

Polymer technology

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Introduction to polymers

The word polymer comes from Greek. It's a compilation of *poly-*, meaning many and *meros* meaning parts. It indicates that we deal with large molecules, or macromolecules.

Their mere size governs how they interact with one another and their neighbours. This is referred to as intra- and intermolecular forces, where covalent bond is the normal intramolecular force that ties the polymers together. Intermolecular forces are what makes the polymers interact with one another. In polymeric materials it is usually van der Waal's (also called London dispersion forces), dipole-dipole or hydrogen bonding.

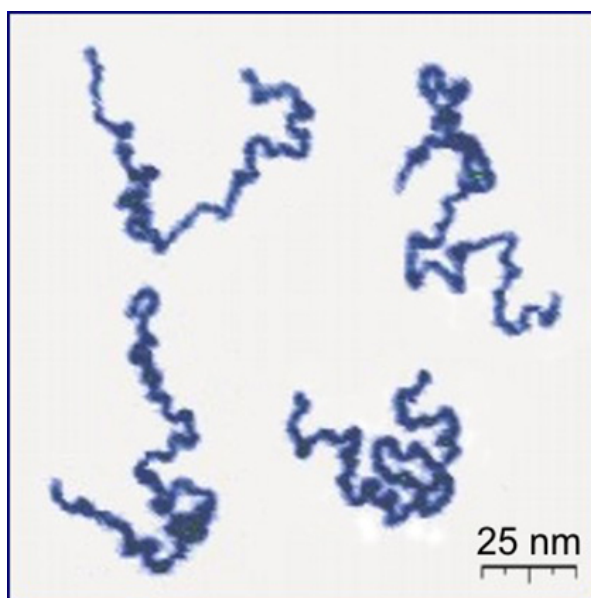


Figure 1: Atom force microscopy image of actual dissolved polymers (Roiter, Y. and Minko, S. AFM Single Molecule Experiments at the Solid-Liquid Interface: In Situ Conformation of Adsorbed Flexible Polyelectrolyte Chains, Journal of the American Chemical Society, vol. 127, iss. 45, pp. 15688-15689 (2005))

[Wikimedia](#) / [CC BY-SA 3.0](#)

[Intermolecular Forces in Polymers](#) (YouTube, 8:05)

[Polymer](#) (Wikipedia)

Task: Seek information on the relative strength of the four forces mentioned in the paragraph above.

[see answer at the end of this resource]

Polymers are by no means a recent manmade invention. Evolution has formed lots of different polymers and continues to do so. Deoxyribonucleic acid, most often abbreviated DNA, that carries information about living matter, is in fact a polymer. There are many other polymers in nature, cellulose in all green plants, proteins in animals, enzymes to facilitate chemical processes, latex from the rubber tree and many more.

You may think that the design of synthetic polymers was inspired by nature, but that was not the case. Rather, chance ruled when rubber was cross-linked by sulphur or when Bakelite was formed by impregnating sawdust with phenol-formaldehyde. It was not until the 1920s that the pioneering work of Hermann Staudinger changed the minds of the scientific community to accept the macromolecular concept. From there on it became essential to be able to define and describe polymers.

There are three key concepts to describe polymers:

- constitution
- configuration
- conformation.

Constitution of polymers

Constitution states what atoms the polymer is made from and how they are arranged in relation to one another. This makes up a repeating unit, which simply describes each polymer's lowest common denominator, e.g. for poly(vinyl chloride), PVC, $-\text{[CH}_2\text{-CHCl]}_n-$ or Polypropylene shown in Figure 2.

The constitution also includes information about the polymer's molar mass and molar mass distribution. It also states if it is a homopolymer, consisting solely from one repeating unit or if it is a copolymer with two or more repeating units. Whether the polymer is linear, branched or cross-linked is also part of its constitution.

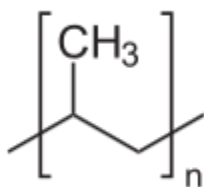


Figure 2. Repeating unit of Polypropylene.

Configuration of polymers

Configuration describes how the repeating units are oriented in relation to one another.

This was set during polymerization. Tacticity is one such parameter. Non-symmetrical repeating units, such as the Propene in Figure 2 can have its substituent, here the methyl group, oriented in different positions. This makes each carbon atom of the polymer with the substituent a chiral centre.

As illustrated in Figure 3 the stretched out polymer has its substituent pointing in either the same direction, which is **isotactic** configuration or in alternating directions which is called **syndiotactic**. If the substituent is randomly orientated the polymer is called **atactic**. Some polymers are also prone to arrange themselves with its substituent on adjacent carbons. This causes a head-to-head coupling.

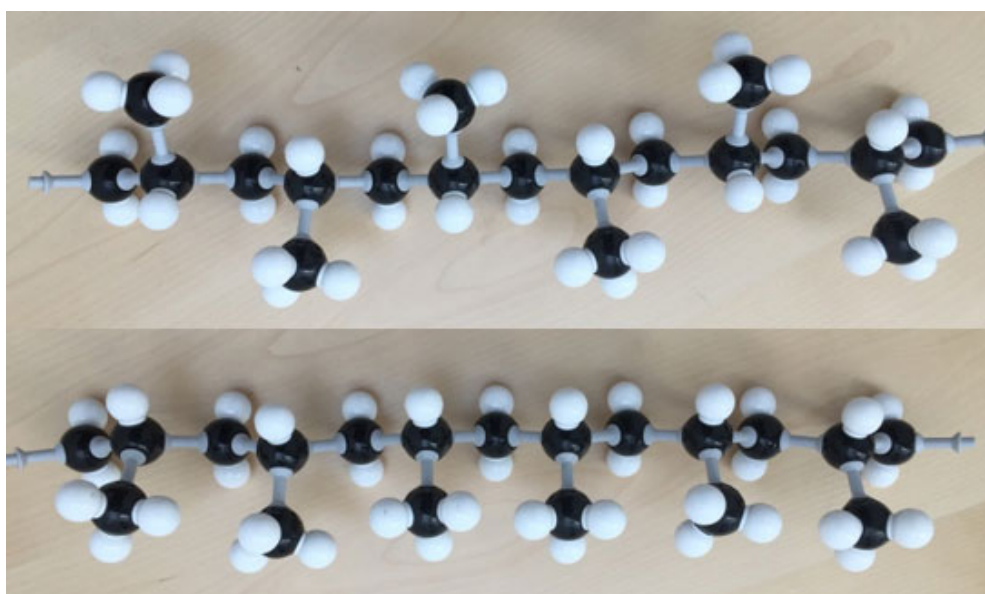


Figure 3. Illustration of syndiotactic Polypropylene, top, and isotactic Polypropylene, bottom
© Anders Persson, University of Borås

Task: Contemplate on the tacticity options for polyethylene, PE, with repeating unit: -
 $[\text{CH}_2\text{-CH}_2]_n$.

[see answer at the end of this resource]

Conformation of polymers

Conformation is the position that each atom of the polymer takes on at a certain given time. In particular the position of atoms on adjacent carbons along the polymer chain, also called backbone, influence what positions that are preferred. The more electronegative and bulky atoms or side groups the more they avoid their proximity. In Figure 4 this is illustrated for a low molecular organic compound.

