Crystallization and Crystallinity

❖ Factors influencing the melting temperature

The melting temperature of polymers is not a fixed constant, in contrast to that of small molecules. For polymers it is influenced by various aspects of the composition of polymer as well as the thermal history of the material. The significant parameters are discussed in detail on the basis of the following points of view:

1. **Conditions of crystallization**
2. **Branching**
3. **Tacticity**
4. **Chain flexibility**
5. **Symmetry**
6. **Interactions between chains or chain segments**
7. **Co-monomers**
8. **Molar mass**

1. <u>Conditions of crystallization:</u>

As a rule of thumb, polymers can crystallize in a temperature range from at least 30 °C above the glass transition temperature to at least 10 °C below the melting temperature. At temperatures that are too low, the mobility of the chain segments is insufficient to allow crystallization. At temperatures that are too high, the segments are too mobile for any crystallization to take place.

Because of the entanglement of polymer chains with one another, polymers, in principle, crystallize relatively slowly, especially when compared to most small molecular substances. Thus, it is possible to control the degree of crystallization by adjusting the rate of cooling. As a general rule, very rapid cooling does not give the polymer enough time to form a highly crystalline material. Indeed, by cooling a polymer extremely rapidly it is even possible to quench polymers that would normally crystallize into a completely amorphous state.

Rapid cooling leads to the formation of a large number of small crystals. Small crystals have a large surface to volume ratio and thus have a relatively large surface energy. As a result, small crystals are energetically disadvantaged in comparison to large crystals. This leads to their melting at comparatively low temperatures. Rapid cooling thus leads to the melting temperature being reduced by up to 30°C. It also leads to polymers with a broad melting range because crystals of very different sizes form, each of which have their own unique melting temperature. If the rate of cooling is

slower, this effect is less developed and the melting range is narrower and more easily defined.

2. Branching:

A compact, branched side group generally leads to a stiffening of the polymer chain and creates an increase in the melting temperature because of the effects that have been explained above (crystallization entropy) (**Fig. 1**).
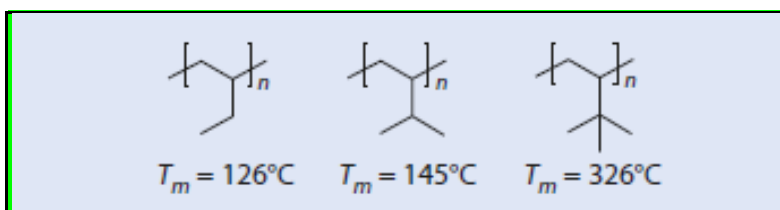

$T_m = 126°C$ $T_m = 145°C$ $T_m = 326°C$

Fig. 1: *Effect of different branching of side chains on the melting temperature*

In contrast to this, long, flexible side chains interfere with the crystal lattice, and thus cause the melting temperature to sink. An example of this can be found in the isotactic α-polyolefins, where the melting temperature drops from polypropylene to poly-1-pentene (**Table 1**). Initially, the melting temperature continues to drop with increasing side chain length. However, after a certain length, it increases again, slightly. This can be observed for side chains that are longer than eight methyl units long, such as poly-1-decene. The reason for this is the increasing influence of the side chains to crystallize on the conformation of the main chain.

Table 1: Influence of length of the side chain on the typical melting temperatures of isotactic α-polyolefins

∞-Polyolefin	Melting temperature T_m(°C)
Polypropylene	170
Poly-1-butene	126
Poly-1-pentene	80

Branching in the main chain also leads to a lowering of the packing density. This lowers the crystallization enthalpy and thus also the melting temperature. Good examples of this are the various branched polyethylenes. Ethylene can be polymerized,

using radical polymerization, to a relatively highly branched material, so called *low-density* polyethylene (PE-LD). This material has a melting temperature of 110 °C, whereas *linear-low-density*-polyethylene (PE-LLD) produced by transition metal catalysis, which has a lower degree of branching, only starts to melt at a higher temperature of around 122 °C.

3. Tacticity

Isotactic polymers usually arrange themselves into helical superstructures so as to minimize the steric interactions between the substituents. In such helical structures, main chain substituents are so arranged as to point away from the helix. The helices themselves are then arranged in the crystal structure in a regular fashion.

In the case of syndiotactic polymers, the main chain substituents are further apart from each other and the main chain takes on a zig-zag conformation (**Fig. 2**). As a general rule, atactic polymers cannot crystallize because of their irregular structures. Because of this, atactic polystyrene (R = C_6H_5) is amorphous, whereas isotactic and syndiotactic polystyrene are crystalline and melt at 240 °C and 270 °C, respectively.
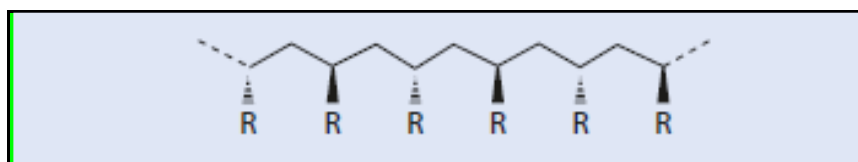

Fig. 2: Zig-zag conformation of a syndiotactic polymer

4. Chain flexibility

The flexibility of the polymer chain has a substantial influence on its crystallization entropy. As has already been stated, the crystalline state is more ordered than the melted state. This loss of entropy is more pronounced the greater the number of conformations that the polymer can adopt in its melted state. This number is, in turn, dependent on the difference in energy between the *trans* and *gauche*. If this energy difference is small, the polymer tends strongly to coil upon itself. Thus, the conformational entropy in the melt is large and the change in entropy on crystallization very unfavorable. This is only overcompensated by the crystallization enthalpy at lower temperatures. Polymer chains that have a small difference in energy between their *trans* and *gauche* forms generally have low melting temperatures (**Table 2**).

Because the crystallization enthalpies for high density polyethylene and poly(tetrafluoroethylene) (PTFE) are very similar, the difference in their melting

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temperatures is a result of the greater tendency of polyethylene to form coils and is thus an entropy effect.

