Partially Crystalline Polymers

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As a corollary to the basic introduction to polymers in their solid state, this chapter deals with partially crystalline polymers. To begin, we need to ask ourselves which polymers are able to crystallize.

Because crystallization involves the transition to a highly ordered state, the entropy of crystallization is negative, that is, unfavorable. This has to be compensated for by a favorable, and thus likewise negative, crystallization enthalpy. Exothermic crystallization requires polymer chains that can interact energetically enough with one another in their crystallized state. This can happen in two different ways: either through symmetrical chains that allow a high packing density or through strong interactions between the chains. Examples of polymers with symmetrical chains are polyethylene or isotactic polypropylene. By contrast, atactic polypropylene cannot crystallize because of its asymmetrical chain. An example of a polymer with strong interactions (in this case hydrogen bonds) between its chains is the polyamide family, particularly polyamide 6.6.

Polymers with especially flexible chains tend to form random coils, as discussed in ► Chap. 2. This is obviously not favorable for crystallization. Therefore, these types of polymers are either amorphous, or crystallization is very slow. Thus, for example, polyisobutene only crystallizes if it is annealed at its ideal crystallization temperature over a long time period.

Crystallization takes place in two stages according to classical crystallization theory, namely, *nucleation* and ensuing growth. For nucleation to take place, crystal nuclei with a critical minimal size first have to form. This process can be induced, for example, by the addition of nucleation agents, and the rate of growth is largely dependent on the temperature.

Both steps significantly influence the morphology of the polymer crystals formed and thus also influence their properties, such as the temperature at which they melt.

5.1 Factors that Influence 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 polymer composition as well as the thermal history of the material. The significant parameters are discussed in detail from the following points of view:

- Conditions of crystallization
- Chain flexibility
- Symmetry
- Interactions between chains or chain segments
- Tacticity
- Branching
- Molar mass
- Comonomers

5.1.1 Influence of the Conditions for Crystallization

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 many crystallization nuclei and thus also to 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.

5.1.2 Influence of 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* conformations (► see Chap. 2). If this energy difference is small, the polymer tends strongly to coil up on 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 5.1).

Because the crystallization enthalpies for high density polyethylene and poly(tetrafluoroethylene) (PTFE) are very similar, the difference in their melting temperatures is a result of the greater tendency of polyethylene to form coils and is thus an entropy effect.

◘ **Table 5.1** 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

5.1.3 Influence of Chain 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. 5.1).

Symmetry-related disorder leads, for example, to *trans*-polybutadiene being crystalline with a melting temperature of 148 °C, whereas *cis*-polybutadiene is amorphous.

5.1.4 Influence of Interactions Between the Chains

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. 5.2). 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).

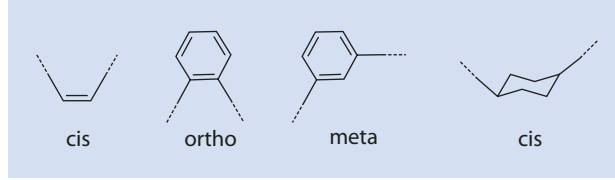

Fig. 5.1 Chain elements that lead to kinks in the polymer chain

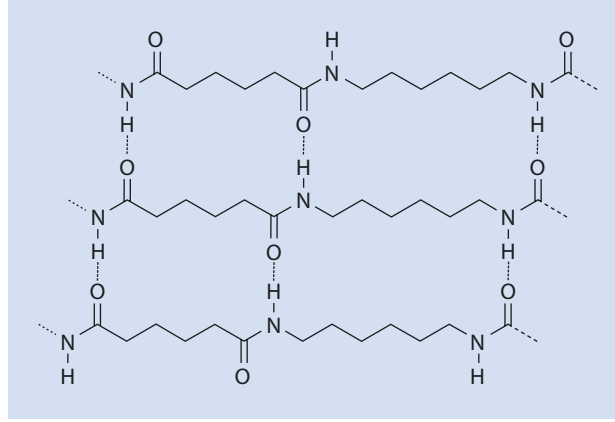

Fig. 5.2 Hydrogen bond network in polyamide 6.6

5.1.5 Influence of 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. 5.3).

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.

5.1.6 Influence of 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. 5.4).

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 5.2) (Jones 1964).

