School of Engineering
Institute of Materials
Laboratory of Macromolecular
and Organic Materials

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Course Notes of Chapter 3.3

Table of Contents

1. Introduction

After our discussion of the amorphous state, we are now bringing some order into the condensed state, i.e., we will talk about the crystalline state or rather the semi-crystalline state, given that even polymers that are capable to properly crystallize (upon cooling from the molten state within a reasonable time frame, for example) are never 100% crystalline.

1.1 What is a Crystal?

A crystal structure is a periodic structure (unlike amorphous solids, quasicrystals, paracrystals, liquid crystals etc.), where the same pattern, "**the unit cell**", is translationally

repeated many times in three dimensions to make a 3-dimensional crystal. The smallest part of the unit cell which can be used to reconstruct the unit cell by symmetry operations is called the "**asymmetric unit**" (Slide 158).

1.2 Which Polymers Crystallize?

It can be assumed that only polymers with a regular chemical structure can form crystals. This would exclude *a priori* atactic polymers, highly crosslinked polymers (thermosets), branched polymers, or random copolymers, for example (Slide 162). With certain exceptions, this is indeed the case. You will find some examples of polymers which crystallize on Slide 151. **These are thermoplastic polymers with mechanical properties comparable to those of glassy amorphous polymers, even though the T_g of some of them is below room temperature** (PE, isotactic PP (iPP), poly(oxymethylene) (POM)). As the structure of semi-crystalline polymers is necessarily heterogeneous, they are often opaque, but not always (a PET bottle is about 30% crystalline!). In general, synthetic polymers absorb little visible light, and a strong scattering requires variations in the refractive index across wavelengths between 400 and 700 nm approximately. The opacity therefore depends on both the morphology and the density difference between the crystalline phase and the amorphous phase.

1.3 How do Polymers Crystallize?

A perfect periodic three-dimensional structure would require a regular stacking of molecules of identical size (because the ends of a chain are chemically distinct from the rest of the chain) in an identical conformation. However, in practice the molecules of a synthetic polymer do not have the same molar mass and, as we have seen, we never observe 100% crystallization, even in the case of "single crystals" prepared from dilute solutions. Indeed, as we will see below, the most common synthetic polymers cannot form large (perfect) crystals.

2. Structures of Crystallizable Polymers

2.1 Polymeric Crystals

Despite the comments in Section 1.3, certain polymers crystallize. Some biomolecules such as pure proteins have well-defined molar masses and sequences and many of them spontaneously adopt unique conformations (unlike random conformations of synthetic polymers), and eventually become “balls” of precise shape in the case of globular proteins. These balls generally constitute the asymmetric unit and can then be regularly stacked to construct a unit cell whose size is of the same order of magnitude as the whole ball (the macromolecule).

The situation is quite different in **conventional synthetic homopolymers**, where **the asymmetric unit can be a part of the constitutive repeating unit, or one or more constitutive repeating units**, because, unlike proteins, the building block repeats itself regularly along the chain. By adopting a regular conformation, the polymer chains can be

Dr. Daniel Görl
daniel.gorl@epfl.ch
lmom.epfl.ch
EPFL STI IMX LMOM
MXG 136, Station 12
CH-1015 Lausanne

stacked in such a way that their constitutive units form a periodic arrangement. If the dimensions of such crystals exceed those of the chains, the ends of the chains will be incorporated defects. However, in most situations of practical interest, such as injection molding, for example, the polymer crystals are relatively small and involve relatively short chain lengths (Slide 153).

According to simple geometric considerations, **the conformations of homopolymers must be generally linear for crystallization**. The chains are fully stretched (zig-zag conformation) or form a regular helix. By convention, we choose the vector $\underline{\boldsymbol{c}}$ of the unit cell to be parallel to the axis of chain orientation in the crystal.