Table 2: **Energy difference between polymers in their *trans* and *gauche* forms**

Polymer (high-density)	Energy difference (*trans/gauche*)	Melting temperature
Polyethylene	$\Delta\varepsilon$ = 3 kJ/mol	T_m = 137 °C
PTFE	$\Delta\varepsilon$ = 18 kJ/mol	T_m = 372 °C

5. Symmetry

Asymmetrical elements in the polymer backbone mean that the polymer chain can no longer fit so well into the crystal structure. The resulting disturbance to the organization of the crystals leads to a lowering of the melting temperature. This effect is especially marked for structural units that lead to a kink in the polymer chain. Examples of this are *cis*-double bonds, *cis*-connected rings or aromatic rings, which have a polymer backbone chain linked to them at their *ortho* or *meta* positions (**Fig. 3**). Symmetry-related disorder leads, for example, to *trans*-polybutadiene being crystalline with a melting temperature of 148 °C, whereas *cis*-polybutadiene is amorphous.
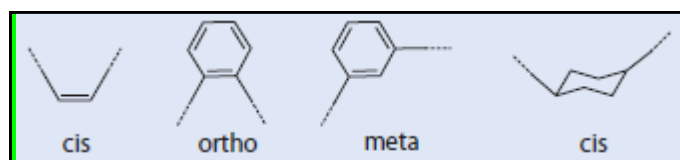

cis   ortho   meta   cis

Fig. 3: Chain elements that lead to kinks in the polymer chain

6. Interactions between chains or chain segments

Examples of interactions between polymer chains and/or between different segments of one and the same chain are dipole–dipole interactions and hydrogen bonds (**Fig. 4**). Thus, as mentioned above, polyamide 6.6 forms a strong hydrogen bond network throughout the whole material. In this polymer the alkylene chains between the groups that operate either as donors or acceptors are of equal lengths and an ideal network develops.

As a result of this, polyamide 6.6 melts at a temperature of roughly 267 °C (compared to high density polyethylene, which does not build any hydrogen bonds and melts at temperatures as low as 137 °C).
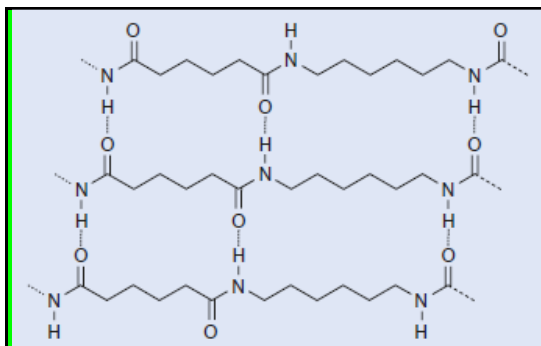
Fig. 4: *Hydrogen bond network in polyamide 6.6*

7. Co-monomers

Most partially crystalline, linear homopolymers are either characterized by a high melting temperature and a high glass transition temperature or a low melting temperature and a low glass transition temperature. A rule of thumb is that the glass transition temperature (in Kelvin) is roughly 0.7 times the melting temperature. This relationship is also valid for many small molecule substances in that they can also be converted into an amorphous state, such as pharmaceuticals.

For some applications this relatively simple connection between the melting temperature and the glass transition temperature is undesirable. There are some applications for which a material with a low glass transition temperature but a high melting temperature would be considered desirable. The melting temperature of a polymer (as an empirical observation) generally correlates to its E-module. Most partially crystalline polymers are packed in an ordered fashion and have strong interactions between their polymer chains. These properties give rise to a high module. Thus, rigidity, melting temperature, and glass transition temperature are usually closely related to one another.

In the following paragraph we discuss which polymer structures enable the above-mentioned relationship between T_m and T_G (at least within certain boundaries) to be circumvented. The question is, for example, how to produce a soft material (with a low melting temperature) that nevertheless has a high glass transition temperature. The crucial fundamental idea here is that the crystallinity of a material is dependent on whether the chain segments in the crystal structure can arrange themselves in an ordered manner, whereas the glass–liquid transition temperature is more dependent on how mobile the molecules in the polymer chains are.

Let us consider the interactions between the chains of polyamide 6.6 (**Fig. 4**). The polymer chains take on a regular zig-zag conformation in the solid state. It is immediately apparent from **Fig. 4** that because of the regularly ordered structure a very large number of hydrogen bonds can form. This network of hydrogen bonds makes this

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polyamide very rigid and the melting temperature very high. However, if a certain amount of co-monomer is incorporated, for example decane dicarboxylic acid, the regular sequence of hydrogen bonds in the material is significantly disturbed. The resulting disturbance of the crystalline order leads to a drop in both the melting temperature and the module. The glass transition temperature TG, which is essentially dependent on chain flexibility, is only slightly influenced by the incorporation of this kind of co-monomer. Therefore, it is possible, by producing a statistical copolymer, to lower the melting temperature and the module without an equivalent lowering of the glass transition temperature.

One advantage of such materials is their lower processing temperature. As most polymer materials are processed as melts, a lower processing temperature is less aggressive to the material and uses less energy. The general effect of the statistical incorporation of a co-monomer into a polymer can be seen in **Fig. 5**.
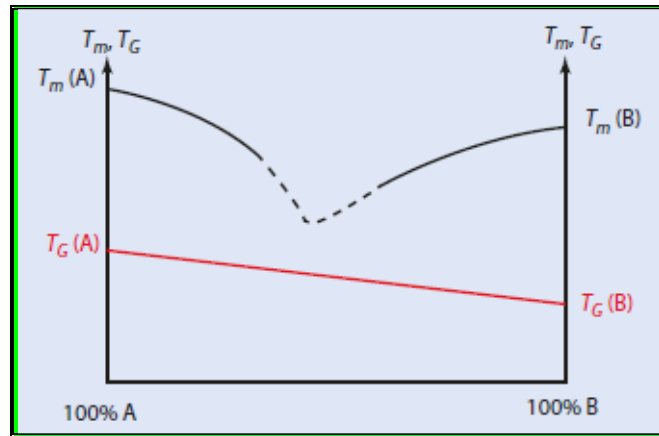

Fig. 5: Idealized description of the change in melting temperature (Tm) and glass transition temperature (TG) as a function of the composition of statistical copolymers of monomer A and B.

$$\frac{1}{T_{AB}} - \frac{1}{T_A} = -\frac{R}{\Delta H_m} \ln x_A$$

T_{AB}	Melting temperature of the copolymer
T_A	Melting temperature of the homopolymer A
ΔH_m	Melting enthalpy of the homopolymer
x_A	Mole fraction of the homopolymer

The figure shows the change in the melting temperature and glass transition temperature of two homopolymers poly(A) and poly(B) when their composition is gradually varied from 100% A to 100% B. Because of the disturbance of the crystal

structure, the melting temperature drops significantly, even if only relatively small amounts of co-monomer are present. The disturbance can be so strong in materials where the co-monomers account for half of the composition that the material does not crystallize at all and remains amorphous.