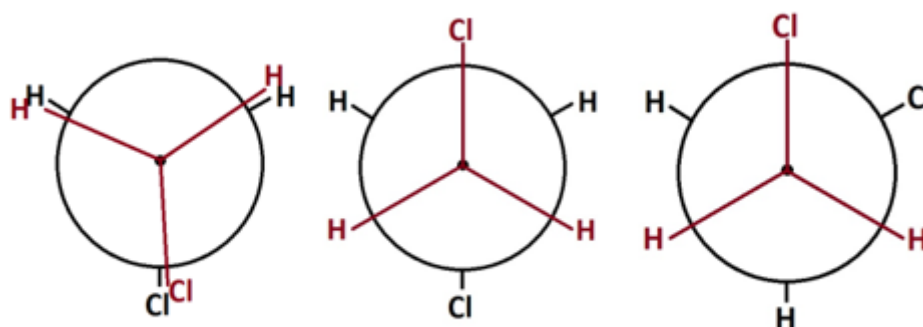


Figure 4. Newman projection of 1,2 dichloroethane molecule in different conformations
 © Anders Persson, University of Borås

The likelihood of taking on the staggered position to the left in Figure 4 drops since a significant energy barrier must be overcome in order to rotate a whole revolution around the two covalently bonded carbons of the backbone. Transferred to a polymer this would give long ranging effects on the preferred overall shape of the whole polymer chain. If a polymer is free to find its preferred conformation it will try to reach its most disordered state. This is governed by the Second law of thermodynamics, which states that nature always moves towards higher entropy. Entropy in polymers can be interpreted as degree of disorder and is one of the major factors that control the behaviour of polymers.

The polymers are constantly moving around. This is called Brownian motion. The higher the temperature the more vigorously the movement becomes. It is just like gas pressure that raises with temperature since the gas molecules increase their velocity with temperature.

Naming of polymers

Polymers are either named according to the monomer that they are polymerized from (e.g. PVC, polymerized from vinyl chloride, $\text{CH}_2=\text{CHCl}$) or they may be named according to functional groups in their repeating unit.

For instance Polyamide, also known by its brand Nylon, has a number of constitutions where the two most common ones are shown in Figure 5 below. The 6 of Polyamide 6 refers to the number of carbons of its repeating unit while the first 6 of Polyamide 66 refers to the number of carbons in between the nitrogens and the second refers to the number of carbons of the rest of the repeating unit.

The [IUPAC](#) rules for naming applies but for these often very complicated molecules this system is not really applicable.

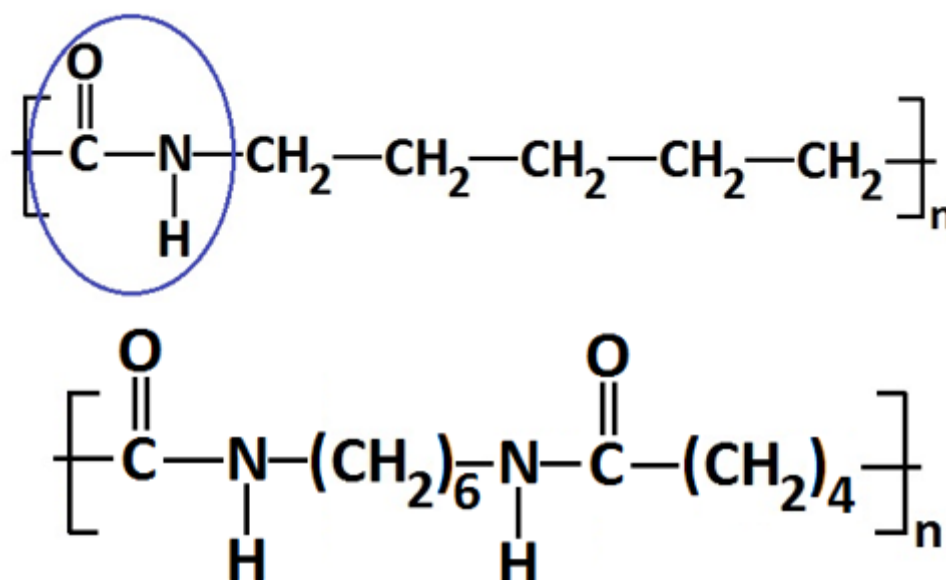


Figure 5. Repeating unit of Polyamide 6 (above) where the amide group is marked with an ellipsoid and Polyamide 66 (below) - Anders Persson, University of Borås

Task: Draw the repeating units of the textile fibre polymers: Acrylic, Polyester and Kevlar.

[see answer at the end of this resource]

Further reading: Study a relevant Polymer Science Textbook such as Young and Lovell *Introduction to Polymers*, 3rd Ed. CRC Press ISBN-10: 0849339294 or a [free on-line textbook such as the one by Mustafa Akay](#) (Download requires significant bandwidth and login).

Molar mass and molar mass distribution

Polymer molar mass and molar mass distribution are essential for many of the physical properties of polymeric materials. They govern their mechanical and processing properties, ability to crystallize, surface energy and density to mention a few. This will be described in more detail further down this module. It takes both quantitative measures and methods to describe molar mass and molar mass distribution.

The molar mass may be quantified by different mean values, of which the two most commonly used are the number-average molar mass, \bar{M}_n , and the weighted-average molar mass, \bar{M}_w . They are defined as:

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} \quad (1)$$

$$\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} \quad (2)$$

The \bar{M}_n is the common average value whereas the \bar{M}_w stresses the high molar mass fraction more. Hence, the \bar{M}_w will be higher than the \bar{M}_n for all non-monodisperse polymer samples. Their ratio \bar{M}_w/\bar{M}_n is actually used as a measure of the molar mass distribution width. It is called PolyDispersivity Index, PDI. The polymer characterization section provides more information on molar mass determination.

Task: Calculate the \bar{M}_n , \bar{M}_w and PDI of a bi-disperse Polyethylene sample consisting of 10 g of 100 000 g/mol and 1.0 g of 10 000 g/mol.

[see answer at the end of this resource]

Polymerization

Polymerization is the process where the polymers are made. They can be divided into two main categories: step-growth and addition polymerisation.

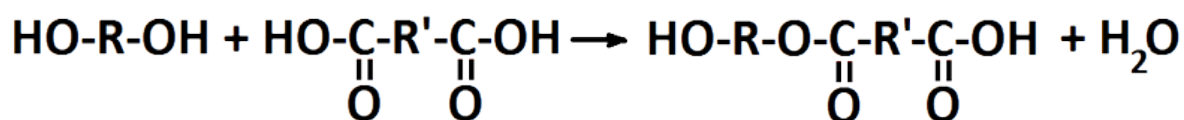
In **step-growth** polymerization, which at first was called condensation polymerization, two different functional groups such as a carboxy acid react with a hydroxyl group to form an ester bond. This is illustrated in Figure 6 on the following page.

Addition polymerization include radical, ionic and coordination polymerization where electrons from double-bond containing compounds are employed to form polymers. These feed stock compounds, often of vinyl type, are called monomers, e.g. vinyl chloride $\text{CH}_2=\text{CHCl}$.

Whereas addition polymerization has the three distinctive steps; initiation, progression and termination that quickly generates a polymer, the step-growth polymerization progresses steadily where the starting compounds first are consumed, forming dimers, then trimers and so on. Hence, the step-growth polymerization needs to reach high conversion for true polymers to be formed whereas addition polymerization may be halted at any time to harvest the formed full-length polymers.

Step-growth polymerization

The reaction between hydroxyl and carboxyl groups to generate an ester bond also gives a bi-product of water. That is why it is called a condensation reaction and it is also an equilibrium reaction that may run backwards, i.e. hydrolysis. In order to give high conversion and M— the water has to be removed.



Ester synthesis from a diol and a diacid where R and R' denotes unspecified organic compounds.

The relation between conversion, p, and degree of polymerization, DP— is described by the Carother's equation:

$$\overline{DP} = \frac{1}{(1-p)} \quad (3)$$

The degree of polymerization is the ratio of \bar{M}_n to the molar mass of the repeating unit M_0 , and p is the consumption of either reactive group, e.g. the hydroxyl groups in the example above. Equation 3 tells that it will take 99 % conversion to reach a degree of polymerization of 100. This is equivalent to a \bar{M}_n of 12 200 g/mol for PA66 shown in Figure 5, which is a reasonable molar mass for that particular polymer.