The example shown in Slides 157 and 159 is the most stable crystalline form of PE: the PE chains adopt a zig-zag conformation in an *orthorhombic* unit cell (a cubic box with $\underline{\boldsymbol{a}}$, $\underline{\boldsymbol{b}}$ and $\underline{\boldsymbol{c}}$ being perpendicular to each other and of different lengths). The asymmetric unit is half of a CH_2 group. **The repetition of the unit cell and its content in space generates the periodic structure.** In this case, the space group of orthorhombic PE is Pnam (see your crystallography courses if you have taken any) and, as shown on Slide 158, symmetry operations associated with this space group can be applied to the half of the constitutive repeating unit in order to build the unit cell. In other words, half of a CH_2 group is all we need to construct a crystal made up of extremely long chains in a zig-zag conformation.

We immediately see that **we cannot reproduce that with a random copolymer or a strongly branched or crosslinked polymer**, and indeed these types of polymers are basically incompatible with the formation of crystals. Nevertheless, we can always accommodate a low degree of branching, crosslinking or irregular chain sequences (including the chain ends) as long as the crystal is not too large (so that these irregularities can be accommodated in the amorphous matrix) or if these defects are incorporated in the crystal.

Sequence irregularities include configurational irregularities. A very important example of such irregularities is the case of atactic vinyl polymers, which we already have encountered a couple of times during our course. In the presence of bulky substituents such as the CH_3-group of PP or the benzene group of PS, we see that **isotactic and syndiotactic polymers can adopt a regular conformation** that minimizes the steric repulsion of the substituents. To this end, an isotactic PP chain, for example, can form a helix with three repeating units per helix turn, from which it will crystallize. The substituents of syndiotactic PP are, however, already far apart of each other in a zig-zag conformation, so that it crystallizes from this form and different from isotactic PP (in fact the stable crystalline form of syndiotactic PP involves yet another type of helix whose energy is lower than that of the zig-zag conformation). What about atactic PP? **In the case of atactic PP there is no regular conformation which prevents all the CH_3 groups from touching each other and therefore it can not crystallize.**

However, atactic poly(vinyl alcohol) can crystallize because the presence of the OH-substituent does not affect the chain conformation, both isotactic and syndiotactic sequences prefer a zig-

Dr. Daniel Görl
daniel.gorl@epfl.ch
lmom.epfl.ch

EPFL STI IMX LMOM
MXG 136, Station 12
CH-1015 Lausanne

zag conformation (hydrogen-bonding interactions between the OH groups may be the dominating effect here). Note, however, that the resulting structure is not chemically periodic, which is somewhat contrary to the strict definition of a crystal.

2.2 Stability and Melting Temperature

Why do polymers take the trouble to get into such regular conformations to crystallize? This allows them to better optimize their conformational energies and their intermolecular interaction (to maximize the value of the cohesive energy) with respect to the random conformations of the amorphous state. Thus, they can reduce (in general) their volume and their internal energy, and therefore their enthalpy. On the other hand, as we go to a much more ordered state, there is a significant loss of entropy. Thus, at constant pressure, the crystalline phase will only be stable if the temperature is below a "thermodynamic" melting point, T_{m0}, where the amorphous phase is in equilibrium with the crystalline phase. T_{m0} is therefore given by

$$\Delta G = \Delta H - T_{m0}\Delta \mathrm{S} = 0 \qquad (1)$$

where ΔG is the "Gibbs free energy", ΔH is the "melting enthalpy" and ΔS is the "melting entropy". The changes of these two quantities during the transition from the crystalline state to the amorphous state are referring to a unit volume of the crystal. So, if the cohesion is dominant (so if the value of E_{coh} is large), and the entropy change is small, T_{m0} will be higher than otherwise. We will now consider the effect of the chain structure on ΔH and ΔS, and therefore on T_{m0} in starting with ΔH.

2.2.1 Melting Enthalpy and Structure

To increase ΔH as much as possible, the cohesive energy (i.e. its absolute value) must be reduced as much as possible and the conformational energy of the crystal relative to that of the amorphous state. For this purpose, the chains are adopting either a zig-zag conformation or an equivalent regular, helical conformation. The chains can then be approximated as a very high form factor cylinder. We know that the ideal stacking of a set of perfect cylinders corresponds to a hexagonal lattice where the cylinders are aligned and the projections of the axes of the cylinders form an equilateral triangle. Often, pseudo-hexagonal arrangements (orthorhombic, monoclinic or triclinic), are strongly favored in crystalline polymers because true macromolecules never represent perfect cylinders. It is certainly difficult to reconcile the very anisotropic form of a cylinder with a cubic lattice, for example. The packing can become less favorable in cases where the low energy conformations are not very compact, i.e. in presence of very large side groups for example, or if the polymer is intrinsically non-linear in nature (compare *trans* and *cis* 1,4-polyisoprene from the first week, for example).