The linear interpolation of the glass transition temperatures shown in **Fig. 5** is a simplification and generally only approaches the real case when the co-monomers are chemically very similar to one another. The effect of copolymerization on melting temperature can be approximately (without proof) estimated as follows:

The different variables that influence melting temperature mentioned above are responsible for the slightly different melting temperatures listed in the literature for chemically identical polymers. The differences can be ascribed especially to molar mass, the degree of branching, tacticity, and the thermal history of the material (cooling rate, tempering). Therefore, it is untrue that any one of the listed values is more or less correct than any of the others.

8. Molar Mass

The ends of the chains are, in comparison to the segments within the chain, relatively mobile. This mobility interferes with the crystal lattice and reduces the degree of crystallization. The resulting drop in melting temperature at low molar masses is a thermodynamic effect. This thermodynamic effect can, however, be superimposed by kinetic effects, because polymers with very large molar mass crystallize very slowly. It is possible, especially if the rate of cooling is fast, that polymers with high molar masses show lower crystallinity than their analogues of lower molar mass. **Table 3** lists the melting temperatures of isotactic polypropylene of differing molar masses

Table 3: Influence of molar mass (M) on melting temperature (T_m) using isotactic polypropylene as an example

M (g/mol)	T_m (°C)
905	93
1050	105
1340	110
2000	114
14,000	154
30,000	170

❖ Criteria of tendency to crystallize

The tendency to crystallize depends upon the following:

1. Structural regularity of the chains that leads to establishment of identity periods.
2. Free rotational and vibrational motions in the chains that allow different conformations to be assumed.
3. Presence of structural groups, capable of producing lateral intermolecular bonds (van der Wall forces) and regular, periodic arrangement of such bonds.
4. Absence of bulky substituents or space irregularity, which would prevent segments of the chains from fitting into crystal lattices or prevent laterally bonding groups from approaching each other close enough for best interaction.

Natta and Carradini postulated three principles for determining the crystal structures of Polymers. These are:

1. It is possible to assume that all mer units in a crystal occupy geometrically equivalent positions with respect to the chain axis. This is known as the Equivalence Postulate.
2. The conformation of the chain in a crystal is assumed to approach the conformation of minimum potential energy for an isolated chain oriented along an axis. This is the Minimum Energy Postulate.
3. As many elements of symmetry of isolated chain as possible are maintained in the lattice, so equivalent atoms of different mer units along an axis tend to assume equivalent positions with respect to atoms of neighboring chains. This is the Packing Postulate.

❖ Morphology of crystalline polymers

A 100 % crystalline material is never produced after the cooling period because polymer chains are so entangled in the molten state. Thus, in partially crystalline polymers there are always both crystalline domains and amorphous domains present. Polymer single crystals can only be obtained from very dilute (less than one per thousand) solutions but this is not of technological relevance.

In practice, polymers are often processed from the melt and crystallization takes place from a very viscous system. The entanglements prevent a perfect crystal structure from being formed. This leads to the proportion of the amorphous domain varying in size. The crystalline areas often form lamellae, typically less than 100 nm thick. The main chain of the polymer is usually orientated orthogonally to the plane of the lamellae, resulting in an "accordion-like" structure.

The question as to how the polymer chains fold at the ends of the lamellae has not been conclusively resolved. There are essentially two models (**Fig. 6 and 7**). According to current hypotheses, the first, regularly folded model (**Fig. 6**) is obtained from a dilute solutions, whereas the second model, also known as the "switchboard model" (**Fig. 7**) is obtained from the melt. The thickness of the crystal lamellae increases with the crystallization temperature. Whereby, the number of repeat units in the main chain is, as a general rule, markedly below 100.

It is crucial for crystallization that the polymer coils cannot disengage themselves from their entanglements with neighboring chains during the crystallization process. Thus one should not envisage that a complete polymer chain separates from the melt and orders itself into a regular crystal lattice. Instead, it should be assumed that the polymer chain must, without significantly moving away from its position, fit itself into the crystal lamellae alongside segments of other chains. This is often described as a solidification of the polymer chain. This process itself does not require a long range reorientation of the polymer chain.
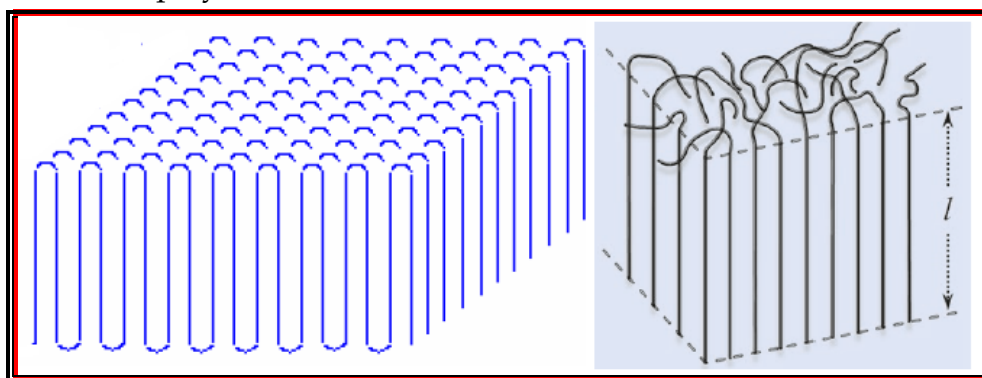

