation modulus and compliance, with both values being equal.

I.15.2 W.L.F. equation (Williams-Landel-Ferry equation)

The derivation of a master curve can only be done after choosing a reference temperature, Tr. This temperature is chosen arbitrarily because any temperature is valid. However, it is preferable to choose this temperature within the polymer's operating range. In 1955, L. M. Williams, R. F. Landel, and J. D. Ferry published a paper showing that, if the reference temperature is chosen judiciously, it is possible to obtain a universal curve that gives the variation of (a_T) as a function of ($T - T_{ref}$). Measurements were taken on 17 different polymers, each with a unique reference temperature, to superimpose the curves (refer to the figure below).



In general, for each polymer studied, the shape of the curve is given by the relationship:

$$\log a_T = \frac{C_1^r (T - T_r)}{C_2^r + T - T_r} \tag{19}$$

C_1^r , C_2^r are two constants that depend on the reference temperature (Tr) and the nature of the polymer. Williams, Landel, and Ferry then proposed choosing the glass transition temperature (Tg) as the reference temperature. Therefore, the relationship becomes :

$$\log a_T = \frac{C_1^g (T - T_g)}{C_2^g + T - T_g} \tag{20}$$

Landel and Ferry observed that in this case, the two constants vary little with the nature of the polymer; they are respectively equal to (17.4 and 51.6). The relationship of (a_T) as a function of Tg is valid for several amorphous polymers. There is another method to calculate the translation factor a_T: we will take Ts = Tg + 50 °C as a reference point. The relationship then becomes :

$$\log a_T = \frac{C_1^s (T - T_s)}{C_2^s + T - T_s} \tag{21}$$

With : C_1^s **= 8,86 et** C_2^s **= 101,6**. Initialement C_1 et C_{2g}.

For amorphous thermoplastic polymers, the Williams-Landel-Ferry (W.L.F.) The equation is valid only within a temperature range between Tg and Tg + 100 °C. This range corresponds to the one in which the polymers are highly deformable. Beyond Tg + 100 °C, the material is practically liquid.

I.15.3 Values of the constants in the W.L.F. equation

Polymère	C_1^g	C_2^g	**T_g (°K)**
Polyisobutylene	16,6	104	202
Natural rubber	16,7	53,4	200
Polyurethane	15,6	32,6	238
Polystyrene	14,5	50,4	373
Polymethyl methacrylate (PMMA)	17,6	65,5	335
Universal constants	17,4	51,6	-

I.16 linear viscoelasticity

The mechanical response of a solid is entirely defined by establishing the relationship between stress and strain. The most basic form of this relationship is linearity, which characterizes the behavior of an elastic solid governed by Hooke's law:

$$\sigma = E\varepsilon \qquad (22)$$

In the case of liquids, this analysis is no longer possible because they do not have a defined shape. In fact, the viscous behavior of liquids is characterized by the rate at which they deform under specific conditions. A relationship is established between stress and the rate of deformation. When this relationship is linear, it is said that the substance is a viscous liquid. This type of behavior is defined by Newton's law.

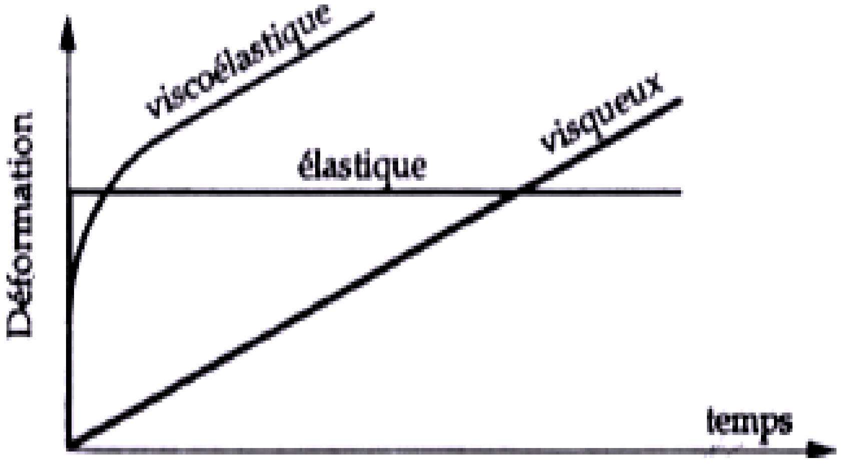
$$\sigma = \eta\left(\frac{d\varepsilon}{dt}\right) \qquad (23)$$

η : represents the viscosity of the material.

By definition, a material exhibits linear viscoelastic behavior when the characteristics of an elastic solid and a linear viscous liquid coexist simultaneously. Through experimental observation, it is known that many materials exhibit viscoelastic behavior. Nevertheless, it is not an exaggeration to say that viscoelasticity is the primary mechanical characteristic of polymers. We make the simplifying assumption that viscoelasticity in polymers is linear. This assumption implies that the relationship between stress and strain remains constant, irrespective of the material's evolution during deformation. In other words, we assume that the impact of chain orientation during deformation is insignificant; this assumption is only applicable in the scenario of small deformations.

I.16.1 Phenomenology

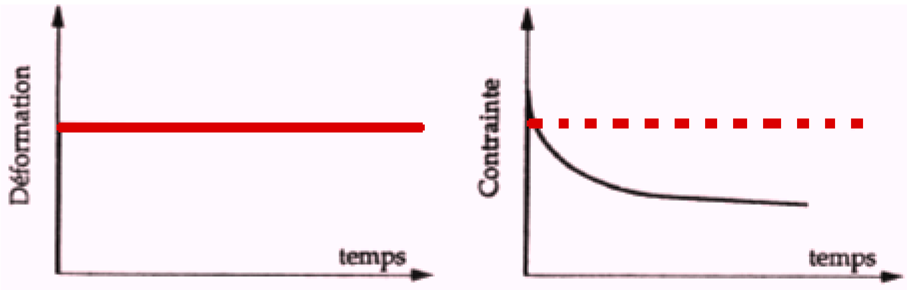
According to the temperature and duration of stress application, most polymers exhibit a range of behaviors, ranging from elastic solids to viscous liquids. The purpose of this phenomenological study is to investigate the viscoelastic response of a polymer to a specific stimulus over time and at different temperatures. In this course, we will focus on studying the influence of time. In a very schematic manner, the viscoelastic behavior can be summarized by plotting the deformation curve over time for the elastic solid, the viscous liquid, and the viscoelastic body when they are subjected to a constant load (see figure: intermediate behavior of the viscoelastic body). Viscoelastic behavior represents a compromise between the elasticity of an ideal solid (represented by a spring with modulus E or G) and the viscosity of a Newtonian liquid (represented by a viscosity damper). In rheology, it is often defined as an assembly of springs and dampers in series and parallel, allowing for the representation of various linear viscoelastic behaviors. These models, while practical, are not directly related to the actual material structure. In a schematic manner, the viscoelastic behavior can be summarized by plotting the deformation curve over time of the elastic solid, viscous liquid, and viscoelastic body when subjected to a constant load (see figure).



We observe that the viscoelastic body exhibits behavior that is predominantly elastic at the beginning and predominantly viscous at the end; between these two extremes, it displays intermediate behavior. To illustrate this phenomenon of viscoelasticity, two simple types of tests are used: relaxation and creep.

I.16.2 Relaxation test

By definition, a relaxation test involves quickly subjecting a sample to a deformation that is kept constant under isothermal conditions. The stress is subsequently measured over time (refer to figure: Stress-Strain System in the case of a polymer relaxation test; the dashed line illustrates the behavior of an elastic body).