Task: Make a \bar{M} graph as function of conversion for the PA66 example.

[see answer at the end of this resource]

It is also essential that the molar ratio, r , between the two reactants, for the current example $r = [\text{OH}]/[\text{COOH}]$, is kept very close to one throughout the whole polymerization process. The Carother's equation can be modified to cover also non-unity r values as:

$$\overline{DP} = \frac{(1+r)}{(r+1-2rp)} \quad (4)$$

It may both be difficult to measure very accurately and to find chemicals that are sufficiently pure. Common analytical grades are in general 98.5% pure. The composition of the 1.5% residue is very important to the outcome. Presence of mono-functional compounds will stop propagation.

Task: What \bar{M} can you expect if you try to make PA66 from a 1,6-hexamethylene diamine of 98% purity with 100% pure adipic acid that is totally consumed if you happen to neglect the molar imbalance upon charging?

[see answer at the end of this resource]

There are a number of ways to manage the difficulties of maintaining equimolar ratio in order to reach high molar mass. Interfacial polymerization, salt dehydration, ester interchange polymerization and step polyaddition are examples of such strategies.

Addition polymerization

During addition polymerization monomers are added to the growing polymer one by one. It has three distinctive steps; initiation, propagation and termination. An initiator is formed that attacks a monomer. Depending on the chemical nature of the monomer the initiators may be a radical, a cation or anion. The electronegativity of the monomer determines what

initiator is stabilized. If the monomer has substituents or side groups they govern the preferred polymerization mechanism.

Radical polymerization was the first commercially utilized of the three and it is still used to make the big bulk plastics such as Low-Density Poly(Ethylene), LDPE, PVC, Poly(Styrene), PS and Poly(Methyl methacrylate), PMMA. Heat, radiation or chemical reactions generate two radicals by scission of a labile covalent bond. The radicals then attack double bonds of the two monomers that form monomer radicals that readily attack new monomers. This propagation phase is usually very rapid and short and ends by termination where the radical is extinct by some kind of termination reaction.

Benzoyl peroxide initiation

Radical ethylene propagation steps

Two radicals may react with one another, i.e. combination termination, resulting in one long polymer. The two free electrons may also end up at one of the two radicals to give two polymers where one of them has a double bond at its end. This is called disproportionation. Different polymers are more or less prone to either of the two termination processes. Another termination process of a growing radical is if it is transferred to another species; an initiator, a monomer, another polymer or a solvent molecule. These are all called chain transfer reactions. Thus the polymers' molar mass, molar mass distribution and linearity are determined by their relative rate constants and how they compete with combination and disproportionation. In case of chain transfer to a polymer, i.e. reaction along its backbone it generates a branching point, something that is common for e.g. LDPE. For LDPE the active site may also jump along the growing polymer, so called back-biting, causing further branching.

Task: Draw a graph that shows how the molar mass increases with conversion for step wise and radical polymerization.

[see answer at the end of this resource]

Coordination polymerization

In 1963 German and Italian scientists were rewarded the Nobel Prize for their invention of catalysts with ability to catalyse and coordinate how vinyl monomers such as ethylene and propylene approach the active site. Thereby stereospecific polymers such as isotactic PP, shown in Figure 3, and non-branched polyethylene, HDPE, could be polymerized. Radical polymerization could only render atactic PP and branched LDPE respectively. Since then a new class of coordination catalysts called metallocene catalysts has been developed. Besides exceptional stereo-specificity they can also accomplish block-sequences of different tacticity, e.g. isotactic blocks and atactic ones that alternate and if they are long enough they will phase separate due to their different ability to crystallize.

Rubber elasticity

Elastomers have a unique set of properties: immediate deformation and recovery, fully reversible deformation, and exceptional deformability. The vulcanization process of latex from the rubber tree by sulphur was independently discovered by the American Goodyear in 1839 and the British citizen Hancock in 1843 but it was not until about a century later that the chemistry and physics behind the discovery was revealed. The sparse covalent network that was formed when sulphur linked some of the double bonds of adjacent cis-Polyisoprene polymer molecules together rendered a single molecule with the following features: high molar mass in-between cross-links yet dense enough to restrict flow, high conformational mobility and very weak and intermolecular attraction. Without going into detail about the thermodynamics behind the rubber elasticity, the reader still needs to grasp the concept of order and disorder and that every spontaneous process moves from order to disorder.

Degree of disorder is defined as entropy. When a rubber elastic material is stressed it readily deforms due to the high molecular mobility and the weak intermolecular attraction. In an

ideal elastomer there is actually no difference in intermolecular attraction in the unstressed and deformed state. The deformation stretches the polymers and orients them along the stress direction. With the orientation they become less disordered, or expressed in thermodynamic terms – lower entropy.

As soon as the stress is released the elastomer returns to as disordered a state as possible. Hence, it immediately retracts. The large deformability comes from the scarce cross-linking density that permits a high degree of deformation before the polymers in-between the cross-links become totally stretched out. Most rubbers are in fact quite close to the ideal state.

Task: Search and describe the molecular design strategy behind thermoplastic elastomers.

[see answer at the end of this resource]

Amorphous polymers and the glass transition

The glass transition is when a material changes its conformational mobility drastically. For polymeric materials it takes place at a certain temperature. This temperature, the glass transition temperature, T_g , is linked directly to a coordinated conformational mobility of the polymer back-bone. It has been suggested that it is 20 to 50 repeating units that are thermally activated. This transition can take place in materials without ordered, so called amorphous materials. If the amorphous material consists of a single phase it will be transparent. In semi-crystalline polymers that consist of both crystalline and amorphous phase, the amorphous phase will still have a glass transition. An amorphous thermoplastic will change its Young's modulus about three decades during its glass transition.

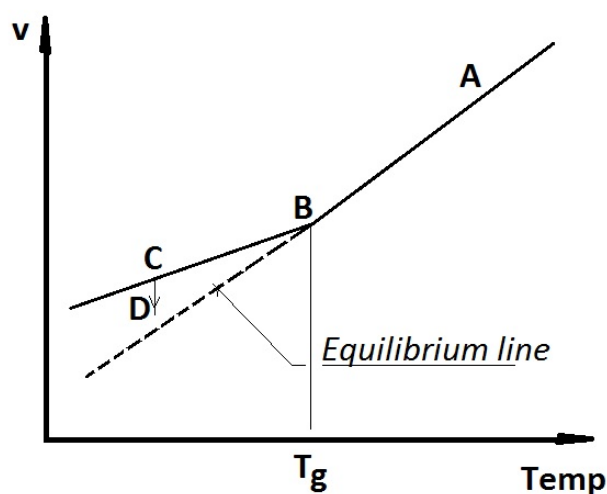


Figure 7. Schematic graph of specific volume - temperature for an amorphous polymer.
© Anders Persson, University of Borås

Each polymer has its own unique T_g . The glass transition is not a primary phase transition, such as melting or vaporisation, hence there is no phase transition heat involved. This makes T_g determination difficult. Changes of physical properties such as shrinkage/expansion, permeability, mechanical properties or cohesive energy density have to be studied. Figure 7 shows how a schematic amorphous material behaves upon cooling from A to B where the shrinkage alters pattern at the T_g . The shrinkage continues at a lower rate from B to C where the cooling is halted. If the temperature is kept constant for prolonged time the material will densify (C to D) since it will try to become as disordered as possible. The atoms will also come closer together. Both these driving forces move the material towards the equilibrium line, which is a continuation of the shrinking line above T_g . The space for conformational mobility decreases. This is often referred to as free volume reduction, which is called physical ageing.