Fig. 6: Lamella model for polymer crystallization

The amorphous areas of a polymer above the glass transition temperature should be envisaged as a (highly viscous) liquid or melt. In contrast to this, the transition to a liquid in the crystal domains only takes place at the melting temperature. As the melting temperature is higher than the glass transition temperature, between T_G and T_m two phases coexist in partially crystalline polymers, one of which is liquid and one solid. In terms of the right hand sketch in **Fig. 7**, this means that in this temperature range there are solid crystal lamellae surrounded by a liquid, amorphous phase. We are dealing with a stable, two phase system, in which crystallites coexist with a chemically identical melt—and this below the melting temperature. This extremely unusual situation, which, of course, is impossible to replicate with small molecules, leads to outstanding mechanical properties.
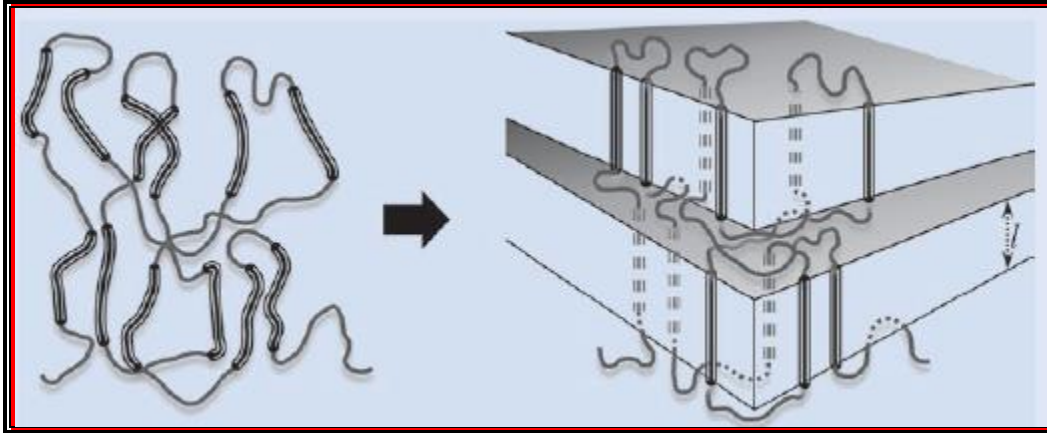
Fig. 7: Switchboard-model of polymer crystallization. Segments that have been incorporated in the crystal lamellae are highlighted

For example, if strain is applied to the material, such as some kind of impact, the liquid phase dissipates the energy and the material does not break. This explains the ductility of many partially crystalline polymers between T_m and T_G. We are thus dealing with a material that in some respects is similar to a highly viscous liquid. However, of course, the material as a whole cannot flow because, as can be seen in **Fig. 7**, the polymer chains are generally integrated into more than one crystallite, which prevents any macroscopic flow. The crystal lamellae of partially crystalline polymers often build superstructures, and an example of this is the so-called spherulites with spherical superstructures as shown in **Fig. 8**.
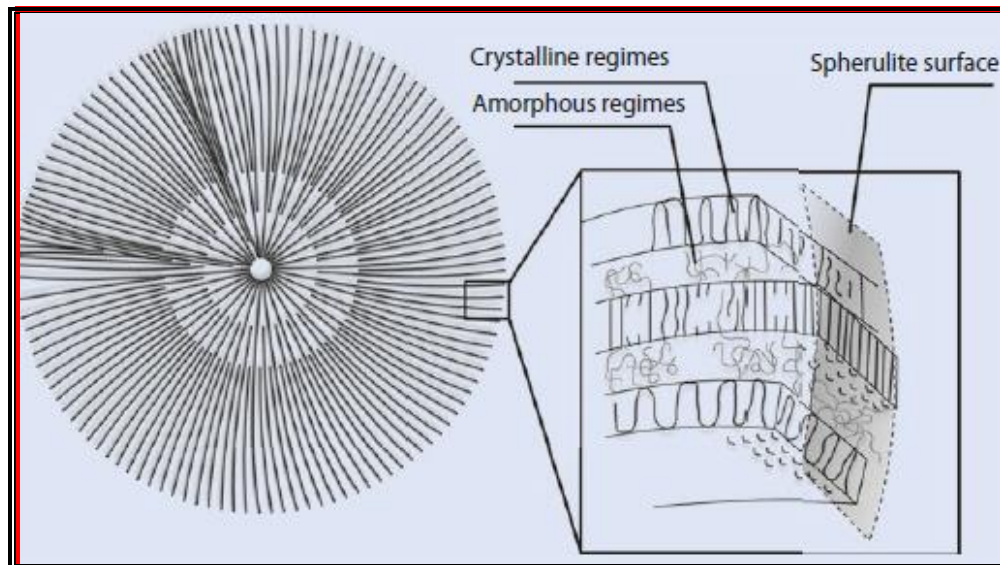

Fig. 8: Superstructure (spherulite) of a partially crystalline polymer

❖ Determination of glass transition temperature (T_G) and melting point (Tm)

Below, the most important methods for determining the glass transition temperature and the melting temperature are presented. These can be classified according to static and dynamic procedures.

Static procedures

Static procedures are based on the measurement of a material property, such as density, volume, heat capacity, or refractive index, as a function of temperature. In these procedures, the sample is slowly heated to maintain equilibrium, and the change of the respective intrinsic property is measured. Examples are dilatometry and the measurement of the refractive index.