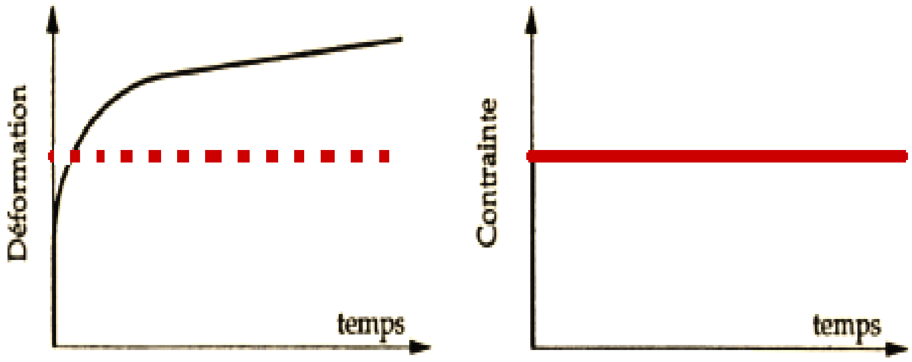
In general, stress decreases over time. If the sample's shape remains unchanged over time, it constitutes pure relaxation. In the most common case, deformation is uniaxial, but it can also occur in shear. However, given that the deformation ε_0 is constant, the relaxation modulus E(t) can be calculated, which is defined by the following relationship:

$$E(t) = \frac{\sigma(t)}{\varepsilon_0} \tag{24}$$

If there is no irreversible viscous deformation, the value of E(t) approaches a constant at infinity, known as the relaxed modulus.

I.16.3 Creep test

A creep test applies stress to a sample at a constant temperature, observing deformation over time (see figure: Stress-Strain System during a polymer creep test; dashed line shows elastic body behavior).



In creep testing, uniaxial stress is commonly applied, but shear stress can also occur. This test includes internal relaxation and viscous deformation mechanisms. With low loads, internal relaxation dominates, especially in small deformations. A correlation with relaxation test results is feasible in such cases. In contrast, large deformations lead to rapid, irreversible viscous deformation. With a constant constraint G, the creep compliance D(t) can be calculated using the given equation.

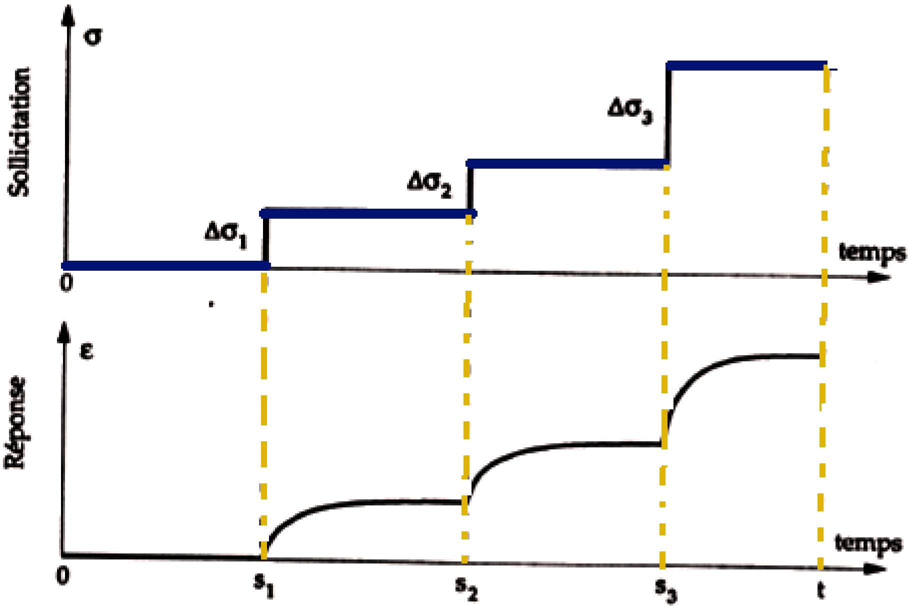
$$D(t) = \frac{\varepsilon(t)}{\sigma_0} \tag{25}$$

The field of linear viscoelasticity is studied using fundamental stresses specifically, simple elongation and simple shear. By focusing solely on these two types of loading, the concept of linear viscoelastic behavior can be concisely described by the following relationships:

	Elongation	**Cisaillement**
Module de relaxation	$E(t) = \frac{\sigma(t)}{\varepsilon_0}$	$G(t) = \frac{\sigma(t)}{\gamma_0}$
Complaisance de fluage	$D(t) = \frac{\varepsilon(t)}{\sigma_0}$	$J(t) = \frac{\gamma(t)}{\sigma_0}$
$E(t) \neq \frac{1}{D(t)}$ **&** $G(t) \neq \frac{1}{J(t)}$		

I.17 Boltzmann’s superposition principle

In 1876, Ludwig Boltzmann introduced the superposition principle, stating that the stress or deformation of a viscoelastic material is influenced by the history of all applied stresses. Each new load independently contributes to the final deformation, which is the sum of all contributions. This principle was the first to characterize viscoelastic behavior; it is known as Boltzmann's superposition principle.



Considering a viscoelastic material undergoing a mechanical test with three creep stages; each stage corresponds to a stress change $\Delta\sigma_1$, $\Delta\sigma_2$, $\Delta\sigma_3$, applied at times s_1, s_2, s_3, respectively (as shown in the figure depicting the material's creep behavior following the Boltzmann superposition principle). Utilizing the principle of superposition, we can express this as:

$$\varepsilon(t) = \Delta\sigma_1 D(t-s_1) + \Delta\sigma_2 D(t-s_2) + \Delta\sigma_3 D(t-s_3) \tag{26}$$

Where, D $(t-s_i)$ represents the creep compliance at time $(t-s_i)$; In the case where there are (n) creep levels, we would obtain the following relationship:

$$\varepsilon(t) = \sum_{i=1}^{n} \Delta\sigma_i D(t-s_i) \tag{27}$$

We can then easily generalize this relationship if we now consider a large number of stress increments ($d\sigma$) (very small). We then obtain :

$$\varepsilon(t) = \int_{-\infty}^{t} D(t-s\ ) d\sigma(s) \tag{28}$$

Which can be written in the form:

$$\varepsilon(t) = \int_{-\infty}^{t} D(t-s\ ) \frac{d\sigma(s)}{ds} ds \tag{29}$$

Using a similar approach, for a relaxation test, we find that the total stress at time t is given by:

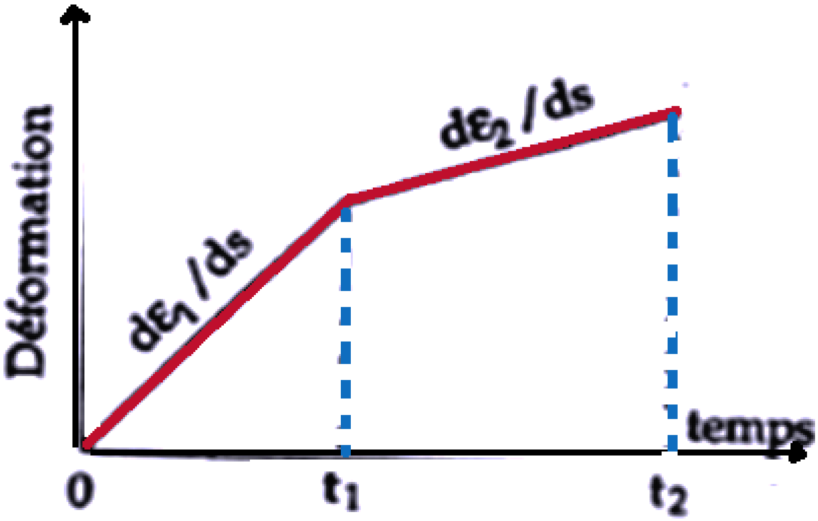
$$\sigma(t)=\int_{-\infty}^{t} E(t-s)\frac{d\varepsilon(s)}{ds}ds \tag{30}$$

Where E (t – s) represents the relaxation modulus at time (t – s).