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

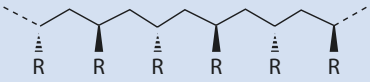

Fig. 5.3 Zig-zag conformation of a syndiotactic polymer

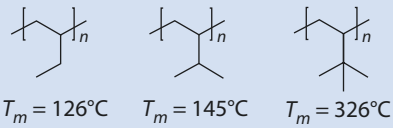

Fig. 5.4 Influence of different branching of side chains on the melting temperature.

Table 5.2 Influence of length of the side chain on the typical melting temperatures of isotactic α-polyolefins

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

this is the increasing influence of the side chains to crystallize on the conformation of the main chain.

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. As is shown in ▶ Chap. 14, 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.

5.1.7 Influence of 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 5.3 lists the melting temperatures of isotactic polypropylene of differing molar masses (Natta et al. 1964).

5.1.8 Comonomers

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

◘ **Table 5.3** 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

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 abovementioned 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. 5.2). The polymer chains take on a regular zig-zag conformation in the solid state. It is immediately apparent from Fig. 5.2 that because of the regularly ordered structure a very large number of hydrogen bonds can form. This network of hydrogen bonds makes this polyamide very rigid and the melting temperature very high. However, if a certain amount of comonomer 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 T_G, which is essentially dependent on chain flexibility, is only slightly influenced by the incorporation of this kind of comonomer. 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 (▶ see Chap. 17), a lower processing temperature is less aggressive to the material and uses less energy.

The general effect of the statistical incorporation of a comonomer into a polymer can be seen in Fig. 5.5.

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 comonomer are present. The disturbance can be so strong in materials where the comonomers 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. 5.5 is a simplification and generally only approaches the real case when the comonomers are chemically very similar to one another.

The effect of copolymerization on melting temperature can be approximately (without proof) estimated as follows:

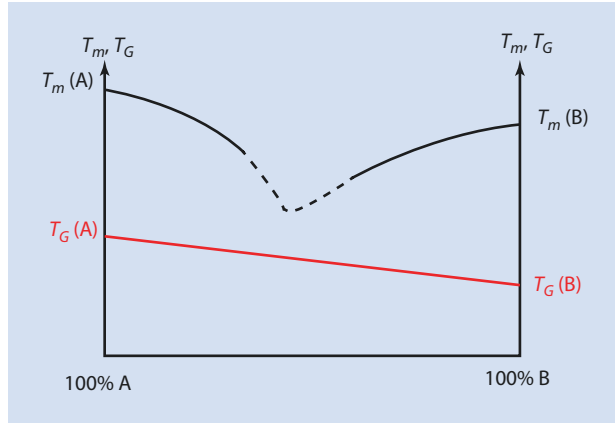

Fig. 5.5 Idealized description of the change in melting temperature (T_m) and glass transition temperature (T_G) as a function of the composition of statistical copolymers of monomer A and B. Further explanations are given in the text

$$\frac{1}{T_{AB}} - \frac{1}{T_A} = -\frac{R}{\Delta H_m} \ln x_A \tag{5.1}$$

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

A comparison between statistical and block copolymers can be found in ▶ Sect. 7.2.1.

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.

