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

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Course Notes of Chapter 3.3

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1. Semicrystalline Polymers

Crystallization in polymers is always partial and heterogeneous, leading to complex morphologies. Even polymers that crystallize efficiently from the melt never reach full crystallinity. Such materials are referred to as **semicrystalline polymers**.

Because semicrystalline polymers contain regions of different density and refractive index at the microscopic scale, they often appear **opaque** due to light scattering. However, exceptions exist: for example, PET bottles (~30% crystalline) remain transparent because their structural features are smaller than the wavelength of visible light.

1.1 Characteristics of Polymeric Crystals

A crystal is a periodic solid in which an identical structural motif, the **unit cell**, repeats in three dimensions. The smallest building block from which the unit cell can be generated by symmetry operations is called the **asymmetric unit** (Slides 171–173).

In polymers, perfect three-dimensional periodicity would require all chains to have identical molar mass, chain ends, and conformations. Such conditions are never met in real synthetic polymers. As a result, **polymer crystals are always imperfect**, even under ideal conditions such as crystallization from very dilute solution. The resulting morphology consists of **crystalline lamellae embedded in amorphous regions**, giving rise to the characteristic semicrystalline texture of most crystallizable polymers.

The crystalline structure of polymers differs from that of small molecules because of chain connectivity and conformational flexibility. Biopolymers such as proteins, with precisely defined sequences and molar mass, can form unique three-dimensional conformations from which they crystallize. In this case, the entire macromolecule may constitute the asymmetric unit.

Synthetic homopolymers, in contrast, crystallize when their chains adopt regular conformations, typically zig-zag or helical, that can be periodically stacked. By convention, the chain axis defines the *c*-axis of the unit cell. Typical examples include polyethylene (PE), isotactic polypropylene (iPP), and poly(oxymethylene) (POM) (Slide 166). **These thermoplastics show mechanical properties comparable to those of glassy amorphous polymers, even when their glass transition temperature T_g lies below room temperature.**

As shown on Slides 172–175, crystalline PE adopts an all-*trans* zig-zag conformation within an orthorhombic unit cell (space group *Pnam*), whose asymmetric unit consists of half a –CH2– group. From this minimal building block, the entire three-dimensional crystal can be reconstructed by applying the symmetry operations of the space group.

Structural irregularities in the backbone sequence, branches, crosslinks, or chain ends disrupt this periodicity. Consequently, random copolymers, branched polymers, and highly crosslinked networks (thermosets) generally do not crystallize significantly (Slide 177). However, small amounts of such irregularities can be tolerated if they are expelled to the amorphous regions and if the crystalline lamellae remain sufficiently small.

A particularly illustrative case of configurational regularity is **tacticity** in vinyl polymers:

- **isotactic PP** crystallizes via a 3_1-helix (3 repeat units per helix turn), driven by steric repulsion between the methyl groups.
- **in syndiotactic PP**, the alternating substituents minimize steric hindrance, which allows the polymer to crystallize from an extended zig-zag conformation, which is enthalpically more favored than a helical one (which would contain *gauche* states).
- **atactic PP** lacks configurational regularity and does not crystallize.

Interestingly, atactic poly(vinyl alcohol) can crystallize despite its stereochemical disorder, because hydrogen bonding between –OH groups dominates the packing and stabilizes a regular zig-zag arrangement for both atactic and syndiotactic sequences. The resulting structure is not strictly chemically periodic but exhibits long-range positional order and is therefore functionally crystalline.

1.2 Polymer Melting Temperature

Polymers crystallize because ordered chain arrangements minimize the internal energy by optimizing both chain conformations and intermolecular interactions. This enthalpic gain ($\Delta H < 0$) comes at the cost of configurational entropy loss ($\Delta S < 0$), as the system becomes more ordered. The crystalline phase is therefore stable only below a thermodynamic melting temperature T_{m0}, defined by equality of the free energies of the crystalline and amorphous phase:

$$\Delta G = \Delta H - T_{\mathrm{m0}} \Delta S = 0 \quad , \tag{1}$$

where ΔG is the Gibbs free energy change, ΔH the melting enthalpy, and ΔS the melting entropy.

When crystallized slowly from dilute solution, some polymers (e.g. PE) form **single crystals** in the shape of thin platelets (**lamellae**), typically ~10 nm thick but several µm wide (Slide 179). Electron diffraction reveals that the polymer chains are oriented approximately perpendicular to the lamellar surface. Because the fully extended chain length is much greater than the lamellar thickness, chains must fold back at the lamellar surfaces. The detailed nature of these folds remains debated, but their presence introduces an energetic penalty associated with the fold surfaces, characterized by a **surface free energy σ_{e}**.