If the atoms that make up the polymeric material come closer to one another it will also give more intermolecular bonds per volume unit, also called the cohesive energy density. Furthermore, the temperature is altered during the measurements and then changes in cooling/heating rate are coupled to the measurement methodology and maybe also other aspects of the method. For instance, the kink in the shrinkage curve of Figure 7 will move to a lower temperature in case it gets more time to take on a more disordered state and higher cohesive energy density. To make it even more complicated upon heating the sample that

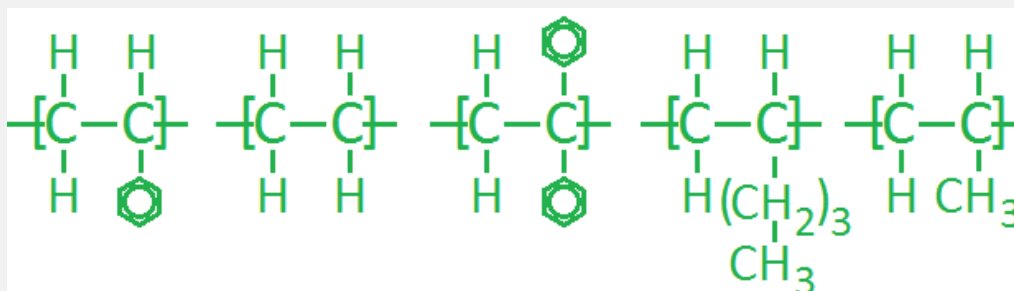
was slowly cooled will register with a higher T_g upon heating since its conformational mobility is restricted by its lower free volume. Hence, text book data on T_g 's can scatter quite significantly.

Polymer constitution is the determining factor for the actual glass transition temperature of a particular polymeric material.

Table 1. Constitutional factors of the polymer repeating unit that:	
raise the T_g	reduce the T_g
<ul style="list-style-type: none"> • Rigid elements of the polymer back-bone such as para-phenylene • Sterically impeding side groups • Ability to form intermolecular attraction. 	<ul style="list-style-type: none"> • Flexible side groups • Symmetrically arranged side groups.

Besides the factors in table 1 there are also a number of parameters that influence the conformational mobility of the polymeric material. The extreme of intermolecular attraction is when they have turned intramolecular, i.e. formation of covalent cross-links in-between polymer molecules. A similar extreme in terms of conformational mobility reduction due to intermolecular attraction is when a polymer crystallizes. Crystallization may take place both of the polymer back-bone or if the side groups are long enough to form crystalline domains by themselves. High molar mass also raises the T_g due to the relative absence of polymer end-groups that facilitate conformational mobility. Low molecular compounds absorbed by the polymeric material will reduce the T_g . They will work as internal grease and are often referred to as plasticizers. In PVC this is utilized to turn a rigid material into something rubberlike.

Task: Sort the following polymers in terms of increasing glass transition temperature.



Suggested order with numbering from left to right:

- 1) 2-4-5-3-1
- 2) 2-5-4-3-1
- 3) 2-5-4-1-3
- 4) 2-4-5-1-3

[see answer at the end of this resource]

Crystallinity and semicrystalline polymers

The driving force behind crystallization is best explained in a thermodynamic context. A polymer will crystallize in case it can form sufficiently strong and frequent intermolecular attractions to compensate for the loss in disorder in the phase transition from disordered to ordered. It is a primary phase transition going from liquid to solid. The change in Gibbs free energy, ΔG , is expressed as:

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

The heat of crystallization, ΔH , which is exothermal, thereby renders a negative value. Also the change of ΔS , where S is a measure of the systems disorder, is negative since crystallization makes the system less disordered. Hence, ΔH has to compensate for the loss of ΔS at a certain crystallization temperature in order to reduce Gibbs free energy. The lower the crystallization temperature, T , the smaller the term $-T\Delta S$ becomes and the potential to reduce Gibbs energy increases. During heating melting of the crystalline structure will occur at a temperature where ΔG equals zero. This constitutes its melting

temperature $T_m = \Delta H/\Delta S$. For polymers with strong and dense intermolecular attraction or for polymers that are rather rigid, thereby do not lose quite as much disorder during their transition they get high T_m 's. For rigid polymers that form strong and dense intermolecular attraction the T_m becomes very high; typical of high performance polymers. It is also that there is a substantial margin between the T_m and T_g to enable the necessary polymer diffusion for crystallization to take place. As a rule of thumb the highest crystallization rate is accomplished right between the T_m and T_g , i.e. $(T_m+T_g)/2$.

A crystalline structure can be described by an ordered 3D structure where, in this case the polymer has arranged itself. The smallest common denominator can be described as a unit cell usually in the form of a cubic, rhombic or distorted rhombic configuration. They take on the configuration that enables the most intermolecular bonds. This may be associated with all-trans or perhaps a helix- conformation. Depending on the degree of supercooling and the cooling-rate during crystallization they will form lamellas of varying folding length. As illustrated in Figure 8 the ordered sequences are linked to amorphous sequences. A polymer can never be completely crystalline, hence they are called semicrystalline. Since the polymer may start to crystallize at more than one spot at once, their diffusion will be restricted.

[Polymer crystallization](#) (YouTube, 0:16)

Even if very high degree of crystallinity can be accomplished upon precipitation of a polymer solution they always contain end groups that affect the crystallization. This is also the case upon crystallization from the molten state. Hence, polymers with a lot of end-groups, which is found for low molar mass linear and for branched polymers renders low degree of crystallinity. Also in cases of very high molar mass polymers the number of entanglements will reduce polymer diffusion needed to accomplish high the degree of crystallinity. Hence there is an optimum in terms of molar mass and thermal history for each polymer.

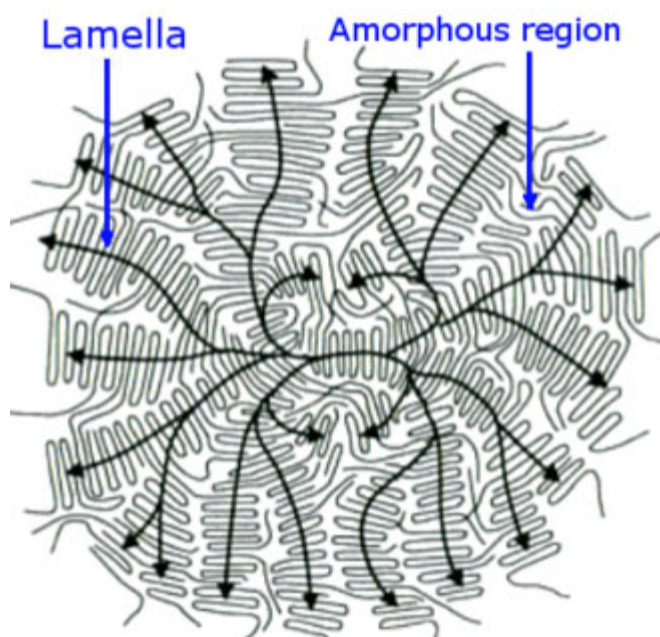


Figure 8. A schematic spherulite of a semicrystalline polymer. Arrows indicate where it was nucleated and how it grew. [Materials scientist at Wikimedia](#) / [CC BY-SA 3.0](#)

Task: How can you easily determine whether a polymeric material is semicrystalline or amorphous?

1. It floats in water.
2. It is really brittle.
3. Its mix of crystalline and amorphous domains makes it opaque or even white.
4. It is completely transparent since it's semicrystalline.