For example:

Let's consider a simple tensile test where two different strain rates were applied successively, as shown in the following diagram. The expression for the stress at time (t_2) is then given by the sum of the following integrals:

$$\sigma(t_2)=\int_{0}^{t_1} E(t_2-s)\frac{d\varepsilon_1}{ds}ds+\int_{t_1}^{t_2} E(t_2-s)\frac{d\varepsilon_2}{ds}ds \tag{31}$$



Exercises

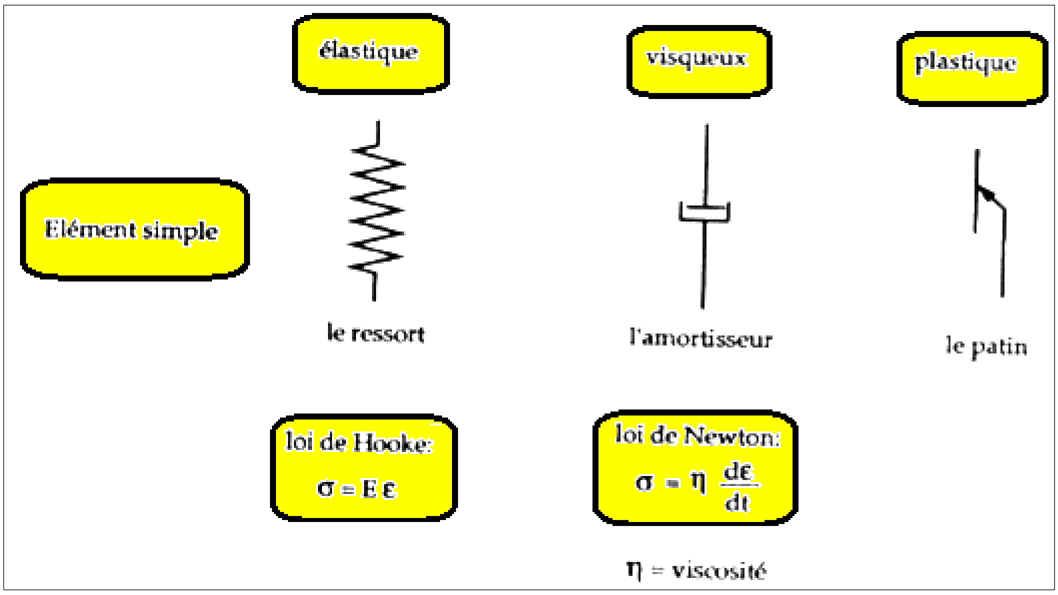
Exercise I-17

Let a stress of 7.6 MPa be applied to a polymer material under constant deformation. After 40 days at a temperature of T = 20 °C, the applied stress decreases only to 4.8 MPa. When the same polymer is heated to a temperature of T = 40 °C, a relaxation time of 50 days is recorded.

1. Calculate the relaxation time for this material at T = 20 °C.
2. What would be the stress after 60 days at T = 20 °C?
3. Determine the activated energy of this polymer material based on the recorded relaxation stress.

I.18 Rheological models

The mechanical behavior of any material can be modeled either structurally or analogically.Structural modeling makes it possible to understand the mechanisms responsible for deformation related to the molecular nature of a material. On the other hand, analog modeling can only simulate macroscopic behavior, unrelated to this molecular nature. The most classic instruments of analogue modelling are rheological models. The rheological models constitute an imaged representation of the one-dimensional mechanical properties of a body, thanks solely to the combination of simple elements. These simple elements are three in number (figure: *simple elements that make up the rheological models*).



The spring represents a purely elastic mechanical behavior where any inertia effect is negligible. The deformation of this element is established instantly as soon as an external force is applied. Obviously, a material strictly obeying such behavior does not exist, because there is always a certain inertia. The damper consists of a piston that can move in a cylinder filled with a viscous liquid. Unlike the spring, it cannot react quickly to a solicitation. The mechanical behavior of polymers is usually modeled by a combination of only two simple elements: the spring and the damper. The most common are:

I.18.1 Maxwell model

In order to simulate the mechanical response of a viscoelastic body, J.C. Maxwell proposed a rheological model composed of a spring and a damper mounted in series; such a combination is called a Maxwell model (figure: *Maxwell model*).

In the spring the stress (σ_1) and the deformation (ε_1) are united by the relationship

$$\sigma_1 = E\varepsilon_1 \tag{32}$$

For the damper, the stress (σ_2) and the deformation (ε_2) are linked by the relationship:

$$\sigma_2 = \eta\left(\frac{d\varepsilon_2}{dt}\right) \tag{33}$$

Consider the total stress σ and the total deformation ε. As the elements are in series, the stress is identical in the spring and in the damper; hence ($\sigma = \sigma_1 = \sigma_2$) For the same reason, the total deformation is equal to:

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \tag{34}$$

We can write as follows:

$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_1}{dt} + \frac{d\varepsilon_2}{dt} \tag{35}$$

$$\begin{cases} \dfrac{d\varepsilon_1}{dt} = \dfrac{1}{E}\dfrac{d\sigma_1}{dt} \\ \dfrac{d\varepsilon_2}{dt} = \dfrac{1}{\eta}\sigma_2 \end{cases} \tag{36}$$

With, ($\sigma = \sigma_1 = \sigma_2$), we can have the following relationship:

$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_1}{dt} + \frac{d\varepsilon_2}{dt} = \frac{1}{E}\frac{d\sigma_1}{dt} + \frac{1}{\eta}\sigma_2 = \frac{1}{E}\frac{d\sigma}{dt} + \frac{1}{\eta}\sigma \tag{37}$$

In the case of simple stresses, this differential equation (relaxation or creep test)

I.18.1.1 Maxwell Model Behaviour in a Relaxation Test

By definition during a relaxation test the deformation remains constant ($\varepsilon = \varepsilon_0$, $\frac{d\varepsilon}{dt} = 0$), equation (6) becomes as follows:

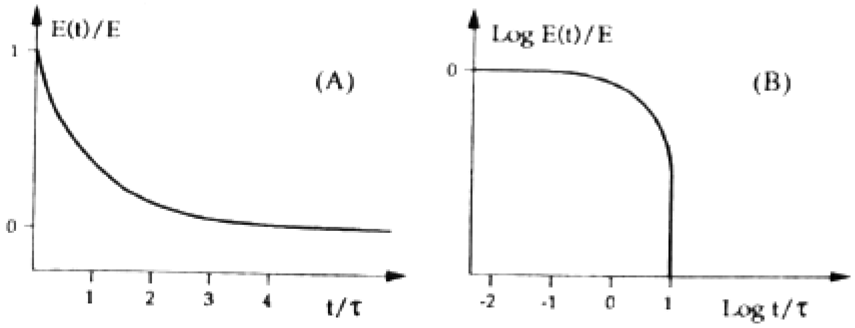
$$\frac{d\sigma}{\sigma} = -\frac{E}{\eta}dt \qquad (38)$$

At ($\sigma = \sigma_0$, $t=t_0$) we will have a solution of the following form:

$$E(t) = E\exp(-\frac{t}{\tau}) \qquad \text{avec} \qquad \tau = \frac{\eta}{E}$$

τ : *Relaxation time*

The graphical representation of this relationship illustrates the behavior of the Maxwell model during a relaxation test, the figure below shows an *Illustration of the behavior of the Maxwell model during a relaxation test, (A) linear scale; (B) log-log scale*. We notice that for a very small time compared to the relaxation time, the model behaves as if it were a spring alone. On the contrary, for a significantly longer time the model reacts as a shock absorber alone. For a time, comparable to the relaxation time, the model's response involves both the spring and the damper.



représentation du modèle de maxwell lors d'un essai de relaxation.

I.18.1.2 Maxwell model behavior during a creep test

By definition the stress is kept constant; hence $\sigma = \sigma_0$, and $\frac{d\sigma}{dt} = 0$.

