

Physics of Solid Polymers – Part 3

SEMICRYSTALLINE POLYMERS

Polymers are never 100% crystalline. They are said to be **semicrystalline**. This was established early, using X-ray diffraction (XRD).

In a “powder” X-ray diffraction experiment, the sample is irradiated by an X-ray beam and a detector moves on a circle and records diffracted intensity as a function of the diffraction angle 2θ (**Figure 1**).

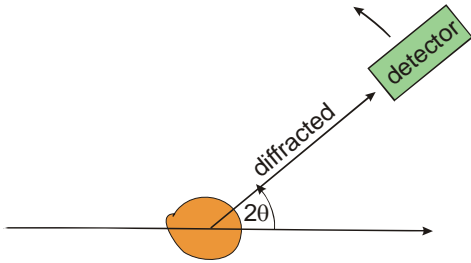


Figure 1 Geometry of powder X-ray diffraction

Diffractograms of a crystalline material consist of sharp peaks (“reflections”) due to constructive interference of X-ray waves on the atomic grating of the crystals (**Figure 2** top). Diffractograms from liquids or glasses have one or two broad maxima (“diffuse scattering”) (**Figure 2** middle). A typical semicrystalline polymer produces a diffractogram that contains both sharp “reflections” and diffuse scattering (**Figure 2** bottom).

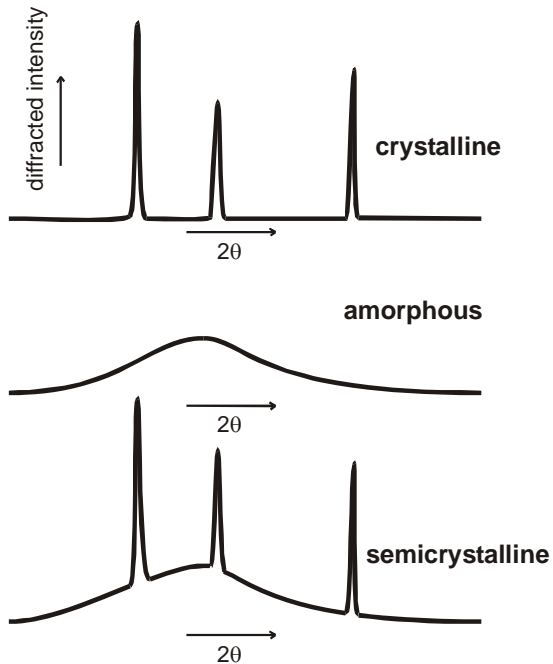


Figure 2 Typical diffractograms

A crystalline and a noncrystalline (amorphous) phase are present. The crystalline fraction (by weight or by volume) is known as **degree of crystallinity** or simply **crystallinity**.

Crystallinity by volume (volume crystallinity):

$$X = \frac{v_c}{v_c + v_a} = \frac{I_c}{I_c + I_a}$$

v_c, v_a are volumes of crystalline and amorphous phases. I_c, I_a are integrated intensities under all the crystalline and diffuse peaks, respectively, in the X-ray diffractogram. The above equation is based on the principle that a volume of a material scatters a fixed fraction of X-ray photons, irrespective of its phase. The photons scattered on crystals are concentrated in narrow angular regions, whereas those from the amorphous phase are spread broadly.

Thus XRD is the only absolute (primary) method of determining X , and it can be applied directly to a new or unknown polymer.

In crystallizable polymers below melting point X can be as high as 85% (0.85) in linear polyethylene and as low as 0% in aromatic polymers - e.g. poly(ethylene terephthalate) (PET) quenched from melt to below T_g . PET can reach 50% crystallinity on annealing above T_g .

Aromatic thermoplastics like poly(ether ether ketone) (PEEK) have X of typically only 0.2 – 0.3.