[see answer at the end of this resource]

Polymer analysis and characterization

Polymers may be analysed and characterized by many different means. Methods may be based on physical properties such as response to waves that may be spectroscopic or mechanical, microscopy, solution properties or thermal characteristics.

Spectroscopic methods are based on interactions between the samples and waves of different frequency and intensity. Commonly used spectroscopic methods include Fourier Transform Infrared Spectroscopy, **FTIR**, where infrared light is absorbed by different parts of

polymer functional groups. It is the different covalent bonds that absorb infrared light. Fingerprints for each individual polymer can be compared to tabulated standard spectra in order to identify polymers. The method is sensitive enough to reveal effects of thermal or chemical manipulations.

Nuclear Magnetic Resonance, **NMR**, is another spectroscopic method that can reveal structural details about the polymers such as presence and degree of branching, head-to-head coupling, cross-linking and even degree of crystallinity. Determination of the crystalline unit cell is best determined by Wide Angle X-ray Scattering, **WAXS**, while e.g. interlamellar distances may be determined by Small Angle X-ray Scattering, **SAXS**. WAXS can also be used to determine the degree of crystallinity in a semicrystalline polymer sample.

Another method, which is very versatile, Differential Scanning Calorimetry, **DSC**, can also be used to determine the degree of crystallinity as the ratio of the sample's endothermal of melting to the endothermal of the perfect crystal. However, this requires knowledge of the sample's identity and also that the crystallinity does not change during heating up to the temperature where melting starts. DSC also provides T_g data and the crystallization can be studied. A small sample is put in an aluminium pan that is sealed and put on a heating plate. An empty and sealed pan, put on another heating plate is used as a reference. The two pans, either kept in the same or separate ovens, are then kept at the same temperature and the energy needed to accomplish that is registered upon temperature manipulation. Examples of such manipulations are shown in Figure 9 where the T_g is revealed together with the T_m and crystallization temperature T_c and the heats of melting and crystallization.

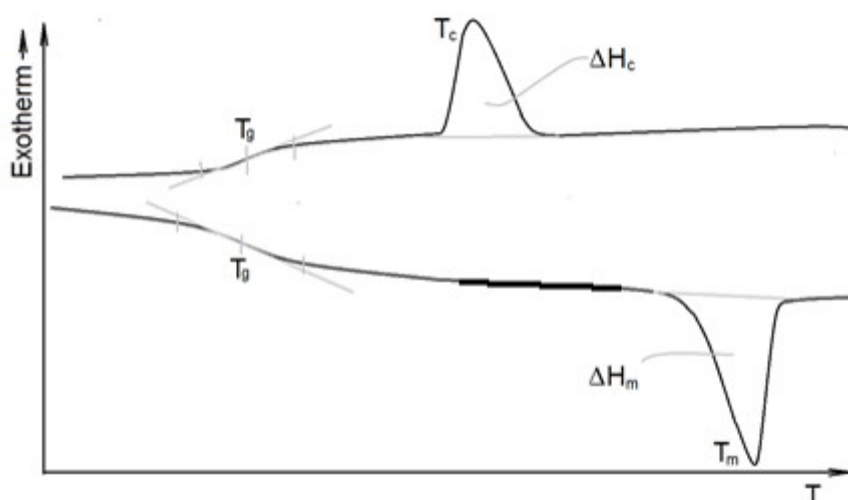


Figure 9. Schematic DSC thermographs of a semicrystalline sample that has been through a heating and a cooling ramp

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In cases with samples of low conformational mobility, such as highly crystalline ones, the glass transition may be difficult to detect since the step of altered thermal conductivity seen in Figure 9 becomes insignificant. In that case other methods may be called upon. One such method which is related to the glass transition is Dynamic Mechanical Thermal Analysis, **DMTA**, where a sample is harmonically deformed and the time lag between applied stress and deformation is monitored as a function of temperature. It is the polymeric materials' viscoelastic properties and their temperature dependence that is registered. More on this is presented in the section on Mechanical properties and viscoelasticity below. That section will also contain information about tensile testing. Thermal Gravimetric Analysis, **TGA**, is basically a very sensitive balance contained in an oven with an atmosphere that may be inert or oxidising. In this way volatile components of the samples may be quantified and thermal decomposition kinetics can be described.

It is also essential to have quantitative data on molar mass and molar mass distribution of linear and branched polymers. There are a few options to measure that but the dominating one is Size Exclusion Chromatography, **SEC**. A diluted polymer solution is injected into a porous column that is flown through by a liquid mobile phase that will bring the dissolved polymers through the column until detected after the column. Higher molar mass also means bigger volume in the solution and the bigger the polymer coils, the fewer column pores will be big enough to contain them and thereby slow them down through the column.

Thus the biggest polymers come first and the smallest at the end. A series of well-known molar mass references are utilized to make up a calibration curve to relate the actual samples to.

There are several other characterization techniques that cannot be covered here. Examples of those are different microscopic techniques, density measurements, permeability, dielectric properties, heat and electrical conductivity, etc.

Task: Imagine that you need to determine what polymeric material a specific artifact is made from. What non-destructive method would you choose?

1. DSC
2. DMTA
3. NMR
4. FTIR

[see answer at the end of this resource]

Mechanical properties and viscoelasticity

One of the big advantages of thermoplastic materials is that they enable shaping into very intricate geometries in a single operation, for instance by injection moulding. In order to save material and to keep process cycle times as short as possible, i.e. required cooling time, the dimensions of the products should be minimized at all times. However, to make sure the product will withstand the loads and deformation it will face in service, it must be possible to simulate the stresses and strains generated and to compare these to tabulated mechanical properties data. Primarily there is a need to quantify tensile and shear properties but also long term data are highly relevant to judge whether or not the product will fulfil its requirement specification. Polymeric materials most often have time dependent mechanical properties. This is called viscoelasticity, which may be linear or non-linear. The former case is valid up to the point where also stress dependence appears. Above that stress the attainable simple and robust linear viscoelastic models lose validity.

Tensile testing is the most common and convenient way to determine a material's short term mechanical properties. A sample with a uniform cross sectional area is clamped at a certain distance between clamps that are pulled apart with a linear velocity while registering force [N], elongation [ΔL] and contraction [Δt] using load cell and extensometers respectively. These parameters are normalized by dividing the force by cross-sectional area to get the normal stress, σ_0 , and the elongation by the original length to get the normal strain, ϵ . By the use of Hook's law, Eq. (6) the Young's modulus can be determined.

$$\sigma = E \cdot \epsilon \quad (6)$$

Based on the transverse strain also the Poisson's number, ν , can be determined. From the Young's modulus and the Poisson's number also the shear modulus, G , may be calculated from equation (7).

$$E = 2G(1+\nu) \quad (7)$$

The Poisson's number is in the range of 0 to 0.5 where the upper limit, only found in rubber, means that there is no volume change. For all other materials a deformed sample increases its volume. Figure 10 illustrates a schematic tensile testing graph of a typical ductile polymeric material. From the linear initial part of the curve the Young's modulus can be determined. The ultimate stress and strain are given by the curve end-point while the yield stress is where the initial linear part levels off and the sample starts to deform permanently.

Thermoplastic polymers, as their name indicates, are highly sensitive to temperature and go through a number of stages as illustrated in figure 11. At low temperature, indicated by I in the figure, is the glassy state, II – the transition zone with T_g at the inflection point, III – the rubbery plateau and finally IV – the viscous zone. Each material has its characteristic figure 11-type curve and there are also structural and morphological factors that alter its appearance. Higher molar mass extends zone III to higher T . The drop of E in the transition zone, which for an amorphous polymeric material is about 1000 times, is less and less pronounced with increasing degree of crystallinity. A similar pattern is seen with increasing degree of cross-linking.