1. Dilatometry:

The rate of volume expansion of a polymer with temperature depends on whether the polymer occupies the glassy, rubbery, thermoplastic or liquid states. Thus, the change of slope of a volume vs temperature plot can be used to identify the glass transition (**Fig. 9**). In practice a dilatometer is used for these measurements, and the position of the capillary meniscus is plotted as a function of temperature.
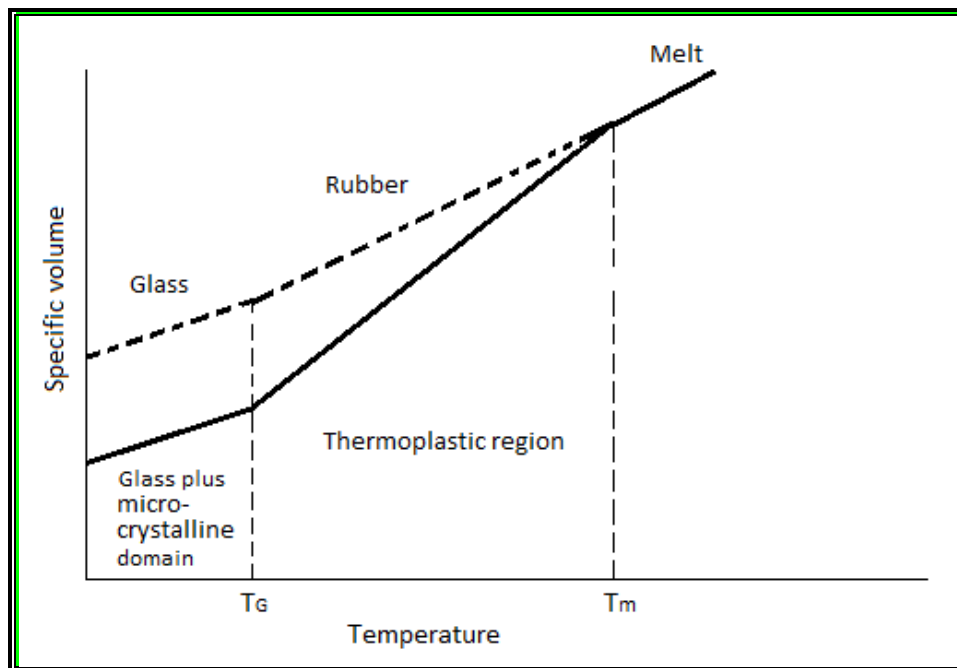

Fig. 9: Variation of specific volume of a crystalline polymer (solid line) and an amorphous modification of the same polymer (dashed line) as a function of temperature. Transitions are indicated by abrupt changes in the slopes of the lines.

2   Measurement of the refractive index

In this method discontinuity in the curves of the volume or refractive index is observed as a function of temperature at the glass transition temperature (**Fig. 10**).
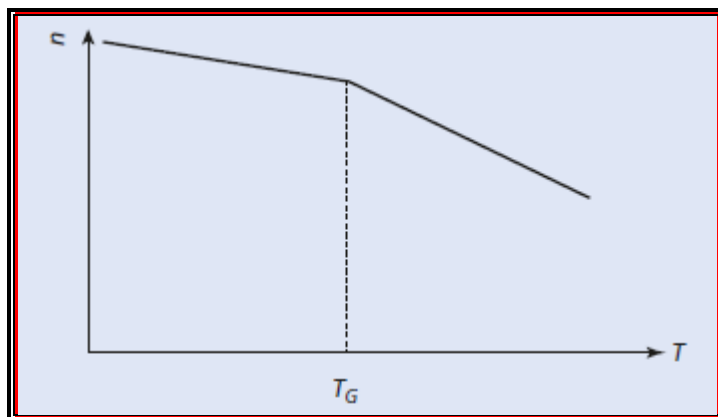

Fig. 10: Refractive index of a polymer as a function of temperature

3.   Differential scanning calorimetry (DSC)

However, in general, the preferred method is differential scanning calorimetry (DSC). The principle of DSC is that a sample is heated at a constant rate and the heat flow required maintaining this defined rate is measured. The heat flow correlates with the heat capacity c_p of the sample, i.e., the amount of heat necessary to produce a given change in temperature. As mentioned above, we observe an abrupt increase in heat capacity c_p at the glass transition temperature, whereas, at the melting point the latent heat ΔH_m (the heat of melting) is required. Thus, the temperature of the sample does not change during the melting process, even though heat is absorbed. This is valid until the moment when the crystal lattice is completely "broken" and the transition to an isotropic melt has occurred. Formally, the heat capacity tends to infinity during the melting process so that a peak results in the DSC (**Fig. 11**). From the area under this peak the heat of melting for the sample can be calculated. Alternatively, if ΔH_m is known, the degree of crystallization can be determined.

DSC is a method frequently used both in industrial and academic laboratories. Its advantages lie in the very small amount of sample material required (approximately 5 mg). Furthermore, the technology is well established and the available devices are quite robust and easy to use. In particular, sample preparation is also relatively simple. The sample has to be placed in a measuring vessel — usually a disposable aluminum pan.
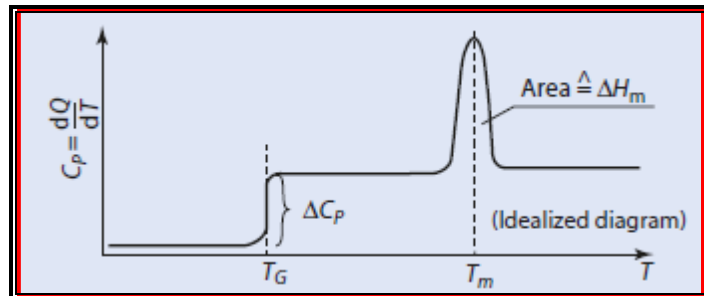
Fig. 11: *Heat capacity as a function of temperature on heating for semi crystalline polymers as observed with DSC*

The disadvantages of DSC lie in its limited sensitivity. Not every phase transition is resolved. Moreover, the measuring curve is sometimes difficult to interpret. Thus, the curve in **Fig. 11** is an idealized DSC curve rarely generated by real polymers. Measured DSC curves are often not parallel to the axes, but arched or curved, so that it is sometimes hard to discern the individual transitions correctly.

DSC provides the possibility of varying the heating rate and hysteresis can be observed for first-order phase transitions. Particularly large hysteresis is observed for the crystallization peak, associated with the transition from a melt to a crystalline phase. This is because crystallization requires the formation of crystal-nuclei. This process requires a certain time so that, at a very high cooling rate, the crystallization temperature can be significantly undershot.