Slide 161 shows again the example of PE compared with that of poly(tetrafluroethylene) (PTFE). PTFE is an interesting system because the fluorine atoms are very large compared to

Dr. Daniel Görl
daniel.gorl@epfl.ch
lmom.epfl.ch

EPFL STI IMX LMOM
MXG 136, Station 12
CH-1015 Lausanne

the hydrogens in PE and therefore very bulky. So, although the polymer backbone structure is based on CC single bonds, PTFE is required to adopt a very compact helical conformation and is very little mobile (PTFE is therefore a very rigid polymer). We can consider PTFE as a perfect cylinder. The crystalline lattice of PTFE is therefore hexagonal. In contrast, PE is less "cylindrical" and its lattice is therefore pseudo-hexagonal rather than perfectly hexagonal.

In case of strong specific interactions, ΔH can be very high. Slide 173 shows the example of aliphatic polyamides, where the formation of a regular conformation optimizes the chain packing and the orientation of amide groups for hydrogen bonding interactions. This is not possible in the amorphous state. Thus, the chains of PA66 (or Nylon 6,6) form layers of parallel chains in zig-zag conformation linked via intermolecular hydrogen bonds. These layers can stack together to form the three-dimensional crystalline structure of this polymer, whose melting enthalpy and therefore the melting point are much higher (see Equation 1) than those of PE, for example, despite their broadly similar chemical structures and rigidity (see 2.2.1). Indeed, if we "dilute" such hydrogen bonds (amide groups) by increasing the number of CH_2 per repeating unit, the melting temperature gradually decreases towards that of PE. This may remind you that we observe the same trend with regard to T_g.

2.2.1 Melting Entropy and Structure

The more rigid the chain, i.e. the higher C_∞, the smaller the change in ΔS during crystallization and the higher will be T_{m0} for a given value of ΔH according to Equation 1. Indeed, if a chain is already very rigid in the amorphous state, its conformations deviate from the typical random coil structure and may be significantly outstretched. We therefore imagine that the loss of entropy (or disorder) is relatively low upon crystallization. Though this is a bit of a simplistic picture, you should therefore be able to order the polymers of Slide 151 with respect to their T_{m0} just by looking at their structures - are they rigid chains, or do they contain groups capable of strong specific intermolecular interactions, or both at the same time? Here too, we notice the same trends as for T_g, which implies that T_{m0} and T_g are globally correlated in synthetic polymers (Slide 175).

3. Polymeric Single Crystals

3.1 Morphology of a Crystalline Lamella

One can prepare single crystals or "lamellae" of certain polymers by isothermal crystallization from extremely dilute solutions so that the chains are not entangled. Slide 164 shows the example of PE in xylene. We speak of lamellae, **because these crystals are present in the form of plates of regular geometry** which reflects the shape of their unit cell (so diamond-like in the case of PE[1] but hexagons in the case of POM), whose lateral dimensions

[1] In fact, they are initially hollow pyramids, but upon transfer to a carbon film for transmission electron microscopy measurements, they collapse. Hence, the small ridges at the surface of the single crystal shown on Slide 164.

Dr. Daniel Görl
daniel.gorl@epfl.ch
lmom.epfl.ch

EPFL STI IMX LMOM
MXG 136, Station 12
CH-1015 Lausanne

can reach µm, **but the thickness is of the order of ca. 10 nm only**. Electron diffraction indicates that the axes of the chains are approximately perpendicular to the plane of these lamellae. Because the length of a stretched PE chain is typically 1000-10,000 nm, **the chains must fold back when forming these single crystals**. The sketch on slide 165 shows how a single crystal might look at the chain scale. Here we show chains going out and going into the crystal by making a sharp turn. The exact nature of these folds remains a subject of controversy because it is difficult to observe them directly. However, the fact that chains must come out of the crystal at more or less regular intervals implies that even a single crystal of this type is not 100% crystalline.