Fold surfaces reduce the stability of thin lamellae and therefore lower the observed melting temperature T_{m} relative to the equilibrium value T_{m0}. This surface-to-volume effect of chain folds on thermodynamic stability is quantified by the **Gibbs-Thomson** relationship:

$$T_m = T_{\mathrm{m0}} \left(1 - \frac{2\sigma_{\mathrm{e}}}{\Delta h_v \cdot l}\right) \quad , \tag{2}$$

where Δh_v is the melting enthalpy per unit and l is the lamellar thickness. For typical lamellae ($l \approx 10$ nm), T_{m} lies 30–50 °C below T_{m0}.

1.3 Kinetic Control of Lamellar Thickness

Polymers crystallize into lamellae due to a **kinetic** compromise. During crystallization, small ordered regions (nuclei) form and dissolve continuously. Only those exceeding a **critical size**, determined by the competition of volume free energy gain and surface free energy cost, can grow further. This nucleation process involves an **activation barrier** that depends on lamellar thickness: it is high for both very thin and very thick lamellae and reaches a minimum corresponding to the most probable thickness observed experimentally (see the Reader on *Polymer Melting Temperature* for details).

If crystallization occurred exactly at T_{m0}, both the critical nucleus size and activation barrier would become infinite, and the nucleation rate would approach zero (Slide 183). Hence, **polymer crystallization requires undercooling ($\Delta T = T_{\mathrm{m0}} - T$), which provides the necessary driving force.** In practice (e.g. injection molding), crystallization becomes sufficiently rapid at supercoolings of several tens of degrees, yielding lamellae with typical thickness around 10 nm.

The overall crystallization rate N is governed by two opposing effects (Slide 184):

- increasing supercooling increases the driving force and nucleation rate.
- decreasing temperature increases viscosity, which slows down chain mobility and crystal growth.

A simplified empirical relation illustrates this competition between kinetics and driving force:

$$N = N_o \exp\left[-\frac{A}{T - T_o}\right] \exp\left[-\frac{\Delta G^*}{kT}\right] \,, \tag{3}$$

Here, the first term accounts for the temperature dependence of chain mobility (viscosity), and the second term is a Boltzmann factor for overcoming the activation barrier ΔG^*. As a result, N passes through a maximum between T_{g} and T_{m0} and tends towards zero at both limits.

2. Factors Influencing the Melting Temperature

The equilibrium melting temperature T_{m0} of a polymer is determined by the balance between the enthalpic gain (ΔH) and entropic loss ($\Delta \mathrm{S}$) associated with crystallization:

$$T_{\mathrm{m0}} = \frac{\Delta H}{\Delta \mathrm{S}} \,, \tag{4}$$

Any factor that increases cohesive energy or reduces the entropy change upon melting will therefore raise both T_{m0} and the observed melting temperature T_{m}.

2.1 Structural Factors Affecting the Melting Enthalpy (Δ*H*)

The melting enthalpy represents the total energy required to disrupt the intermolecular cohesion and depends primarily on how efficiently chains pack and how strong their intermolecular interactions are.

a) Chain Packing and Conformation

In the crystalline state, polymer chains adopt conformations that minimize internal energy, most commonly zig-zag (all-*trans*) or regular helical. These conformations maximize van der Waals contacts and lead to dense, often pseudo-hexagonal packing. True hexagonal packing occurs for chain conformations with nearly cylindrical cross-sections, such as in PTFE, where bulky fluorine atoms enforce a tight helix. By comparison, the parallel all-*trans* configured chains in PE deviate slightly from this ideal geometry, resulting in an orthorhombic (pseudo-hexagonal) lattice.

Packing becomes less favorable in polymers with bulky side groups or intrinsically kinked backbones (e.g. *cis*-1,4-polyisoprene), reducing cohesion and thus both ΔH and T_{m0}.

b) **Specific Intermolecular Interactions**

Strong interactions such as hydrogen bonds greatly increase ΔH (Slide 188). For example, in polyamides (e.g. PA 6,6), chains may adopt extended zig-zag conformations that allow formation of highly ordered hydrogen-bonded layers.

Diluting such groups by inserting additional –CH2– units between the amide linkages progressively lowers both ΔH and T_{m0}, approaching values typical of non-polar polymers like PE.

c) Molar Mass

Increasing molar mass raises ΔH because longer chains provide more cohesive energy per macromolecule and reduce the fraction of end groups that disturb crystal packing. This effect saturates above a certain chain length, where ΔH approaches an asymptotic value corresponding to infinitely long chains (Slide 190).

At the same time, higher molar mass reduces the overall crystallinity due to lower chain mobility (see Equation 3).

d) Branching

Branching increases viscosity at a fixed molar mass and, if excessive, prevents crystallization altogether. In PE, controlled branching is therefore used to tune the degree of crystallinity (Slide 191).

2.2 Structural Factors Affecting the Melting Entropy (ΔS)

The melting entropy reflects the difference in conformational freedom between crystalline and amorphous states. Factors that reduce the disorder of the melt (or increase order in the amorphous phase) will reduce ΔS and thereby increase T_{m0} for a given ΔH.

a) Chain Stiffness

Rigid polymers, characterized by a high characteristic ratio C_∞, exhibit small entropy changes upon melting because their chains are already conformationally restricted in the amorphous state (Slide 186).