4. Differential thermal analysis (DTA)

Differential thermal analysis (DTA) the most popular technique like differential scanning calorimerty (DSC) for the measurement of glass transition temperature (T_G) and crystal melting temperature (T_m). The DTA method requires the heating of a small amount of a polymer sample at a constant rate of temperature increase. The temperature of the polymer is compared continuously with the temperature of a control substance, such as alumina, which itself undergoes no transitions in the temperature range being scanned. The temperature difference between the polymer and control material is then a function of the different specific heats of the two substances. The specific heat of a polymer changes rapidly as a transition region is approached with exothermic changes being characteristic of glass transitions (**Fig. 12**). Endotherms indicate first-order transitions (melting temperatures). Two advantages of the DTA method are that only a small amount of polymer is required and the measurement is quite rapid. Also, the transition temperature can be identified to within 1 or 2°C. A

disadvantage is that highly crystalline polymers may show only weak exotherms that may prove difficult to identify.
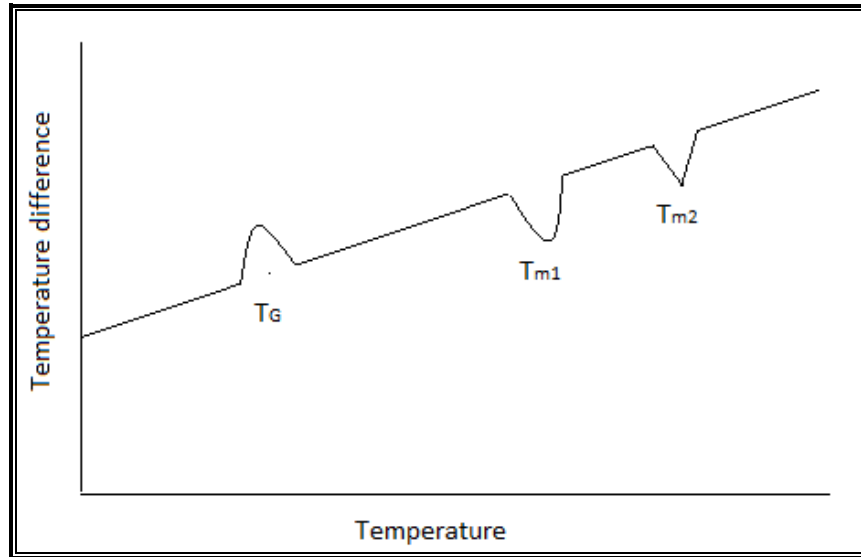

Fig. 12: Differential thermal analysis (DTA) scan of a polymer, showing an exotherm typical of a glass transition and the endoterms that are characteristic of Tm transitions.

Dynamic procedures

In *dynamic mechanical thermal analysis* (DMTA), a sample is subjected to periodic sinusoidal, mechanical stress, for example, by a periodic tensile or torsional movement. This is accomplished at a frequency *f* and with a stress *σ*. During such measurements it is often observed that the deformation of the material is delayed in time with respect to the applied stress, so that the periodic oscillation of the material and the mechanical excitation are phase-shifted (**Fig. 13)**
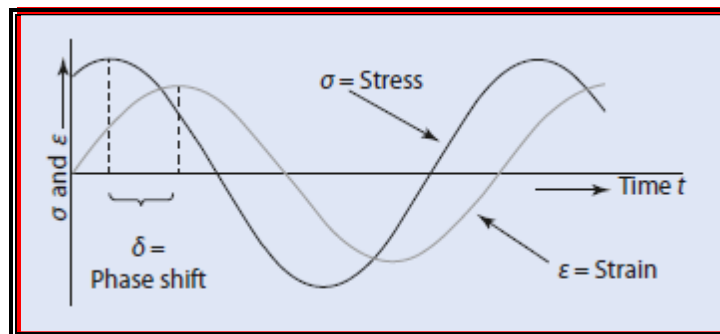

Fig. 13: Periodic progression of stress σ and strain ε

The angle of the phase shift is referred to as δ. Such a periodic oscillation can be – as known from mathematics – represented in the form of complex numbers. Thus, we can define the strain ε as

$$\varepsilon = \varepsilon_0 e^{-i\omega t}$$

and the stress σ as

$$\sigma = \sigma_0 e^{-i\omega t + \delta}$$

In doing so, ε_0 or σ_0 signify the respective amplitudes, ω the angular frequency ($\omega = 2\pi f$), and t the time.

Although Young's modulus represents the ratio of stress and strain for simple systems which obey Hooke's law, a complex E-modulus (E^*) can be defined for these complex cases. The rule is

$$E^* = \frac{\sigma}{\varepsilon} = \frac{\sigma_0}{\varepsilon_0}(\cos\delta + i\sin\delta)$$

The complex modulus E^* thus consists of a real part and an imaginary part, which are referred to as E_1 and E_2 (sometimes also as E' and E''):

$$E^* = E_1 + iE_2$$

E_1 is referred to as the *storage modulus* and E_2 as the *loss modulus*. E_1 is a measure of the energy that can be stored in the system and E_2 a measure of the energy that is lost in the system. The quotient of the moduli E_2/E_1 therefore is given by $\sin\delta/\cos\delta$, i.e., $\tan\delta$ – this is designated the *loss factor*, and describes the ratio of dissipated to stored energy.

Without proof, it can be shown that the loss factor can be written as

$$\tan\delta = \frac{E_2}{E_1} = \frac{1}{\omega\tau}$$

Here, τ denotes the relaxation time of the system.

If E_1 and E_2 are plotted as a function of temperature for materials going through the glass transition, the typical graph shown in **Fig. 14** is obtained.