Equation (6) can then be written: $$\frac{d\varepsilon}{dt} = \frac{\sigma_0}{\eta} \qquad (39)$$

By integrating this equation from 0 to t, it comes that

$$\varepsilon(t) = \frac{\sigma_0}{\eta} t + cst \tag{40}$$

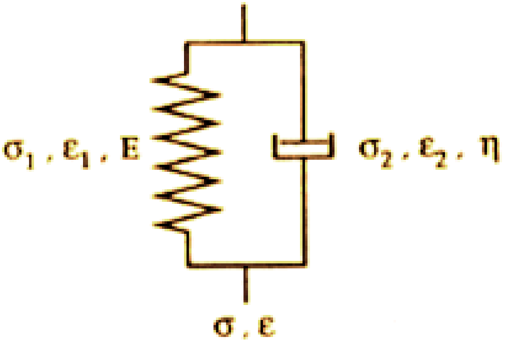
To define the integration constant, the boundary conditions (t = 0, $\varepsilon = \varepsilon_0$) are set. We obtain:

$$\varepsilon(t) = \frac{\sigma_0}{\eta} t + \frac{t}{\eta} \tag{41}$$

Example: Shown that: $D(t) = \frac{1}{E} + \frac{t}{\eta}$

I.18.2 Voigt model

The viscoelastic response of a material to mechanical stress can also be presented by a model composed of a spring and a damper mounted in parallel (this combination is called a **Voigt model** (also called a Kelvin or Voit-Kelvin model).



Modèle de Voigt.

Given that this time the elements are in parallel, the deformation must be the same in the spring and in the damper; hence $\varepsilon = \varepsilon_1 = \varepsilon_2$. For the same reason, the total stress is equal to the sum of the spring and damper stresses; hence $\sigma = \sigma_1 + \sigma_2$. Since the two relationships below are still applicable, we obtain the fundamental equation of the Voigt model:

$$\sigma = E\varepsilon + \eta \frac{d\varepsilon}{dt} \tag{42}$$

$$\frac{d\varepsilon}{dt} = \frac{\sigma}{\eta} - \frac{E\varepsilon}{\eta} \tag{43}$$

The Voigt model is used to describe viscoelastic behavior during creep tests, but it can hardly be applied for relaxation tests, since it is impossible to instantly impose a finite deformation on it; the necessary stress would be infinite. The relaxation modulus for the Voigt model is then reduced to the following relationship:

$$\mathrm{E}(\mathrm{t}) = \mathrm{E} \tag{44}$$

I.18.2.1 creep test

Given that by definition the constraint is kept constant, it can always be written that σ = σ_0 and dσ/dt = 0. As an example, when, we get and therefore the characteristic polynomial of splits into.

$$\begin{gathered} \frac{d\varepsilon}{dt} = \frac{\sigma_0}{\eta} - \frac{E\varepsilon}{\eta} \\ E(t) = \sum_{i=1}^{z} E_i \exp(-\frac{t}{\tau_i}) \end{gathered} \tag{45}$$

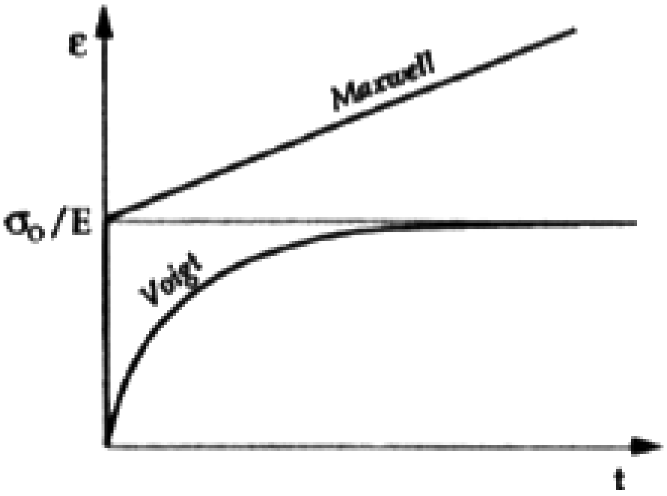
The solution to this differential equation is given by the relationship:

$$\varepsilon(t) = \frac{\sigma_0}{E}\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \tag{46}$$

Hence the creep compliance for the Voigt model is given by the following relationship:

$$D(t) = \frac{1}{E}\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \tag{47}$$

It is now possible to compare the evolution of deformation over time, in creep, of the Maxwell and Voigt models (figure: *Behaviour over time, under constant load, of the Maxwell and Voigt models)*. We can then tell what type of material we can associate these behaviors with. In the case of Maxwell's model, we find that the rate of deformation is constant; it is equal to the slope of the curve, i.e. $\frac{\sigma_0}{\eta}$. This model therefore represents the behavior of a viscoelastic liquid; it is generally called the Maxwell liquid. On the other hand, for the Voigt model we notice that when “t” tends to infinity, the deformation ε(t) tends to σ_o/E. This type of behavior is very similar to that of polymers.



I.19 Generalized Models

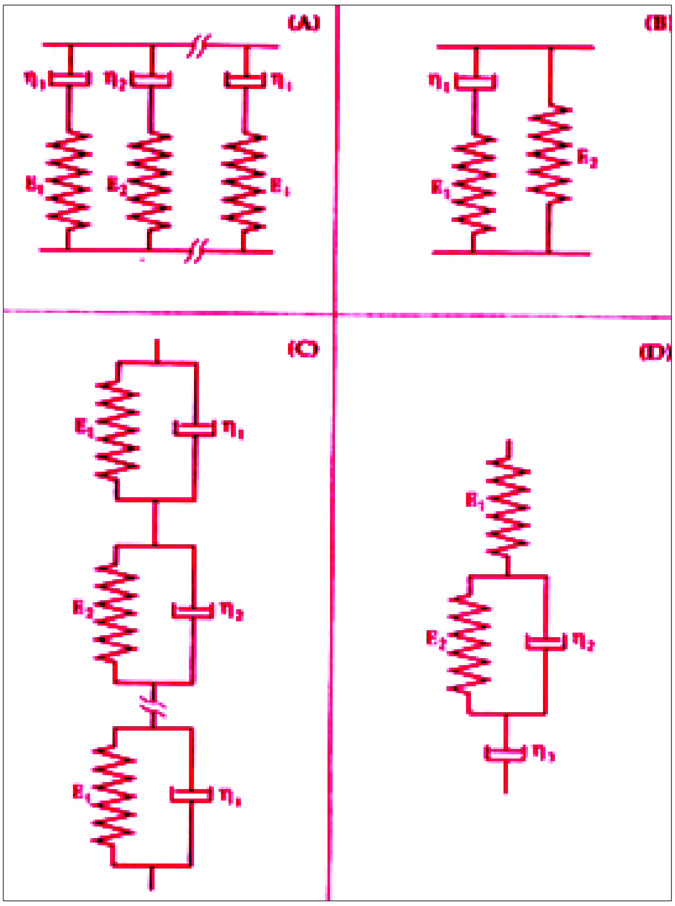
The viscoelastic response of a polymer is in fact much more complex than that obtained with the two previous models (Maxwell and Voigt). As an example, we note that for each of these two models, there is only one relaxation time constant (t). In the case of polymers, this would imply that all the chains must be rearranged in the same way and at the same time; this does not correspond to reality. Thus, these two models cannot give a good approximation of the behaviour of polymers.

To try to overcome this shortcoming, more sophisticated models have been proposed, combining a greater number of simple elements. We will limit ourselves to the models obtained by generalising Maxwell's and Voigt's models.

The generalization of Maxwell's model consists in the parallelization of a given number of Maxwell's models. The model obtained is then called the generalized Maxwell model or Maxwell-Wiechert model (Figure A). If this model is subjected to a relaxation test, the relaxation modulus of the set is obtained by the sum of the moduli of each of the Maxwell elements, namely:

$$E(t) = \sum_{i=1}^{z} E_i \exp(-\frac{t}{\tau_i}) \tag{48}$$

By using only two Maxwell elements (z = 2) and replacing one of these two elements with a simple spring, we obtain a set called the Zener model (figure B). With this model, the behaviour of a highly cross-linked polymer can be simulated. Indeed, this behavior is characterized by an instantaneous elasticity followed by a delayed elasticity phase; the deformation remaining in all cases fully reversible.