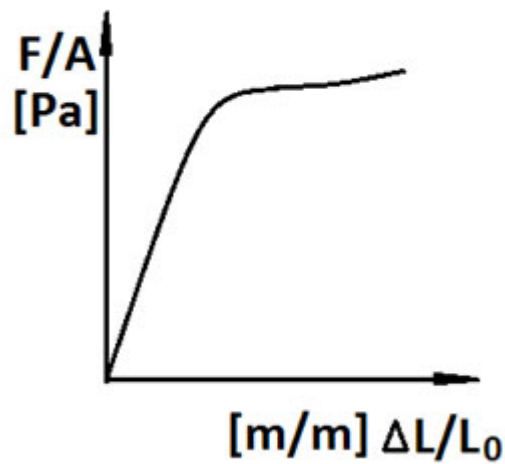


Figure 10. Schematic stress-strain curve from tensile testing © Anders Persson, University of Borås

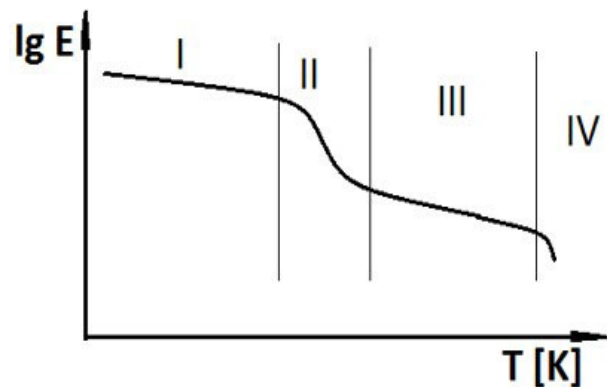


Figure 11. Schematic temperature dependence of Young's modulus for an amorphous thermoplastic material © Anders Persson, University of Borås

Task: Find approximate Young's modulus values of HDPE, PET (bottle and fibre) and Kevlar.

[see answer at the end of this resource]

The pattern seen in Figure 11 may actually also be attained by exchanging the temperature for loading time. This is a manifestation of viscoelasticity and is based on the fact that deformation depends upon conformational rearrangements and with time the likelihood that the polymers will move in a way that releases stress. Accordingly harmonic loads of different frequencies will follow a similar pattern since frequency is reciprocal time, i.e. low frequency is equivalent to long loading time.

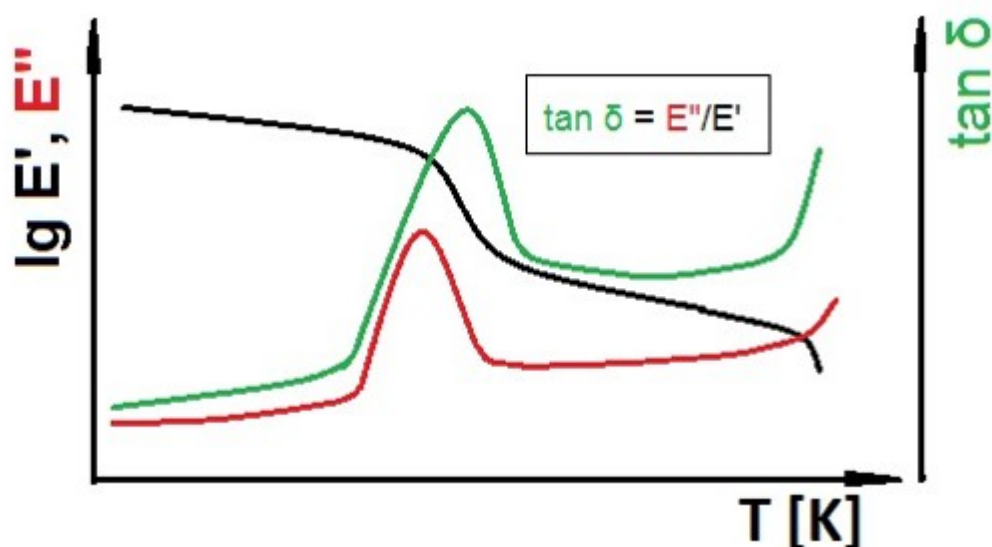


Figure 12. A schematic illustration of DMTA data
© Anders Persson, University of Borås

A very powerful way to describe viscoelasticity and thermal behaviour is DMTA. It is based on the fact that the response to an applied stress will cause a deformation time lag for a viscoelastic material. Alternatively, a deformation is applied and the stress will lag behind in the same way. By this methodology the storage modulus (in phase with the applied stimulus), E' and the loss modulus (half a cycle behind the stimulus), E'' can be determined. Furthermore, the ratio of E''/E' , which in vectorial terms becomes $\tan \delta$. The vectorial sum of E' and E'' , becomes E^* , which is the normal E that a material responds by without any details on lag effects.

As shown in Figure 12 the $\tan \delta$ peak is very pronounced and it is related to the T_g . There is no consensus what should be the designated parameter for the T_g , the E' inflection point, the E'' or $\tan \delta$ peaks. They are all also both frequency dependent and heating rate dependent. A further limitation of DMTA is that it requires mechanical integrity of the samples. Thus, T_g is difficult to study for a completely amorphous sample. Accordingly the melting of a semicrystalline sample is not attainable unless it is also cross-linked or contains some other kind of reinforcement.

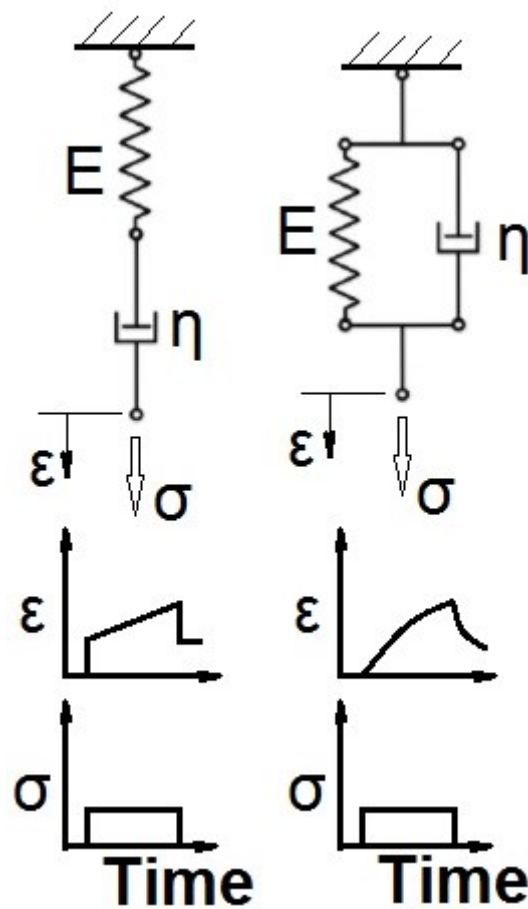


Figure 13. Schematic description of Maxwell (upper left) and Kelvin-Voigt (upper right) viscoelastic models and descriptions of their strain responses to creep © Anders Persson, University of Borås

Other commonly used manifestations of viscoelasticity are creep and stress relaxation tests.

During a creep test a sample faces a constant stress and the strain is monitored while a stress relaxation test means that a sample is faced by an immediate deformation followed by stress monitoring.

There are two simple mathematical models that can mimic these responses where the Kelvin-Voigt best mimics the creep behaviour while the Maxwell best describes stress relaxation. Both models are presented in Figure 13. Figure 14 illustrates the response to a stepwise strain and how the stress in the sample levels off. After a certain time denoted τ , the relaxation time has been reached, which equals the ratio of the dash-pot viscosity η to the Young's modulus E as $\tau = \eta/E$.