It can be seen that the storage modulus drops abruptly across the glass transition. This becomes obvious by considering that the melt after the glass transition is a liquid and as such is generally not able to store energy. By contrast, the loss factor passes through a maximum at temperatures around the glass transition temperature. A maximum of the

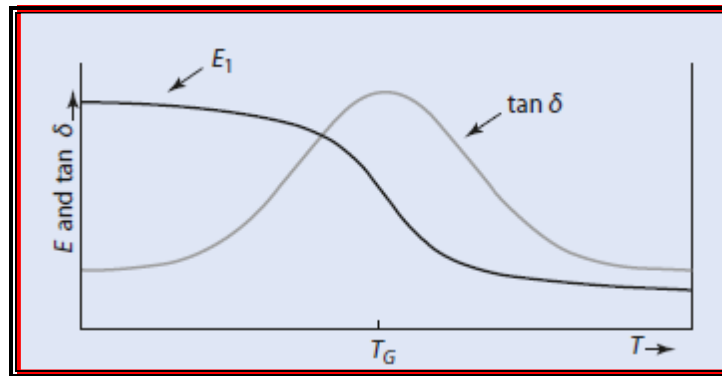loss factor is equivalent to the material being a damping element. This can easily be explained graphically.

Fig. 14: Graph of the storage modulus and the loss factor as a function of temperature

In a thought experiment, one imagines a polymer at low temperature as a hard metal spring. At low temperature the polymer chains are in a glassy solid state, they are not very mobile, and relatively large forces are required for small elongations. In other words, the material can be represented by a hard spring with a relatively high modulus.

As this system passes through its glass transition, the chains become more flexible, the material becomes softer, and the modulus of a spring representing the material is low. A polymer above its glass transition temperature can be represented by a soft metal spring.

Both hard and soft springs have own resonance frequency. As is known from physics, a spring can store a lot of energy in the region of its resonance frequency, and it can be easily excited. With a hard spring, this resonance frequency is relatively high and for a soft spring the frequency is low. However, at their respective resonance frequencies, large oscillations can easily be induced in both springs.

What happens when a material passes through its glass transition? Because polymers always have a certain molar mass distribution, and, in particular, amorphous phases are heterogeneous with respect to their local order, there are both soft and hard springs present in the material close to the glass temperature. Thus, the system no longer finds its resonance frequency and any attempt to store energy in these materials results in much larger energy dissipation. As a consequence, energy dissipation is observed at temperatures close to the glass transition, and thus a high damping of input energy. In an experiment, one would find that a weight hanging on a hard and a soft spring, arranged in series, cannot be excited to a greater, persistent oscillation.

DMTA measurements are designed to measure the storage and loss moduli of the sample as a function of temperature whereby the glass transition can then be identified

from the position of the maximum in the loss modulus curve.

This can be achieved by heating a sample with a constant frequency and measuring the phase shift between the stress and strain curves. However, in practice it is simpler to vary the frequency rather than the temperature. This leads us to the so-called *time-temperature superposition principle*. How are frequency and temperature related?

Let us imagine that we are observing a sample at high temperature. If we put a load on the sample, for example by denting it or pulling on it, then at high temperature the polymer chains have sufficient mobility to respond to the strain by changing their conformation; the material appears soft. The same thing happens when we put a strain on a material at low frequency. The duration of the strain is relatively long and the polymeric material has a relatively long time to counteract the strain. Again, it appears soft. At low tempera- tures or high strain frequencies the opposite is the case. At low temperatures, the mobility of the material is not sufficient to react to the strain by changing its coil conformation. The material appears hard. At high measuring frequencies, the material does not have enough time to react to the strain and it appears hard.

This behavior—the dependence of the mechanical properties on the duration of the applied strain—is by no means limited to polymers. Compare stepping into a water-filled bathtub with a belly flop from a 5-m springboard. You can probably notice dramatically the dependence of the mechanical effect on your body on the speed of your plunge. Similarly, water behaves differently at a bathtub temperature of 37 °C than at −10 °C. Here, low temperatures cause a similar effect to that of short strain durations.

Thus, there is an analogy between measurements at high frequencies and measurements at low temperatures and vice versa. Therefore DMTA measurements can either be carried out at a constant measuring frequency when varying the temperature, or which is more often done technically the temperature is kept constant and the measuring frequency varied. The data are then converted into a temperature curve.

Figure 15 shows the dependence of the storage and loss moduli on the measuring frequency, or more specifically on $\log(1/\omega\tau)$. The maximum of the loss modulus is achieved when this logarithm becomes zero, i.e., when the relaxation time τ is identical to the reciprocal of the measuring frequency. Thus, when the time in which the material can relax is approximately similar to the observation time, the sample is in an intermediate state where the material cannot yet fully relax but the first movements have already started. This state corresponds to the gradual transition from a hard to a soft spring. Exactly here, analogous to the above thought experiment, high damping is observed.
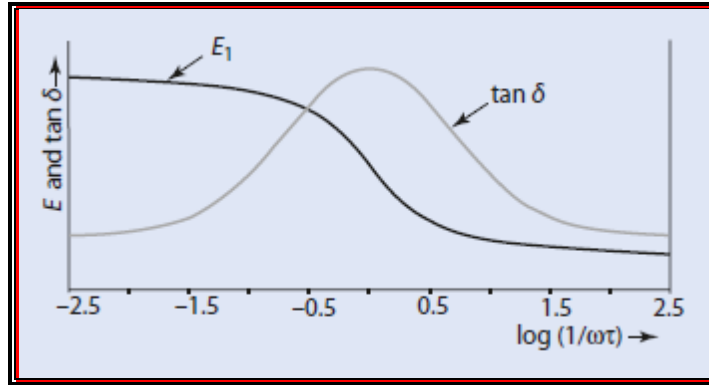
Fig. 15: Graph of storage and loss moduli as a function of frequency

The DMTA suits itself ideally for the detection of very fine phase transitions. This can be shown by the example of polystyrene (**Fig. 16**).