5.2 Morphology of Partially 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.

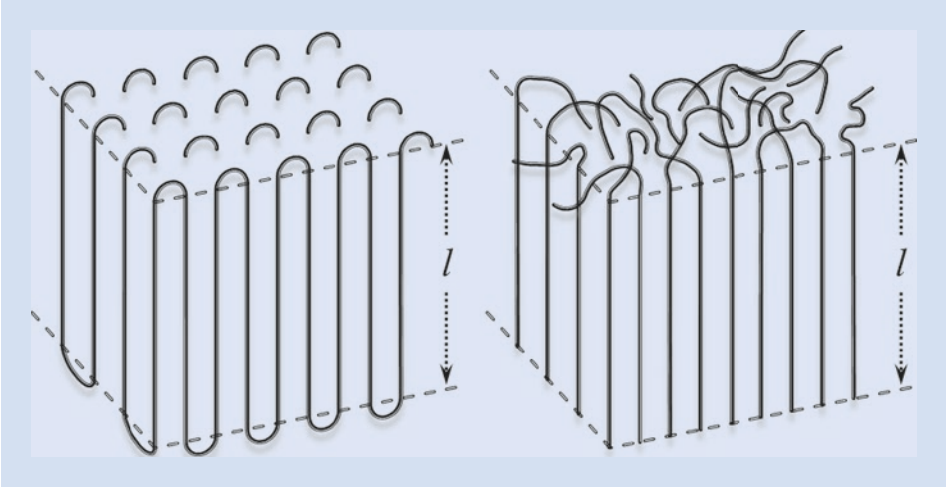

Fig. 5.6 Lamella model for polymer crystallization

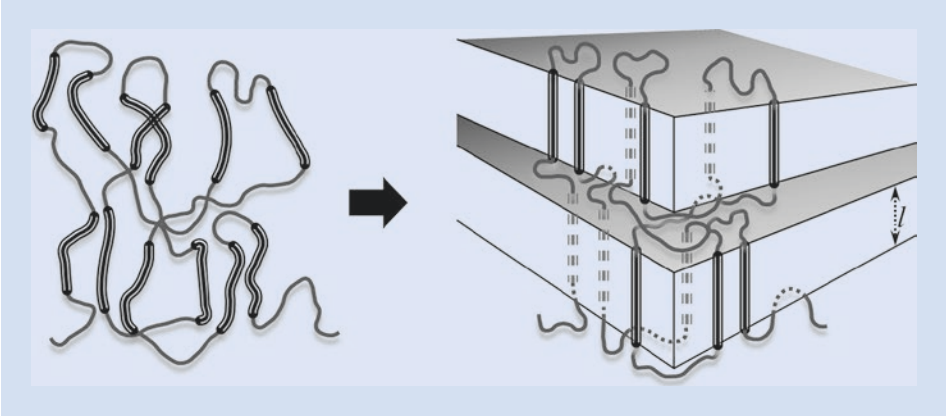

Fig. 5.7 Switchboard-model of polymer crystallization. Segments that have been incorporated in the crystal lamellae are *highlighted*

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 (Figs. 5.6 and 5.7).

According to current hypotheses, the first, regularly folded model (Fig. 5.6) is obtained from a dilute solutions, whereas the second model, also known as the "switchboard model" (Fig. 5.7) is obtained from the melt (Dettenmaier et al. 1980).

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.

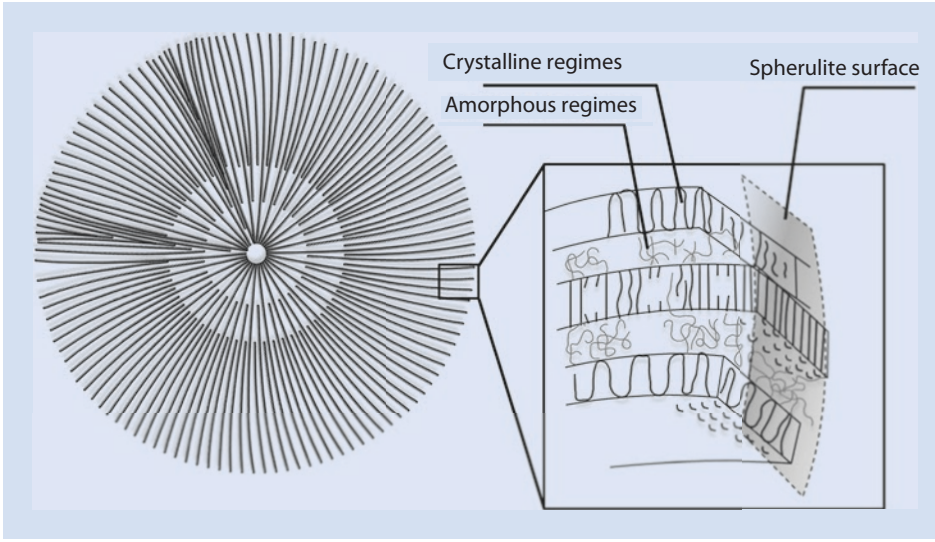

Fig. 5.8 Superstructure (spherulite) of a partially crystalline polymer

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.

The physical chemistry of partially crystalline polymers in the solid state is fascinating. As already explained in ▶ Chap. 4, 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. 5.7, 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. 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. 5.7, 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 (McCrum et al. 1988) with spherical superstructures as shown in Fig. 5.8.