Examples include PTFE, Kevlar, and other aromatic polyamides. By comparison, flexible chains such as those of polyethylene have many accessible conformations in the melt, leading to large ΔS and low T_{m0}.

b) Orientation and Pre-ordering

External orientation by flow or deformation can also lower ΔS, since amorphous chains become partially aligned prior to crystallization (Slide 187). This favors crystallization at higher temperatures and leads to anisotropic morphologies (see below).

Thus, both ΔH and ΔS are influenced by similar structural parameters, rigidity and intermolecular interactions. Polymers with high T_{m0} often also exhibit a high glass-transition temperature T_{g}, reflecting the underlying balance between cohesive forces and conformational mobility (see Slide 189).

3. Morphology of Semicrystalline Polymers

Because of the limited chain mobility in the condensed phase, the degree of crystallinity in polymers rarely exceeds about 50%. Rigid polymers such as polycarbonate (PC) typically remain amorphous under conventional cooling conditions (e.g. injection molding or extrusion), while more flexible polymers like isotactic PP or PET readily form semicrystalline structures. These contain both crystalline lamellae and amorphous regions, which can be glassy or rubbery depending on whether the temperature is below or above T_{g}.

3.1 Spherulites (Slides 195-197)

In the absence of flow or orientation, crystallization from the melt generally proceeds through **spherulitic growth**, producing roughly spherical aggregates of radially oriented lamellae separated by amorphous material. Under polarized light, these structures display the characteristic Maltese-cross pattern due to birefringence. X-ray diffraction and optical analyses show that within each lamella the chain axes are oriented tangentially to the lamellar plane, while the lamellae themselves radiate outward from a common nucleus.

Spherulites form through **repeated lamellar branching and twisting**: as thin lamellae grow, mechanical stress or entanglements can cause local tearing or screw dislocations, generating new lateral surfaces that serve as growth fronts. This process can lead to spiral or helical growth patterns when multiple lamellae develop roughly parallel to one another.

However, the amorphous material between lamellae resists the imposed ordering: the chains there tend to adopt random-coil conformations. The resulting pressure and conformational frustration cause divergence and separation of neighboring lamellae. The cumulative effect of many such local events gives rise to the overall spherical morphology.

Variations of the classical spherulitic texture can occur. For instance, in the α-phase of isotactic PP (which also has other polymorphs), lamellar multiplication occurs partly by twinning. Secondary lamellae grow at nearly 90° to the primary ones, producing a "cross-hatched" texture (Slide 198). This morphology is typical of commercial iPP, which is about 90% isotactic, and is likely linked to interruptions or defects in isotactic sequences.

3.2 Oriented Morphologies

When crystallization occurs under flow or strain, molecular orientation strongly affects morphology. In this case, lamellae tend to grow perpendicular to the direction of chain orientation. Such conditions are common near mold surfaces in injection-molded parts, leading to layered, "stacked lamellar" textures.

Under stronger deformation, such as in fiber spinning or high-shear extrusion, a distinct morphology known as the **shish-kebab structure** forms. Here, lamellae (the "kebabs") nucleate and grow on pre-oriented fibrillar cores (the "shish"), which consist of extended-chain crystals (Slide 199).

At the extreme of molecular orientation, as achieved in **ultra-high molecular weight polyethylene (UHMWPE)** fibers, chains can crystallize almost entirely in extended conformations (Slide 200). This yields nearly perfect extended-chain crystals, very high crystallinity, and outstanding mechanical strength along the fiber axis. The load is then transmitted directly through the covalent C–C bonds of the fully extended zig-zag chains, with minimal contribution from weaker van der Waals interactions. In contrast, isotactic polypropylene, whose chains adopt a helical conformation, exhibits much lower stiffness. In other wods, PE and PP compare like a taut wire and a coiled spring.

4. Summary

- Many polymers can crystallize, particularly those with regular, linear, and periodic chain structures.
- The equilibrium melting temperature T_{m0} is a thermodynamic quantity, while the observed melting temperature T_m depends on lamellar thickness and morphology.
- The degree of supercooling ΔT provides the driving force for crystallization, but the actual process is kinetically controlled.
- The observed lamellar thickness (typically around 10 nm) represents a kinetic optimum, not the thermodynamic equilibrium value.
- T_{m0} reflects a balance between enthalpic stabilization (cohesive interactions) and entropic penalty (loss of configurational freedom). Structural modifications that increase cohesive energy or decrease conformational entropy lead to higher T_{m0}.
- In chain-folded crystals, lamellae are much thinner than the contour length of the chains. The fold surface energy lowers the apparent melting temperature compared to the equilibrium value.
- Semicrystalline polymers crystallized from the melt typically contain both amorphous and crystalline phases. The most common morphology is the spherulite, though under flow or orientation, stacked lamellae, shish-kebab, or extended-chain structures (as in UHMWPE fibers) may form.