3.2 Melting Point of a Crystalline Lamella

It is therefore concluded that the chains of a polymer of high molecular weight fold back to form crystalline lamellae. However, this folding is energetically unfavorable, especially if the chain is rigid. It follows that in general the melting temperature, T_m, of a lamella with thickness l is less than T_{m0}. As l can vary appreciably according to the conditions of crystallization (see the end of this section), the T_m of polymers are not well defined. And since they cannot be obtained under perfect crystal shape, you cannot measure T_{m0} directly. The values given for typical polymer melting temperatures during our class are therefore referring to experimental values much less than T_{m0}.

We try to quantify this effect, for which we can use the sketch of a PE lamella (Slide 166). The enthalpy of this lamella will contain terms related to the surface energy, σ, of the side faces and to the surface energy, σ_e, of the upper and lower faces where the folds are located. So, if the edges of the crystal are of lengths A and B, since melting takes place when the free enthalpy is equal to 0, we can use Equation 1 to get T_m as follows:

$$\begin{aligned}\text{free energy of a lamella} &= (\text{volume of the lamella} \times \frac{\text{enthalpy of a perfect crystal}}{\text{volume}} \\ &- \sigma \times \text{lateral surface} - \sigma_e \times \text{normal surface}) \\ &- (\text{volume of the lamella} \times T \times \frac{\text{entropy of a perfect crystal}}{\text{volume}})\end{aligned}$$

$$\Delta G_{lamella} = 2ABl\Delta H - 4\sqrt{A^2+B^2}l\sigma - 4AB\sigma_e - 2ABlT\Delta S$$

And at T_m, $\quad 2ABl\Delta H - 4\sqrt{A^2+B^2}l\sigma - 4AB\sigma_e - 2ABlT_m\Delta S = 0$

$$T_m = \frac{2ABl\Delta H - 4\sqrt{A^2+B^2}l\sigma - 4AB\sigma_e}{2ABl\Delta S}$$

We can neglect the term σ because typically the folding energy is relatively large and $A, B \gg l$:

$$T_m \approx \frac{\Delta H}{\Delta S}\left(1 - \frac{2\sigma_e}{l\Delta H}\right) = T_{m0}\left(1 - \frac{2\sigma_e}{l\Delta H}\right) \qquad (2).$$

Dr. Daniel Görl
daniel.gorl@epfl.ch
lmom.epfl.ch

EPFL STI IMX LMOM
MXG 136, Station 12
CH-1015 Lausanne

For a typical value of l of 10 nm, we obtain values of T_m which are some 40 K less than T_{m0}!

3.3 Why Lamellae?

One can wonder why polymers crystallize in this form, which is very far from equilibrium, and why l is so small. This is not an easy question and the theories for nucleation and lamella growth are controversial to say the least. Nevertheless, we can admit that there is a kinetic barrier to the nucleation of a lamella from a polymer melt or a solution. Small aggregates containing n cylinders of length l and cross section a^2 (which may originate from longer chain lengths, but folded over) are formed and disappear spontaneously within the polymer. Only by exceeding a critical size, a nucleus continues to grow into a crystal. The change in free enthalpy during formation of such a nucleus at a temperature $T < T_{m0}$ is

$$\Delta G_{nucleus} \approx 2na^2\sigma_e + 4\sqrt{n}la\sigma - nla^2\Delta G(T) \qquad (3),$$

where (from Equation 1) the free energy of melting per unit volume of a perfect crystal will be

$$\Delta G = \Delta H - T\Delta S = \Delta H\left(1 - \frac{T}{T_{m0}}\right) = \frac{\Delta H \Delta T}{T_{m0}} \qquad (4).$$

$\Delta G_{\text{nucleus}}$ will be positive for small nuclei (l, n are small) and will increase with l and n to reach a maximum ΔG^*, which is the activation energy. We can find ΔG^* by differentiation and subsequent integration:

$$\left.\frac{\partial \Delta G_{nucleus}}{\partial n}\right|_l = \left.\frac{\partial \Delta G_{nucleus}}{\partial l}\right|_n = 0 \implies l^* = \frac{4\sigma_e T_{m0}}{\Delta H \Delta T} \implies \Delta G^* = 32\sigma^2\sigma_e\left(\frac{T_{m0}}{\Delta T \Delta H}\right)^2 \qquad (5).$$