Generalized rheological models and their most common derivative. (A): Generalized Maxwell or Maxwell-Wiechert; (B): Zener; (C): Generalized Voigt or Voigt-Kelvin; (D): Burgers

The generalization of the Voigt model consists of a series assembly of a given number of Voigt elements. The model obtained is then called the generalized Voigt model or Voigt-Kelvin model (Figure C). As with the Voigt model alone, this generalised model does not make it possible to study the relaxation of a material. Nevertheless, if it is subjected to a creep test, the creep compliance of the assembly can be calculated by summing the compliance of each of the Voigt elements, namely:

$$D(t) = \sum_{i=1}^{z} \frac{1}{E_i}\left(1 - \exp\left(-\frac{t}{\tau_i}\right)\right) \qquad (49)$$

By using only two Voigt elements (z = 2) and replacing one of these two elements with a Maxwell element, we obtain a set called the Burgers model (figure D). Thanks to this model, the **creep behavior of a thermoplastic polymer** can be qualitatively reproduced. Indeed, this behavior is characterized by an instantaneous elasticity followed by a delayed elasticity phase and by an irreversible deformation.

Exercises

Exercise I-18

The rheological behavior of a polyethylene specimen of length 100 mm and section 40 mm^2 can be represented by a Maxwell model (E=10^9 Pa, η= 7.2 x10^{10} Pa. s). This specimen is subjected to a creep test under 160 kg. The maximum elongation cannot exceed 6% of the initial length

1. after how long does breakage occur?"

Exercise I-19

We propose to study the behavior of a material represented by a spring in series with a Kelvin-Voigt element. The determination of the parameters is carried out by a tensile creep test on a specimen of length 100 mm and section 20 mm^2 under a force of 25 kg. The creep curve presents three zones:

An instantaneous deformation of 1%. and a delayed elongation of 1.7 mm after 100 h and a horizontal asymptom of 1.8 mm.

1. Calculate the parameters and the apparent modulus after 10 hours.

Exercise I-20

We propose to study the behavior of a material represented by a spring in series with a Kelvin-Voigt element. The determination of the parameters is carried out by a tensile creep test on a specimen of length 100 mm and section 20 mm^2 under a force of 25 kg. The creep curve has three zones: an instantaneous deformation of 1%, a delayed elongation of 1.7 mm after 100 hours, and a horizontal asymptote of 1.8mm.

1. Calculate the parameters and the apparent modulus after 10 hours.

I.20 Polymer Damage

The main purpose of this part is to study the mechanical limits of polymers; To do this, we will follow the following plan:

1. Plastic strain ;
2. Damage phenomena: This section deals with the study of phenomena that are related to damage, on a macroscopic scale;
3. Fragile ruptures ;
4. Fracture Mechanicus.

I.20.1 Plastic deformation

I.20.1.1 Definition

Plastic deformation refers to any permanent alteration that surpasses a specific threshold, known as the plasticity threshold. Assessing the plasticity threshold in polymers proves challenging due to their viscoelastic behavior. Plasticity thus represents a rheological property enabling an object to retain its shape post-deformation; it correlates with a deformation mode primarily determined by factors such as temperature, strain, and strain rate. Initially, it is imperative to differentiate between viscous flow and plastic deformation.

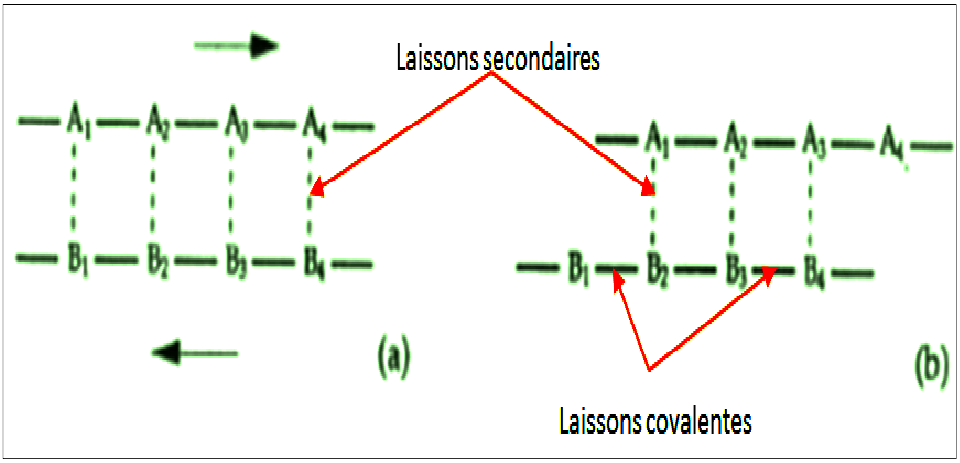
For example: a polymer cup. If it is placed in a furnace at a temperature of about 120 °C, it can be observed that it becomes like a polymer sheet again (initial state of manufacture). From a rheological point of view, this cup is a liquid with a very high viscosity at room temperature. If the temperature is raised, the viscosity decreases, which makes it possible to change the shape of the object without actually transforming its structure. After deformation, the new shape is frozen at room temperature. This behavior is unique to viscous flow.

Viscous flow occurs only in non-cross-linked, amorphous, or very poorly crystalline materials. Amorphous materials do not have a melting point *(fusion is a thermodynamic characteristic related to the transition from an ordered state to a disordered state),* and order does not exist in an amorphous structure. There is an equivalence between time and temperature. This means that our cup will return to its original shape at room temperature, but after an extremely long time. Viscous flow is associated with reversible conformational changes.

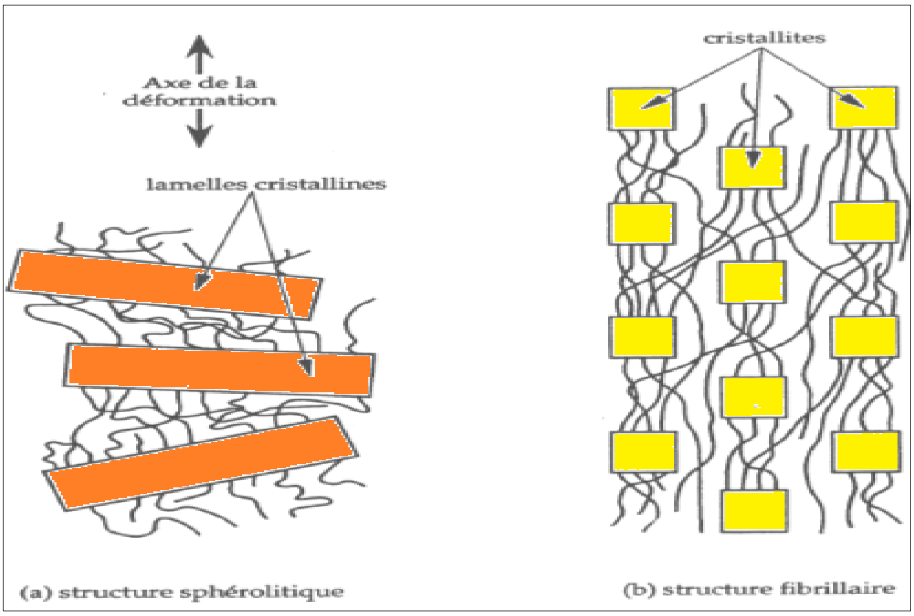
Plastic deformation is a significant transformation of the molecular structure of a material. It is irreversible, it can lead to the ruin of the material, and it concerns both amorphous and crystalline structures. The study of plastic deformation is not only essential for understanding the mechanisms involved in the shaping of the material, but it also makes it possible to model the orientation mechanisms and thus contributes to the improvement of the material. Unlike viscous flow, plastic deformation is associated with molecular mechanisms of deformation.

I.20.2 Molecular mechanisms of deformation

In solid materials, the molecular mechanisms that lead to plastic deformation are related to shears between atomic planes. The relative motion of the atomic planes is the most plausible way to explain the stability and irreversibility of plastic deformation. In metals, the metallic bond makes the cohesion of the material identical in all three directions of space. On the other hand, in polymers, cohesion is strong along chains (covalent bonds), while it is weak between secondary bonds. For this reason, even in highly crystalline polymers where dislocations exist, secondary bonds play no role in the plastic deformation of the material. Plastic deformation in polymers should be considered as the transition from one steady state to another stable state without creating residual stresses that would be fixed, as in the example of the polymer cup, where the stresses are frozen by the lowering of the temperature. The simple diagram below shows the macromolecular structure of a polymer, replacing atoms with monomer units. This results in what is known as plastic shear deformation.