Density of a polymer:

$$\rho = \frac{\text{total.mass}}{\text{total.volume}} = \frac{\rho_c v_c + \rho_a v_a}{v_c + v_a} = \rho_c X + \rho_a (1 - X) = \rho_a + (\rho_c - \rho_a) X$$

Example: polyethylene $\rho_c = 1.00 \text{ gcm}^{-3}$, $\rho_a = 0.85 \text{ gcm}^{-3}$ (note: “ ρ ” is Greek “*rho*”, not latin “*p*”)

In an industrial quality control laboratory, ρ is typically determined using *density gradient columns*. Find out more about them. Measuring heat of fusion by DSC can also be a quick way of establishing X , since $X = \Delta H_f / \Delta H_f^0$, where ΔH_f is the measured heat of fusion (heat of melting) of the polymer and ΔH_f^0 that of a hypothetical 100% crystalline polymer. ΔH_f is determined from the area under the endothermic melting peak in the DSC curve (“thermogram”) where heat flow into the sample (in $\text{mW s}^{-1} \text{mg}^{-1}$) is recorded against time (or temperature) during heating at a constant rate. However, to determine X by DSC, we first need to know ΔH_f^0 . For common polymers ΔH_f^0 can be found in literature. If ΔH_f^0 is not known, we have to determine its value by recording XRD on a series of samples with different X . How?

Other methods of determining X : broad-line nuclear magnetic resonance (NMR), IR spectroscopy (some absorption bands are specific to the crystalline phase). All must be calibrated against absolute X determined by XRD.

Problem: Crystallinities of HDPE and LDPE are typically 0.8 and 0.5. Calculate their densities.

LAMELLAR POLYMER CRYSTALS

Initially it was thought that polymer crystals were fibrillar (“fringed micellae” type), see Figure 3. This was later shown to be wrong, except in special cases (drawn fibres, some polymer gels from concentrated solutions).

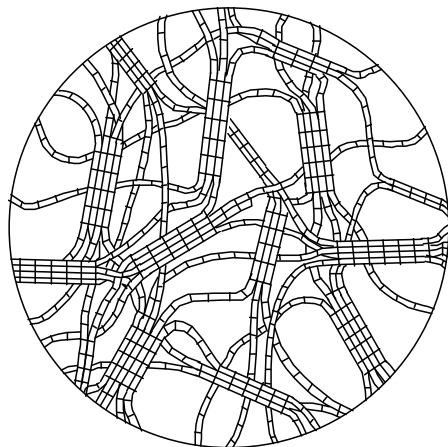


Figure 3 “Fringed micelle” model of semicrystalline polymers. Abandoned today.

The breakthrough in understanding the structure of semicrystalline polymers came when **single crystals** of polyethylene grown from dilute solution were first observed by transmission electron microscopy (Keller 1957).

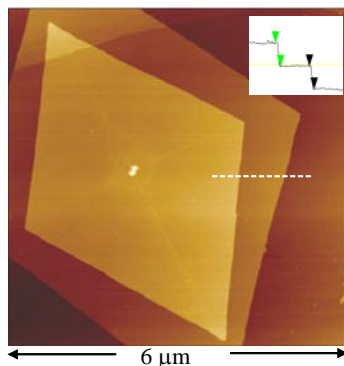


Figure 4 AFM image of polyethylene single crystals grown from dilute solution. Thickness 10 nm. Chains are along viewing direction.

Single crystals are very thin **lamellae** (note: 1 lamella, 2 lamellae!; not “lamellar”. “Lamellar” is an adjective!). Monolayer crystals are **10 nm thick**, several microns wide (see AFM Figure 4). Polymer chains are perpendicular to the layers (electron diffraction!). An extended chain of a typical polymer is ca. 1 μm long, i.e. 100 times the thickness of a crystal lamella. The chains (not the crystals!) **fold back** at the surface of the lamellar crystal. An average length chain folds backwards and forwards many times – see Figure 5.

Most flexible crystallisable polymers form lamellar single crystals from solution. The shape depends on crystallographic symmetry.

MELT-CRYSTALLISED POLYMERS

Melt crystallised polymers were also found to be lamellar (small-angle X-ray scattering (SAXS), transmission electron microscopy of thin stained sections, scanning electron microscopy (SEM) of partially extracted bulk material).

Lamellar stacks - alternating crystalline and amorphous layers.

- Layer periodicity typically $20 < l < 50$ nm (= crystalline + amorphous layer thickness)
- folds are **less regular**, “loose”
- “**tie molecules**” between lamellae - give material mechanical integrity
- l decreases as crystallisation temperature T_c is lowered.