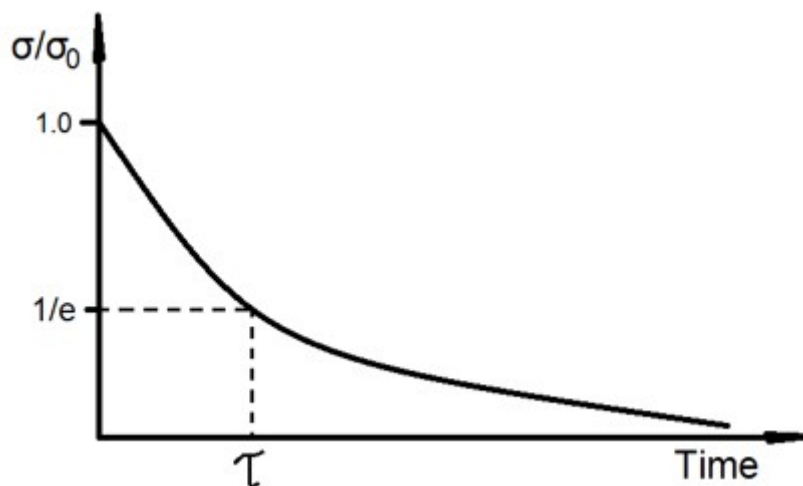


Figure 14. Schematic relaxation curve described by the Maxwell model

© Anders Persson, University of Borås

Mathematically the Kelvin-Voigt and Maxwell models for creep and stress relaxation may be expressed as:

$$\varepsilon = \sigma_0 E (1 - e^{-Et/\eta}) \quad (8)$$

$$\sigma = \sigma_0 e^{Et/\eta} \quad (9)$$

As seen from equations 8 and 9 the parameters are exactly the same. This means that it is enough to conduct one of the two tests in order to be able to predict the other one.

Task: Give a real life example of a situation where a textile faces creep and one example of a stress relaxation situation.

[see answer at the end of this resource]

A polymeric material that has reached the viscous state, zone IV in Figure 11 has lost its mechanical integrity and is now considered a fluid with mainly viscous behaviour. The Kelvin-Voigt and Maxwell models are still valid but with significantly shorter relaxation times than in the solid state. Hence it is more relevant to use a purely viscous fluid as a starting point, i.e. a model with only a dash-pot and also to emphasise shear flow rather than tensile. The stress-deformation behaviour depends on the shear rate, $d\gamma/dt$, a fluid experiences in accordance with equation (10).

$$\tau = \eta \cdot d\gamma/dt \quad (10)$$

Observe that τ denotes shear stress, NOT relaxation time, while $\dot{\gamma}$ is the shear angle and its time derivative is how quickly the angle changes, i.e. $d\gamma/dt$. A fluid that obeys equation (10) is called a Newtonian fluid and has a viscosity, η with unit [Pa s] that is constant at all shear rates. This is rarely the case for polymers that have tendencies to align along the flow field, which causes a viscosity drop since they slide more easily along one another than when they are randomly distributed. Such behaviour is referred to as shear thinning.

Task: Water has a viscosity at room temperature of about 1 mPa s. How does that compare to olive oil and LDPE at 210°C?

[see answer at the end of this resource]

Plastics = Polymers + Additives

Polymers are rarely used as they are directly from polymerization. In order to fulfil functional and aesthetic requirements there is need for thermal stabilizers, antioxidants, UV protectors, lubricants, plasticizers, flame retardants, fillers and reinforcements, colorants and other additives. These additives cause a dilemma. While extending the lifetime of the products, which is good from a sustainability point of view, they may also cause health issues during service and environmental end-of-life challenges and may consume non-renewable resources such as phosphorous for flame retardancy. There are definite challenges for the plastics value chains to manage these issues.

Task: Tyres for the automotive sector are a really big product. How come all tyres are black? What additive makes them black and why is it there?

[see answer at the end of this resource]

Polymeric processing

Thermoplastic processing is dominated by the Archimedes screw, which is a long screw, fitted in a pipe and used to pump liquids, slurries, sewage and other difficult media. For thermoplastic purposes the screw is tightly fitted in a temperature controlled extruder

barrel fed by plastic granules from a hopper and the plastic is heated by the kneading action of the screw combined with external heating of the extruder barrel.

In order to create pressure in the extruder the pitch height of the screw is reduced along the screw from the feeding zone to the melt zone and to the metering zone. For an extruder, the cylinder barrel ends in a filter package and a die to shape the extrudate. This creates a back pressure that helps to melt and homogenize the plastic material. Injection moulding is also based on the Archimedes screw with the added feature to stop the screw and move it axially forward to push molten plastic into a mould in order for it to cool down and take on the shape dictated by the mould cavity.

[Extruder Operation and Control](#) (YouTube, 1:53)

[Injection Moulding Animation](#) (YouTube, 2:58)

The shape of the extruder die determines the shape of the extrudate that may be further manipulated by, for instance, an inner air pressure of a tubular extrudate to make plastic film or by pulling of the multifilament that comes out during melt spinning in order to orient the polymers for improved strength and stiffness. Blow moulding is an intermittent technique used to make hollow objects such as bottles that share some elements of the extrusion process. During the intermittent processes where the screw is moved axially in order to push molten plastic out, there are possibilities and limitations to the process cycle. In particular the injection moulding cycle is rather special. Once the mould is filled, the material shrinks during cooling. In order to handle that shrinkage and make sure the mould is properly filled every time, additional material is squeezed in by overfilling it by adding an after pressure that compresses the molten plastic. A molten plastic is, unlike most low molecular fluids, actually compressible.

[Blown Plastic Sheet Film Process](#) (YouTube, 3:24)

[Blow Moulding](#) (YouTube, 4:57)

[Injection Moulding - Optimizing An Efficient Injection Moulding Cycle](#) (YouTube, 1:46)

Once the mould inlets have solidified it seals the mould and filling of new granules into the screw channel can start while the moulded object continues to cool and be ready for ejection. The limiting factor here is the cooling phase from injection to ejection and it

depends highly on the chosen material. This is affected by the temperature the material has to cool from until it is solid enough for ejection and also whether it crystallizes, a process that requires management of both the exothermal crystallization and cycle time. Plastics are also very poor thermal conductors. If it is possible to choose an amorphous plastic it will usually offer the most attractive process calculus.

There are many other thermoplastic, thermosetting and rubber processes that cannot be covered here.

Task: If you are facing difficulties to fill the mould during injection moulding – how do you value the following options?

1. Turn up the heat of the barrel.
2. Turn up the heat of the nozzle.
3. Increase the rotational speed of the screw.
4. Heat up the mould.
5. Increase the injection rate.

[see answer at the end of this resource]

Polymeric materials and sustainable development

Plastics have a significant stigma to handle as a symbol of products that are used once and immediately discarded – the western way of life without modesty and respect for nature. Plastic products also end up in nature where they harm wildlife and oceans. Their low density and durability are both factors that make plastics a plague.

This is such a paradox since a plastic object, with its low weight, good strength and durability can save a lot of energy if it is used for its full lifetime in suitable applications. Its excellent barrier properties are also important in prolonging the lifetime of groceries and its use in wrapping and trays can save fruit and vegetables from being hurt during transports and so on.

There are two major challenges that need addressing to mitigate the negative impact of polymeric materials. First, the linear economy must become circular for the materials to be

utilized more than once. Here the waste pyramid should be the guiding star meaning that the first option should always be to reuse an object and so on down the steps of the pyramid. Secondly polymers should be based on renewable raw materials rather than fossils. It is up to all producers to consider end-of-life aspects during their design phases. Also consumers need to exert their power by selecting conscious products. This goes for plastic products as well as textiles, which is a fast growing environmental issue. Next to housing, traveling and food, textiles is the fourth most CO₂ intense group of products in Sweden today.