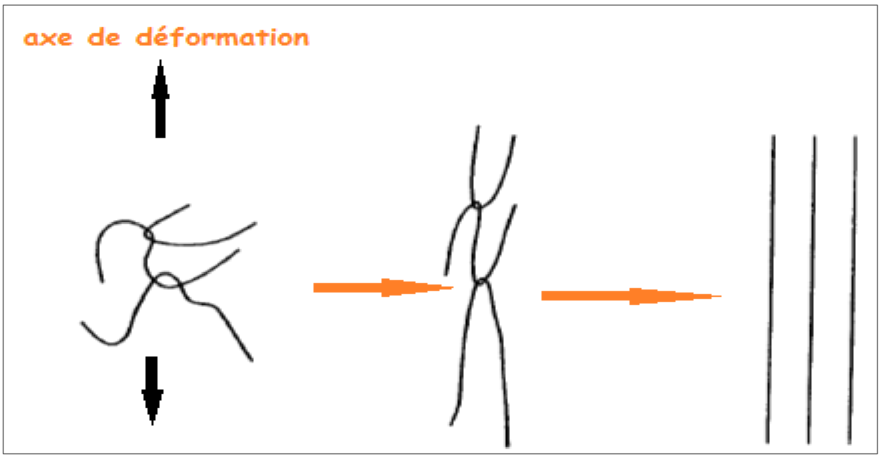


When the number of secondary bonds between two chains is significant, the energy required to simultaneously break them all exceeds that of a covalent bond. The primary mechanisms of plastic deformation in polymers involve extensive reorientation of both amorphous molecular chains and crystalline lamellae. In the context of semi-crystalline polymers, it's important to note that crystallinity typically comprises spherolites, which are composed of crystalline lamellae interconnected by amorphous chains (refer to the figure below).



When subjected to uniaxial stress, this type of polymer initially exhibits an alignment of the amorphous chains, followed by an alignment of the crystalline lamellae, as depicted in Figure a. Subsequently, in a second stage, the largest and most imperfect lamellae undergo breakage. This process is accompanied by a complete reorganization of the distribution of crystal zones relative to amorphous zones, as illustrated in Figure b. At very high strain rates, under conducive conditions, a fibrillar structure identical to that depicted in Figure b is attained. During this stage of deformation, the amorphous zones comprise solely the ends of macromolecular chains. The remaining non-crystalline zones are oriented in such a way that they cannot be appropriately labeled as amorphous; instead, they are classified as part of the mesomorphic phase. It is believed that the mesomorphic phase predominantly governs the mechanical properties of this material type, with the crystallites serving as anchoring points.

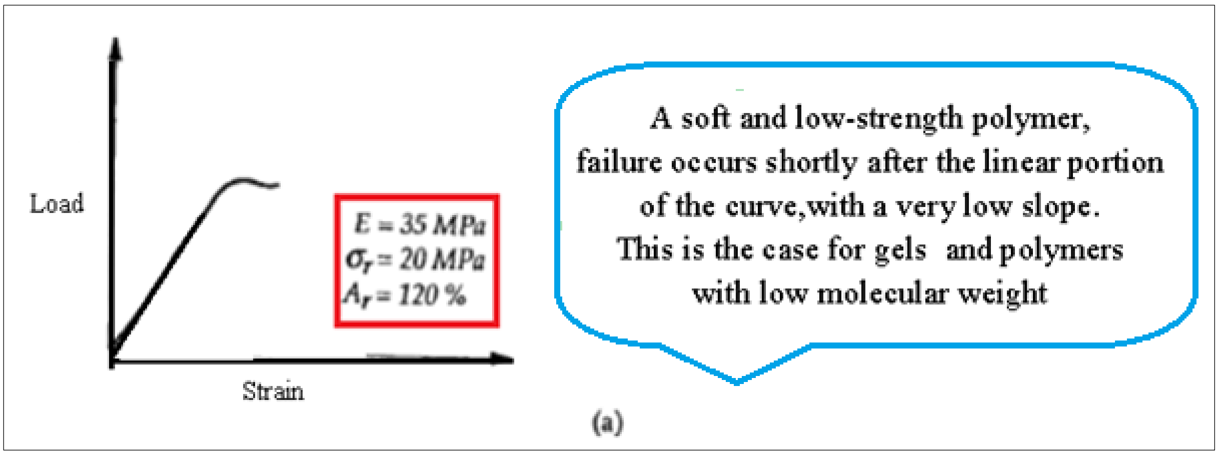
In amorphous polymers, the structural reorganizations related to deformation are not as well understood due to the challenges associated with studying amorphous structures, which are inaccessible by X-ray and electron diffraction. Additionally, it is important to note that an amorphous polymer can be conceptualized as a collection of statistical spheres that intertwine, forming a complex network of entanglements. In this type of material, applying unidirectional tension causes the spheres to reorient and the polymer chains to align, resulting in plastic shear deformation. However, this structural rearrangement is constrained by the presence of entanglements between the chains, which act as cross-linking points, impeding stretching. When the number of entanglements is exceptionally low, a paracrystalline structure can emerge through plastic deformation. Refer to the figure below for a visual depiction of the structural rearrangements in an amorphous polymer induced by unidirectional extension.

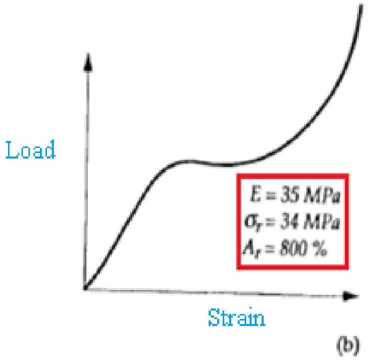


During deformation there is a possibility of disentanglement of some chains. This is especially important when the temperature is high and the chain length, strain rate and density of the entanglement network are low.

I.20.3 Load-strain curve for a tensile test

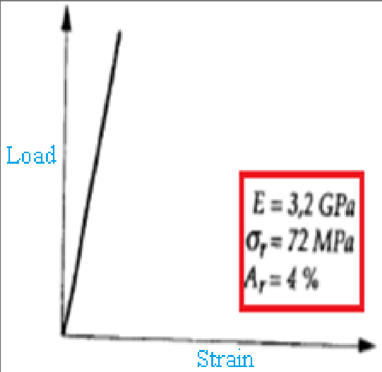
Specimen fracture is said to be brittle when it occurs in the elastic domain after low deformation and high loading. On the other hand, if the fracture is preceded by a plastic deformation that has occurred above a certain deformation threshold, the material is called ductile.





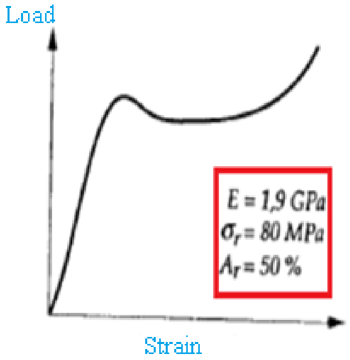
(b)

A soft and resilient polymer: the modulus is low, but the deformation is very significant. This deformation remains almost elastic until the ultimate breaking point. It is worth noting that there is a sharp increase in the slope towards the end of the test. This phenomenon indicates a stiffening of the sample, likely due to a reorientation of the chains along the axis of deformation. This is the case for elastomers.



(c)

A hard and brittle polymer: the modulus is high, but the deformation is low; there is no plastic deformation. This is the case for polystyrene and methyl methacrylate.



(d)

A tough and ductile polymer: it has a high modulus and significant deformation due to extensive plastic deformation. It is common in this case to observe necking in the sample. This is characteristic of polyamides and polyesters."

Part-II: Electrical Properties of Polymers

Electrical properties are determined by the response that a material provides when subjected to an electric field. The application of such a field leads to two distinct types of reaction.