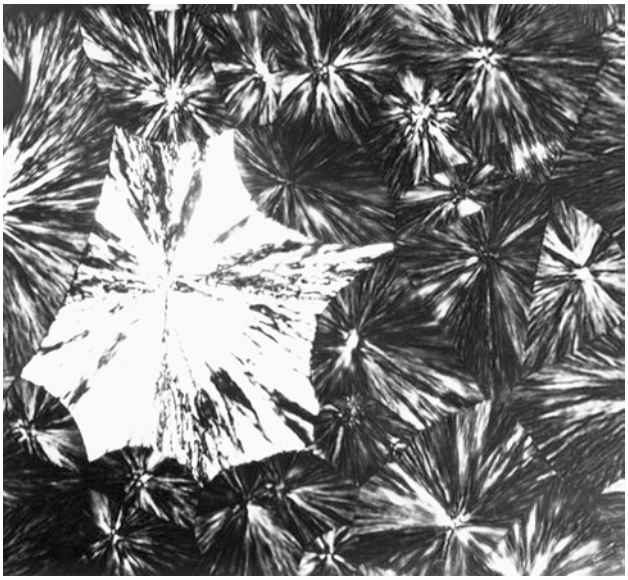

Fig. 5.9 Isotactic polypropylene viewed through a polarizing microscope (dark regions: α-spherulite, light regions: β-spherulite)

As well as the structures shown here, one- or two-dimensional superstructures (fibers or discs) are also observed. These superstructures can be analyzed by a polarizing microscope because they are birefringent (Fig. 5.9).

This image shows isotactic polypropylene. Polypropylene forms two different kinds of spherulites (called α- and β-spherulites) which can be seen in Fig. 5.9.

5.3 Crystallization Kinetics

An analysis and the knowledge of the crystallization kinetics are crucial requirements for a rational processing of a polymer. During the manufacturing process, in which the polymer is generally melted (▶ see Chap. 17), the cooling rate, as has been explained, determines the degree of crystallinity and thus the properties of the resulting material. It is therefore important to know how a polymer crystallizes under any given processing conditions.

The analysis of the crystallization kinetics can, for example, be carried out using a dilatometer (Fig. 5.10), whereby the change in volume of the sample as a function of temperature is measured from the change in the height of a column of mercury (which also serves to contain the sample). For such measurements, the material is tempered above its melting temperature and then rapidly cooled to the desired crystallization temperature. Because the density of the crystals is greater than that of the amorphous domains, a volume contraction accompanies crystallization. By measuring the change in volume with time the desired crystallization kinetics can be determined.

The crystallization of polymers can be described by the Avrami equation:

$$\frac{w_{m,t=t}}{w_{m,t=0}} = \exp\left(-kt^n\right) \tag{5.2}$$

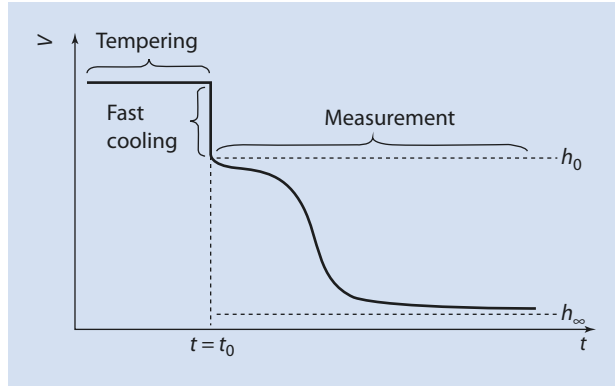

Fig. 5.10 Schematic diagram of the change in volume *V* of a polymer sample over time *t* during crystallization as measured in a dilatometer

Table 5.4 Interpretation possibilities of the Avrami exponent *n*

Growth in the form of....	Slow nucleation ($T \sim T_m$)	Rapid nucleation ($T \ll T_m$)
Fibers	2	1
Discs	3	2
Spherulites	4	3
Complex bundles/coils	6	5

w_m Weight of the non-crystalline melt as a function of time *t*
k Rate constant
n Avrami exponent

This equation describes the weight fraction of the non-crystalline melt at time *t* relative to the original mass of the melt at time t_0. The relation between these two numbers is a function, which, where $n = 2$, corresponds to a Gaussian distribution.

To evaluate the results of dilatometric measurements, the Avrami equation is usually transformed as follows:

$$\frac{h(t) - h_\infty}{h_0 - h_\infty} = \exp\left(-kt^n\right) \tag{5.3}$$

h_0, $h(t)$, h_∞ Height of the column of liquid at time $t = 0$, t and t_∞

From the value of the Avrami exponent, *n*, it is possible to predict what kinds of superstructures form in the melt. The correlations are listed in Table 5.4. However, a difference between slow and rapid nucleation must be taken into consideration.

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