[How the oceans can clean themselves: Boyan Slat at TEDxDelft](#) (YouTube, 11:21)

Task: What strategies are at hand for plastic sorting to enable efficient recycling?

[see answer at the end of this resource]

Answers

Introduction to polymers

Seek information on the relative strength of the four forces mentioned in the paragraph above.

Answer: Covalent (C-C) about 350 kJ/mol, H-bond: 20 kJ/mol, Dipole: 2 kJ/mol, vdW: 2 kJ/mol.

Configuration of polymers

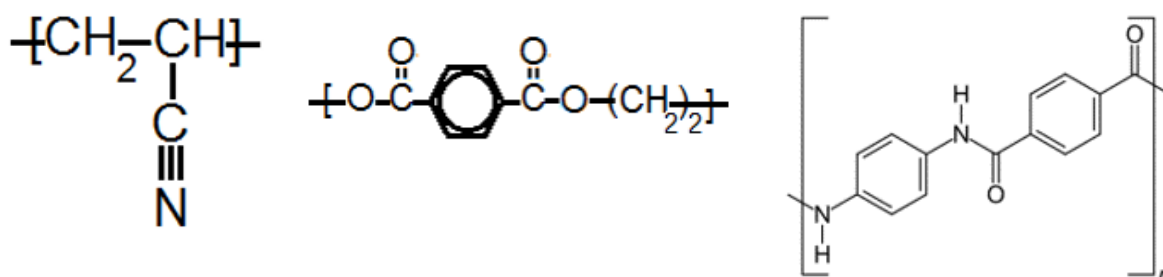
Contemplate on the tacticity options for polyethylene, PE, with repeating unit: $-\text{[CH}_2\text{-CH}_2\text{]}_n-$.

Answer: Since PE does not carry any substituents tacticity is not relevant.

Naming of polymers

Draw the repeating units of the textile fibre polymers: Acrylic, Polyester and Kevlar.

Answer:



Images 1 and 2 by Anders Persson, University of Borås, image 3 - [Wikimedia/public domain](#)

Molar mass and molar mass distribution

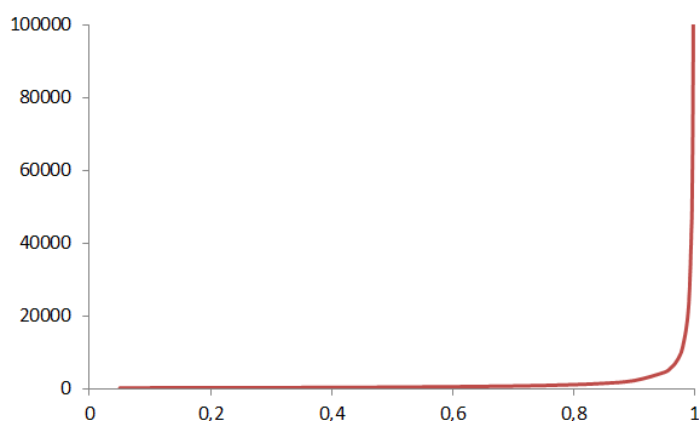
Calculate the \bar{M}_n , \bar{M}_w and PDI of a bi-disperse Polyethylene sample consisting of 10 g of 100 000 g/mol and 1.0 g of 10 000 g/mol.

Answer: $\bar{M}_n = 5.5 \cdot 10^4$ g/mol, $\bar{M}_w = 9.2 \cdot 10^4$ g/mol, and PDI = 1.7

Step-growth polymerization

Make a \bar{M} graph as function of conversion for the PA66 example.

Answer:



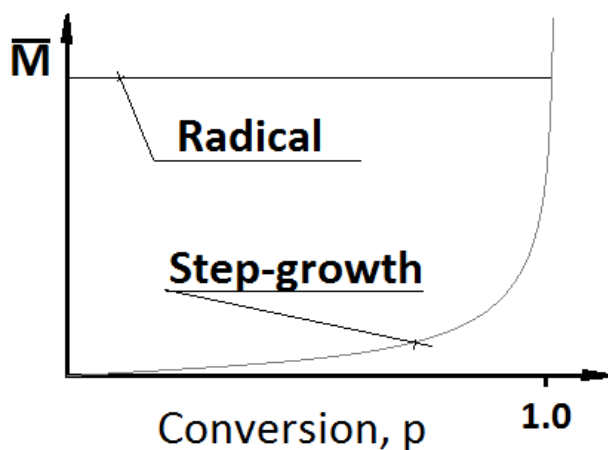
What \bar{M} can you expect if you try to make PA66 from a 1,6-hexamethylene diamine of 98% purity with 100% pure adipic acid that is totally consumed if you happen to neglect the molar imbalance upon charging?

Answer: $DP = \{p = 1, \text{ in equation (4)}\} = (1 + r)/(1 - r) = \{r = 0.98\} = 1.98/0.02 = 99$ and the molar mass of the repeating unit of PA66, $M_0 = 226.32 \text{ g/mol}$ gives \bar{M}_n of 22 kg/mol. Comment: This is a purely theoretical exercise, the conversion p will never be 100%.

Addition polymerization

Draw a graph that shows how the molar mass increases with conversion for step wise and radical polymerization.

Answer: The graph shows how the mean molar mass increases for the polymeric molecules that are formed as a function of conversion for radical and step-grown mechanisms.



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Rubber elasticity

Search and describe the molecular design strategy behind thermoplastic elastomers.

Answer: A three-block copolymer with a long middle block of high conformational mobility at its intended use temperature while the outer shorter blocks should be made out of polymers that are rigid at use temperature. The two different polymers should also be chemically different in order to separate from one another.

Amorphous polymers and the glass transition

Sort the following polymers in terms of increasing glass transition temperature.

Answer: Option 1 is the correct answer since: 2 the lowest since no substituents, 4 lower than 5 due to its flexible side group, 1 and 3 have sterically hindering side groups where the symmetrical side groups reduce the T_g.

Crystallinity and semicrystalline polymers

How can you easily determine whether a polymeric material is semicrystalline or amorphous?

Answer: Answer 3 is correct. As long as the crystal domain size is bigger than $\frac{1}{4}$ of the light wave length the density difference between the two phases will fracture light.

Polymer analysis and characterization

Imagine that you need to determine what polymeric material a specific artefact is made from. What non-destructive method would you choose?

Answer: Answer 4 is correct. It is the only non-destructive option of the four.

Mechanical properties and viscoelasticity

Find approximate Young's modulus values of HDPE, PET (bottle and fibre) and Kevlar.

Answer: HDPE = 1.0 GPa, PET = 3.1 and 12 GPa for bottle and fibre grade, Aramid = 100 GPa.

Give a real life example of a situation where a textile faces creep and one example of a stress relaxation situation.

Answer: Creep may occur for instance on a sail of a sailing boat and a stress relaxation situation may occur when a pair of trousers are stretched over the knees during kneeling.

Water has a viscosity at room temperature of about 1 mPa s. How does that compare to olive oil and LDPE at 210°C?

Answer: Olive oil at room temperature = 60 mPa s, LDPE at 210°C = 400 Pas.

Plastics = Polymers + Additives

Polymer technology

Tyres for the automotive sector are a really big product. How come all tyres are black? What additive makes them black and why is it there?

Answer: The additive is carbon black (incompletely combusted carbon) that blocks UV light from causing oxidation at the tyre's inner parts, adds wear resistance, improves conductivity and regulates the Young's modulus.

Polymeric materials and sustainable development

What strategies are at hand for plastic sorting to enable efficient recycling?

Answer: There are not yet any commercial automatic sorting technologies available.