The nucleation rate, N, is then

$$N = N_o \exp\left[-\frac{A}{T - T_o}\right]\exp\left[-\frac{\Delta G^*}{kT}\right] \qquad (6).$$

We see that the critical thickness l^* and ΔG^* decrease with supercooling ΔT. N increases until the viscosity (the first term in Equation 6) begins to increase sharply near the glass transition. N passes therefore through a maximum between T_g and T_{m0} and tends towards 0 at T_{m0} and T_g.

As l^* is fixed by the folds, a stable nucleus can only grow in the lateral directions (in fact it increases by a factor of about 2 during growth). Thus, the thickness of lamellae is determined *kinetically*[2] - **the polymer crystallizes with the value of *l* which allows it to crystallize as quickly as possible at a given *T*** (it is often assumed that the growth involves secondary nucleation on the lateral surfaces of the lamellae). If we could get crystals at $T = T_{m0}$, they would have an infinite thickness, but we would have to wait an infinite long time for this to happen. **In**

[2] A crystal made up of small molecules can grow more or less rapidly in all directions, and therefore reach an effectively infinite size (i.e. large enough so that the surface energy no longer influences the melting temperature).

Dr. Daniel Görl
daniel.gorl@epfl.ch
lmom.epfl.ch

EPFL STI IMX LMOM
MXG 136, Station 12
CH-1015 Lausanne

most semi-crystalline polymers, crystallization becomes fast enough to occur during injection molding at supercooling, ΔT, of several tens of K, where l^* is on the order of 10 nm.

4 Semicrystalline Polymers

Constraints on the mobility of condensed polymers in the molten state or in concentrated solution imply crystallinity levels well below 100%. Indeed, polycarbonate (PC), is not very mobile due to its rigid chains. It often has a crystallinity rate close to zero for typical cooling rates of industrial processing methods such as injection molding or extrusion. This is why we consider **PC to be an amorphous polymer, even though it can crystallize if given enough time.**

Even soft polymers like isotactic PP often show high levels of crystallinity of around 50% when crystallizing from the molten state. The rest of the polymer is therefore the amorphous state (glassy or rubbery depending on T_g). We are therefore talking about glassy semi-crystalline polymers in the case of polymers such as PET or PLLA.

4.1 Spherulites (Slides 181-184)

In the absence of flow, **the microstructure of a semi-crystalline polymer is typically "spherulitic"**. **A spherulite is a more or less spherical cluster of amorphous material and crystalline matter.** From birefringence measurements, we can show that the axes of the chains and therefore the $\underline{\boldsymbol{c}}$ axis of the crystal phase is tangentially oriented in a conventional spherulite. X-ray scattering measurements or direct observation with a transmission electron microscope, for example, show that **these spherulites contain lamellae with a thickness of approximately 10 nm, separated by amorphous layers of approximately the same thickness** depending on the degree of crystallinity (Slide 182). Like in single crystals, the axes of the chains are generally (or almost) perpendicular to the plane of these lamellae and **the lamellae are therefore typically oriented along the radii of the spherulites**.

Where do spherulites come from? A simple model is presented on the slide 183 where we consider, first, an isolated lamella that nucleates somewhere in the supercooled polymer. The lamella growth occurs by adding chains to the side surfaces. It is assumed that this lamella will increase its surface while keeping a constant thickness l. In a diluted solution with very stable temperature this gives rise to single crystals as on the Slide 164. However, at the molten state the chains are strongly interpenetrated and in constant motion. Our lamella, which has reduced flexural rigidity due to its low thickness, will be pulled in all directions, and will tear easily.