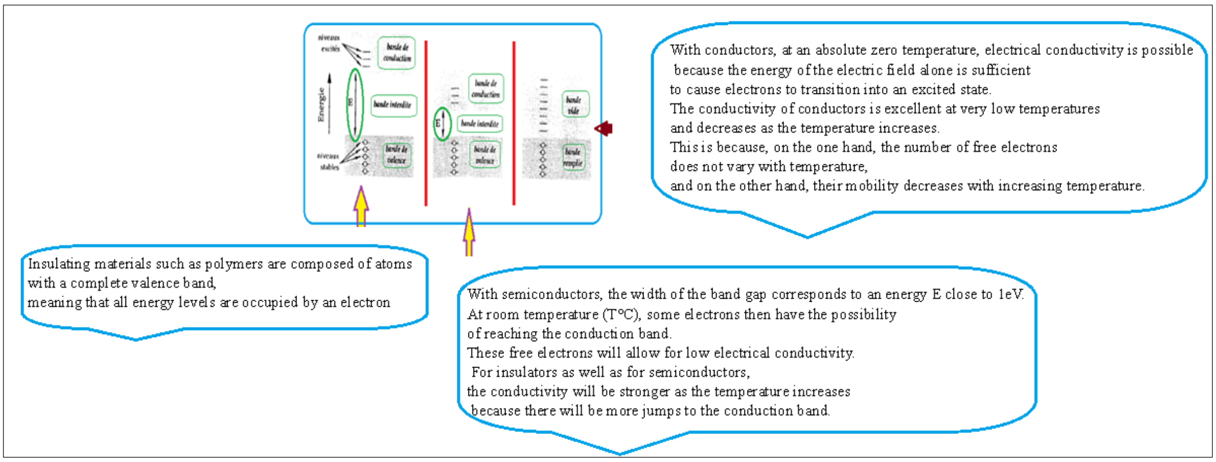
- A flow of electrical charges in the material, which stops as soon as the field is removed, but which nevertheless remains irreversible. In this case, the material is said to be **conductive.**
- The application of this electric field can cause a separation between positive and negative charges, which leads to the formation of a dipole structure, but which disappears when the field is removed. The material is then said to be dielectric (insulating).

Electrical conductivity: Electrical conductivity is a phenomenon that relates to the transport of electrical charges within a material. This flow of charges generates an electric current. The table below shows the Electrical Conductivity at Room Temperature for different materials.	σ $[\Omega\ m]^{-1}$	Semi-conducteurs	σ $[\Omega\ m]^{-1}$
Silver	6,3 x 10^{7}	Pure gallium arsenide	10^{-6}
Copper	5,8 x 10^{7}	Insulating	
Aluminium	3,5 x 10^{7}	Phenoplasts	10^{-9}- 10^{-10}
Steel	0,7 x 10^{7}	Polyamides	10^{-9} - 10^{-12}
Stainless steel	0,2 x 10^{7}	Alumine	10^{-10} -10^{-12}
Graphite	10^{5}	Poly methacrylate Methyle	< 10^{42}
Semi-conducteurs		Polyethylene	10^{-13}- 10^{46}
Germanium pur	1	Polystyrene	< 10_{-14}
Pure Silicon	10^{-3}	Polytetrafluoroethylene	< 10^{-16}

II.1 Conducteurs

Electrical conductivity is a physical property that varies most with the nature of a material at room temperature, it ranges from 10^{8} to 10^{-17} [Q. m] $^{-1}$. Materials fall into three categories: conductors, semiconductors, and insulators.

- **Conductors:** metals with a conductivity of the order of 10^{7} [Ω.m] $^{-1}$.
- **Insulators:** Conductivity is less than 10^{-8} [Ω.m] $^{-1}$.
- **Semiconductors:** germanium, silicon and gallium arsenide, in its pure state their conductivity is low, it can be increased with a very small number of specific elements (doping).
- **Superconductors:** their electrical resistance becomes virtually zero when heated to very low temperatures, as lead at a temperature of 4°K has a conductivity greater than 10^{26} [12.m] $^{-1}$.



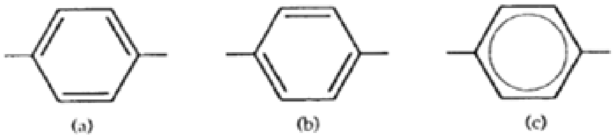
With conductors, at an absolute zero temperature, electrical conductivity is possible because the energy of the electric field alone is sufficient to cause electrons to transition into an excited state.
The conductivity of conductors is excellent at very low temperatures and decreases as the temperature increases.
This is because, on the one hand, the number of free electrons does not vary with temperature,
and on the other hand, their mobility decreases with increasing temperature.

Insulating materials such as polymers are composed of atoms with a complete valence band,
meaning that all energy levels are occupied by an electron

With semiconductors, the width of the band gap corresponds to an energy E close to 1eV.
At room temperature (T°C), some electrons then have the possibility of reaching the conduction band.
These free electrons will allow for low electrical conductivity.
For insulators as well as for semiconductors,
the conductivity will be stronger as the temperature increases
because there will be more jumps to the conduction band.

For the conductivity of polymers, there are two main sources of current conduction: impurities and electron delocalization. Impurities, when they are ionic, will allow the passage of a fairly weak electric current. Electron offshoring is a phenomenon that can be perfectly illustrated with the paraphenylene group:

Double bonds associated with π orbitals can be found at multiple locations within the hexagon (a and b), making it no longer possible to assign the electron of one of these orbitals to a specific pair of atoms; this is known as electronic delocalization. By convention, electronic delocalization is graphically represented by drawing a circle within the hexagon instead of the double bonds (c).



II.2 Factors that influence conductivity in polymers

- **Structure and composition:** Fluoropolymers are considered to be the most insulating. In contrast, polysulfonitride is conductive at room temperature and superconductive below 1.3°K.
- **Additives and impurities:** Additives are usually added in order to increase conductivity. Graphite particles that can be added to any polymer, dopants such as arsenic pentafluoride mixed with polyacetylene and plasticizers are also known to increase conductivity. Impurities are mainly made up of residues from manufacturing aids such as catalysts.
- **Time and temperature:** Conductivity in polymers decreases almost linearly with the time it takes to apply an electric field and increases with temperature.

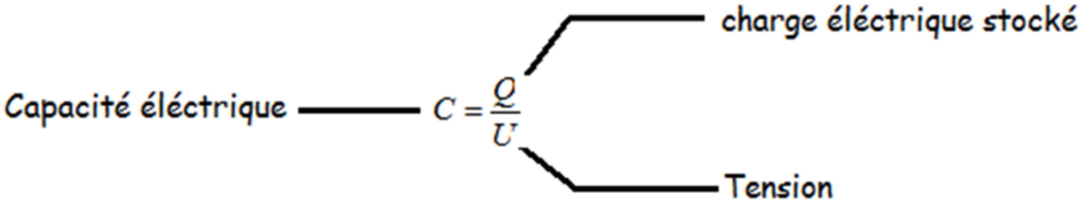
- **Presence of moisture:** Some polymers are known to absorb moisture significantly, leading to a significant increase in conductivity. The combined presence of moisture and a high-voltage electric field can cause the polymer to degrade by hydrolysis. This effect is noticeable with polyesters because hydrolysis causes them to break down into acid and alcohol, which are their two basic constituents.