α:T_G
β: Phenyl groups rotate around the polymer chain
γ: Rotation of head-to-head linkages
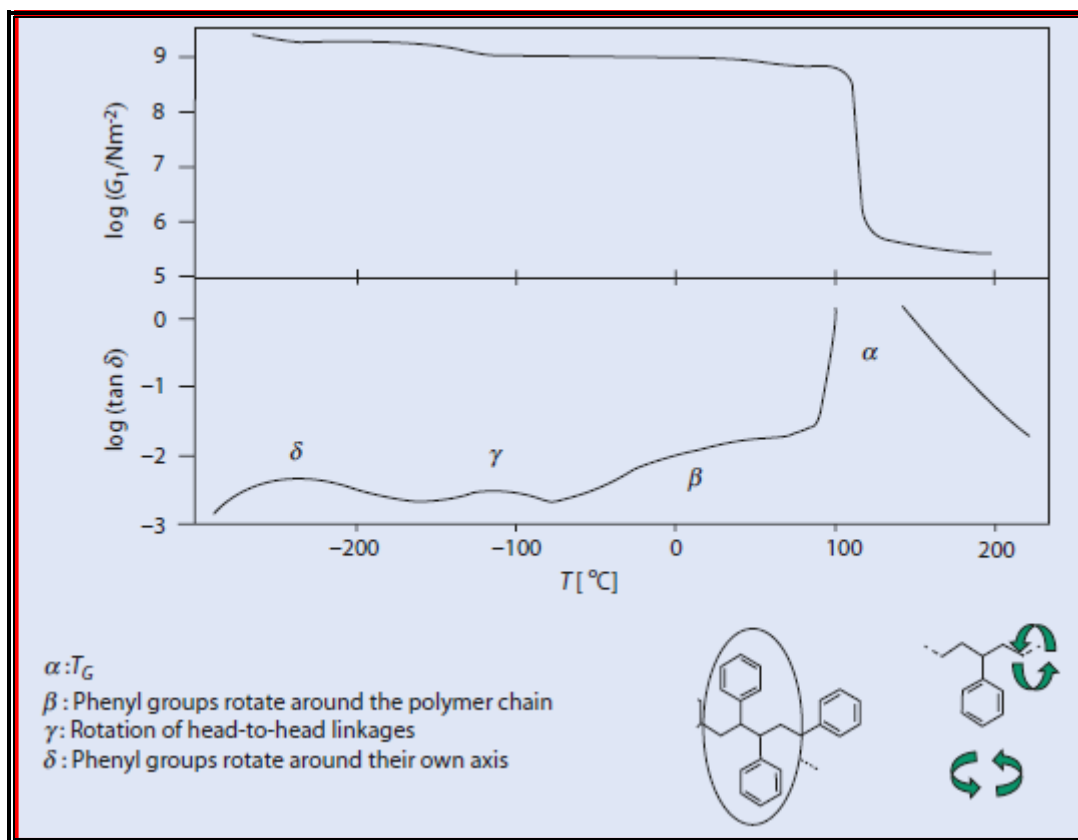δ: Phenyl groups rotate around their own axis

Fig. 16: DMTA measurement of polystyrene

In the upper part of the figure, the dependence of the storage modulus, in this case the shear modulus, on the temperature is shown for polystyrene. One can see a large transition at a temperature of about 100 °C, which corresponds to the glass transition of

polystyrene. The curve at lower temperatures is, however, more difficult to interpret. This region is easier to analyze if the logarithm of the loss factor tan δ is plotted as a function of the temperature (lower part of the diagram). Here we also see a very distinctive maximum at about 100 °C, which can be assigned to the glass transition. However, three additional transitions at lower temperatures can also be identified. These are referred to as the β, γ, and δ transitions. It has been shown that, at the β transition, the phenyl groups stop rotating around the polymer chain. If the sample is cooled below the γ transition, the rotations of head-to-head linkages also become frozen. At the δ transition, the rotation of the phenyl groups around their own axes also ceases. Thus, interestingly, we find further thermal transitions in the material below the main glass transition temperature T_G.

Dielectric thermal analysis (DETA) functions according to principles similar to DMTA. Analogous to DMTA, in DETA an alternating electric field is applied to the sample rather than an oscillating mechanical field. The polarization of the material is measured. Analogous to the DMTA measurements, a phase shift between the polarization and the applied alternating field is observed. At low frequencies or high temperatures, for example, an entire dipolar moiety can orient itself in the electric field. At high frequencies/lower temperatures, only the electrons within the group are displaced. At temperatures around the glass transition temperature there is a non-uniform reaction and high damping results.

In principle, DETA can be used in the same way as DMTA; however, it can only be applied to polymers with dipolar groups. Thus, in combination with DMTA, DETA allows conclusions as to whether dipolar groups are involved in a particular transition. If they are, the transition is observed using both techniques. If not, the transition is only identified using DMTA.

❖ Detection and measurement of microcrystallinity

Nearly all methods, used for the measurement of T_G are also used to measure crystalline melting temperature. However, convincing proof that microcrystalliny exists in a particular polymer requires the use of two additional techniques: optical birefringence and X-ray crystallography.

The optical birefringence technique makes use of a polarizing microscope, preferably fitted with a heating stage for raising the temperature of the sample. When viewed through crossed polarizers, a microcrystalline polymer will show a dark background broken by bright specks which originate from the crystalline domains. Some polymers show a more complex structure in which individual microcrystallites radiate in all

directions from specific points to form spherulites. The structure of each spherulite can be visualized as made up of micricrystals oriented along the radii of individual spheres. The bright specks extinguish or reappear as the sample is rotated relative to the polarizing filter. The specular pattern should persist until the temperature is raised to the crystalline melting point, at which temperature the bright specks or spherulites should be totally extinguished.

The X-ray diffraction approach makes use of the fact that a totally amorphous polymer will not give rise to a sharp diffraction pattern. Diffuse scattering rings only are seen. These resemble the X-ray patterns obtained from liquids. An unoriented microcrystalline polymer will yield an X-ray photograph that consists of sharp rings. Such photographs bear a striking resemblance to Debye-Scherrer "powder" photographs of powdered small-molecule crystalline materials, and for the same reason. The sharp concentric areas or rings result from diffraction by randomly oriented micricrystallites.

An oriented microcrystalline polymer fibre or film will yield a pattern of diffraction spots or arcs. The appearance of amorphous-type patterns and the disappearance of a crystalline-type pattern provide a measure of the crystalline melting temperature. However, it is not uncommon that, as the temperature is raised, one crystalline pattern is replaced by another, and in this way a sequence of T_m values can be measured.