- A tear will create a "giant screw dislocation" with a Burgers vector, $|\boldsymbol{b}| = l$, and new lateral surfaces from which the lamella can grow to form a “spiral”.
- Spiral growth has the effect of generating multiple layers that are more or less parallel to each other. However, there will be amorphous polymer trapped between these

Dr. Daniel Görl
daniel.gorl@epfl.ch
lmom.epfl.ch

EPFL STI IMX LMOM
MXG 136, Station 12
CH-1015 Lausanne

lamellae. The pressure exerted by the trapped amorphous layer, which tries to adopt a statistical conformation, leads to a separation and divergence of the trajectories of the lamellae.

- Other tears will occur in each lamella, which multiply and separate, and so on.

The result in 3D is a ball of more or less radially oriented lamellae, which are separated by amorphous layers, in line with experimental observations. In thin films, the same mechanisms give rather circular objects (truncated spherulites) that can be modeled relatively easily with filamentary "lamellae", which then multiply and separate. The result are regions that are approximately circular on either side of the initial lamella. Note that the semicrystalline film of PC shown on slide 183 was obtained by exposing an amorphous film to a solvent for several days.

4.2 Factors Influencing Lamellar or Spherulitic Morphology

We note that by increasing the molar mass the degree of crystallinity of a sermicrystalline polymer gets reduced because chain mobility decreases and negatively impacts the mobility term of Equation 6 (Slide 176). The same is true for an increased degree of branching, which increases the viscosity for a fixed molar mass (if the degree of branching is too high, the crystallinity rate becomes zero). In the case of PE, we use branching to control the degree of crystallinity (Slide 178).

We also observe spherulitic structures that are quite different from the classical structure described in Section 4.1. For example, in the "α phase" of isotactic PP (there are other polymorphs as well), the multiplication of lamellae occurs partly by twinning; secondary lamellae appear whose trajectories are almost 90° to those of the primary lamellae giving a "crossed" texture (Slide 184). This unusual structure is typical of commercial PP products, which are approximately 90% isotactic. It is therefore perhaps linked to interruptions in those isotactic sequences.

It is also noted that crystallization can be favored, if the polymer is oriented by a flow or strain, because ΔS is reduced. In this case, the lamellae are typically oriented perpendicular to the direction of orientation of the molecules. This leads to textures of "stacked" lamellae in injection moldings (typically found on the surface of casts where the flows are relatively strong). During the manufacture of fibers (processes which imply a very high orientation of the melt), we observe so-called "Shish-kebab" structures (Slide 185), where lamellae nucleate on a core which consists of "extended chain crystals".

The latter dominate the structure of certain so-called "ultra-oriented" fibers. We can prepare ultra-oriented fibers from ultra-high molecular weight polyethylene (UHWPE) (Slide 186), i.e. PE with M_w of up to 3,000,000 g/mol, or even more. The fibers are formed from a very diluted gel so that there is little interaction between the chains. The chains nevertheless form a

Dr. Daniel Görl
daniel.gorl@epfl.ch
lmom.epfl.ch

EPFL STI IMX LMOM
MXG 136, Station 12
CH-1015 Lausanne

continuous network due to their very large size, and can be oriented by applying a deformation to the gel. Under these conditions, the degree of orientation and crystallinity after formation and drying of the fibers are extremely high and the resulting mechanical properties are comparable to those of inorganic fibers in the direction of orientation. This is because the load is directly transferred to the covalent C-C bonds of the chains in their zig-zag conformation, while weaker secondary interchain interactions are exceptionally absent. However, if we try to do the same thing with isotactic PP, the results are disappointing, because the chains crystallize in a helical conformation. At the module level, this is like comparing a stretched wire and the same wire in the form of a spring.

4. Summary

- Many polymers are able to crystallize, in particular chains that are periodic, linear, or capable of forming linear conformations.
- In single crystals the chains fold: monocrystals or "lamellae" are much thinner in ***c*** direction than the length of a chain; fold surface energy leads to substantial reduction in the apparent melting temperature.
- Polymers crystallized from the melt are semicrystalline (often around 50% amorphous). Most common morphology is based on spherulites, but under certain processing conditions, stacked lamellae (fibers) or extended chain structures (UHMWPE) can be observed.

Dr. Daniel Görl
daniel.gorl@epfl.ch
lmom.epfl.ch

EPFL STI IMX LMOM
MXG 136, Station 12
CH-1015 Lausanne