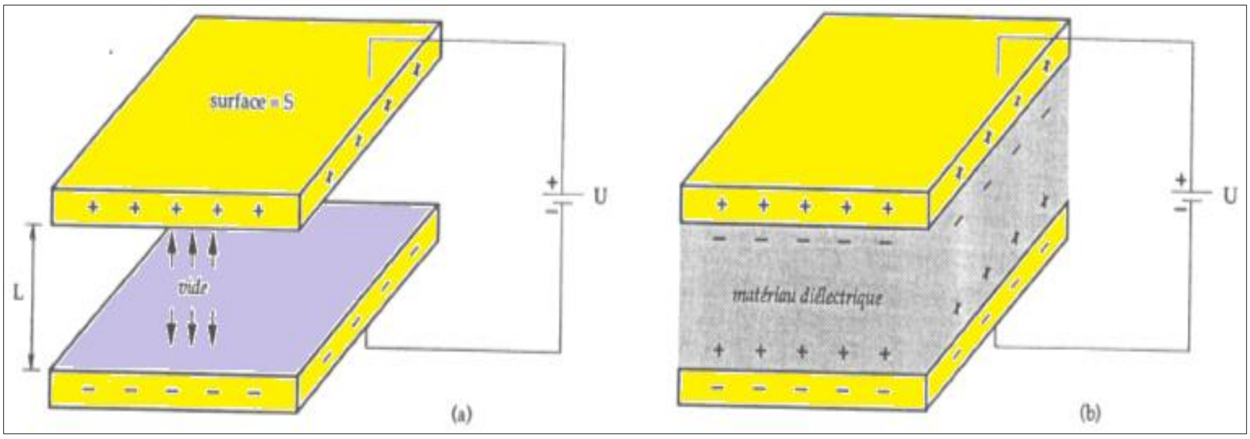
II.3 Dielectric properties

The dielectric properties of a material are essentially estimated by measuring three quantities:

- Dielectric constant,
- dielectric losses,
- dielectric strength.

II.3.1 Dielectric constant





Capacité éléctrique — $C_0 = \varepsilon_0 \frac{S}{L}$

S — surface des plaques

L — distance entre les plaques

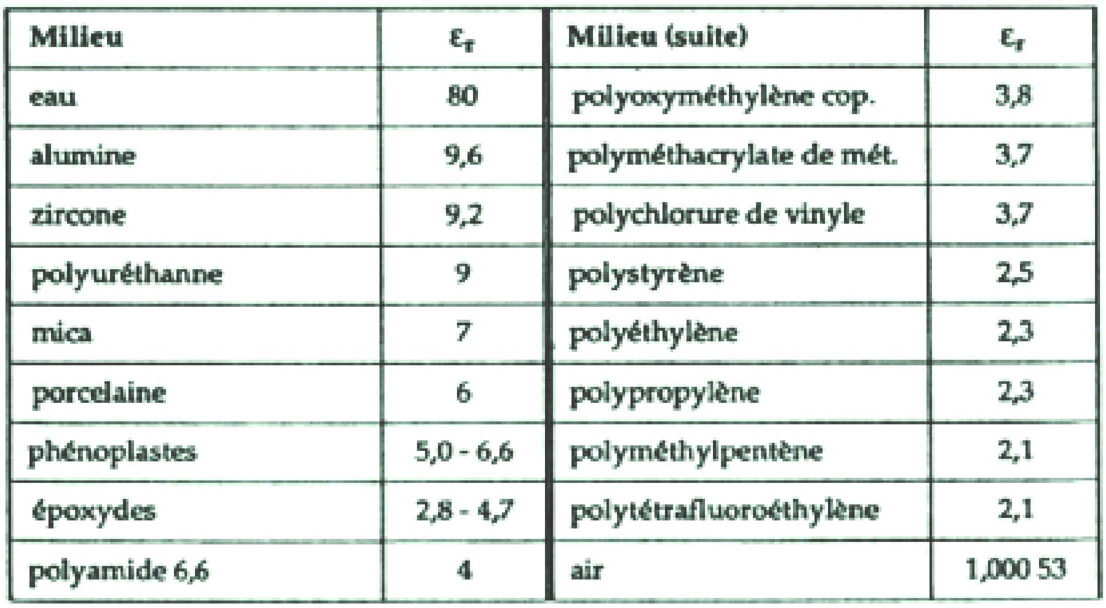
ε_0 — permittivité du vide:8.85*10^{-12} F.m^{-1}

$C = \varepsilon \frac{S}{L}$

ε — permittivité du milieu diéléctrique

constante diéléctrique — $\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$

Constantes diélectriques pour différents milieux à 25 °C

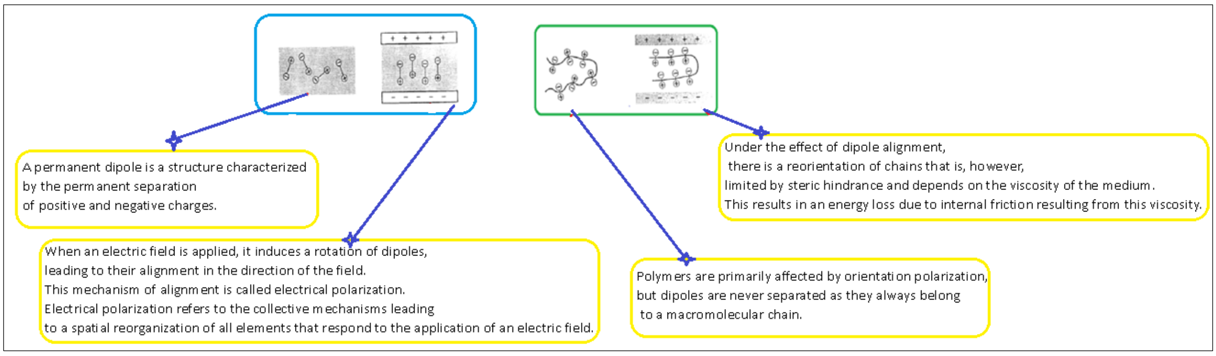


Milieu	ε_r	Milieu (suite)	ε_r
eau	80	polyoxyméthylène cop.	3,8
alumine	9,6	polyméthacrylate de mét.	3,7
zircone	9,2	polychlorure de vinyle	3,7
polyuréthanne	9	polystyrène	2,5
mica	7	polyéthylène	2,3
porcelaine	6	polypropylène	2,3
phénoplastes	5,0 - 6,6	polyméthylpentène	2,1
époxydes	2,8 - 4,7	polytétrafluoroéthylène	2,1
polyamide 6,6	4	air	1,000 53

II.2.2 Dielectric losses (internal friction)

A permanent dipole is a structure characterized by the permanent separation of positive and negative charges. There are four different types:

- electron polarization that causes electron displacements,
- ionic polarization that causes ion displacements,
- orientation polarization which concerns the alignment of the dipoles,
- interfacial polarization, which occurs in the case of two-phase materials (one conductive phase and the other insulating phase).



A permanent dipole is a structure characterized by the permanent separation of positive and negative charges.

When an electric field is applied, it induces a rotation of dipoles, leading to their alignment in the direction of the field. This mechanism of alignment is called electrical polarization. Electrical polarization refers to the collective mechanisms leading to a spatial reorganization of all elements that respond to the application of an electric field.

Under the effect of dipole alignment, there is a reorientation of chains that is, however, limited by steric hindrance and depends on the viscosity of the medium. This results in an energy loss due to internal friction resulting from this viscosity.

Polymers are primarily affected by orientation polarization, but dipoles are never separated as they always belong to a macromolecular chain.

II.2.3 Leakage current

It also contributes to the dissipation of energy. Leakage current is an electrical current that is established due to the presence of electrical charges inside the insulating material. These fillers are mainly ionic impurities and they only play a really important role at high temperatures. In summary, leakage current and internal friction are the two main mechanisms that cause dielectric losses in polymers.

II.2.4 Dielectric strength

When an increasing electric field is imposed on a capacitor, there is a limit beyond which there is a loss of dielectric properties. The material is then conductive and no charge is stored in the capacitor. This limit voltage per unit thickness is called the dielectric strength.

II.2.5 Explanation of the phenomenon of electrical rigidity

When the applied voltage is high enough, a small number of bonds will be broken. This rupture releases electrons that will be accelerated by the field, until they collide with other electrons. They will in turn be freed and so on. This mechanism develops rapidly (chain reaction). This reaction generates a large flow of free electrons, which makes the material conductive. Modern polymers can exhibit a wide variety of special electrical properties such as

- Piezoelectric ;
- Pyro ;
- Ferroelectrics ;
- Triboelectric ;
- Photovoltaic ;
- Photoconductors.

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