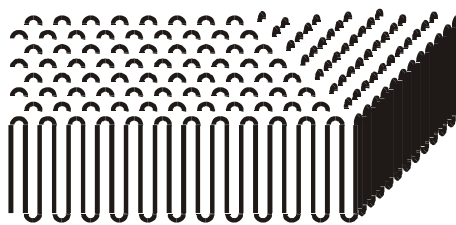
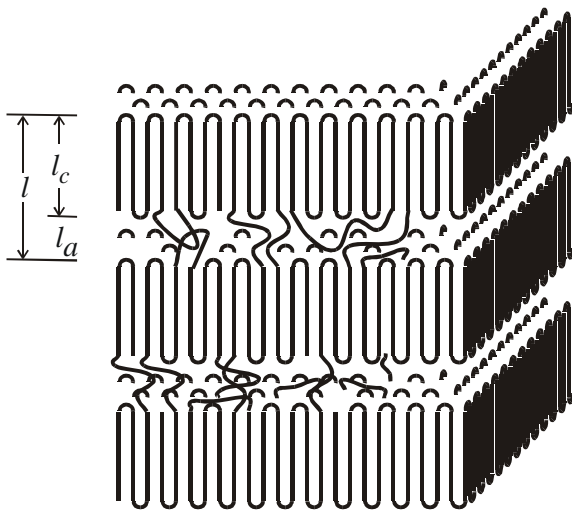


Figure 5 Folded-chain lamella - single crystal from solution



Small-angle X-ray scattering of a bulk melt-crystallized polymer gives a peak in the 2θ range of 1° due to diffraction on the 1-dimensional lattice of stacked lamellar crystals. Here each crystal is a repeat unit with “d-spacing” l in the range 20 – 50 nm. $l=l_c+l_a$, see **Figure 6**. l = “long period”. Note that $l_c/l = X$.

Unlike SAXS, the conventional, or wide-angle X-ray scattering (WAXS) gives periodicities on the scale of atoms, small molecules or monomer units (≈ 1 nm).

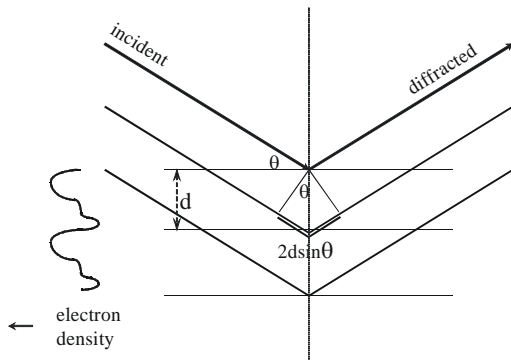
Diffraction angle 2θ is inversely related to the periodicity d , according to the **Bragg equation**:

$$\lambda = 2d \sin \theta$$

(λ = X-ray wavelength). Figure 7 show schematically the derivation of the equation. When θ is such that the waves scattered on neighbouring

Figure 6 A lamellar stack in melt-crystallized polymer

planes are shifted exactly by λ , or $n\lambda$, the two waves will interfere constructively. In all other cases they interfere destructively.



Why small angle?
 $n\lambda = 2d \sin\theta$
 (Bragg equation)
Small d - large θ
 (wide angle XRD) when layers are layers of atoms (d is a fraction of a nm)
Large d - small θ
 (small-angle XRD) when layers are thin crystals - d is of the order of 10-40 nm

Figure 7 Derivation of the Bragg equation

When applied to SAXS of semicrystalline polymers, the layers in Figure 7 are the whole lamellar crystals, rather than atomic planes. A relatively sharp SAXS peak is obtained only if the lamellae form regular stacks. 2θ for SAXS is typically a fraction of 1° .

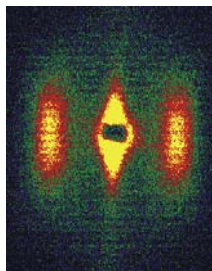


Figure 8 SAXS pattern of oriented *i*-PP. Orientation axis is horizontal. Lamellae are vertical, stacked as on a bookshelf (1st order reflections are the two vertical streaks).

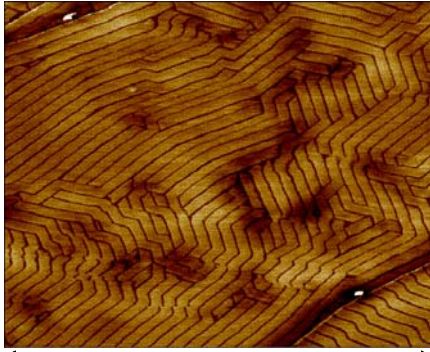


Figure 9 AFM image of 50 nm thick edge-on crystalline lamellae of uniform chain length polyethylene on graphite

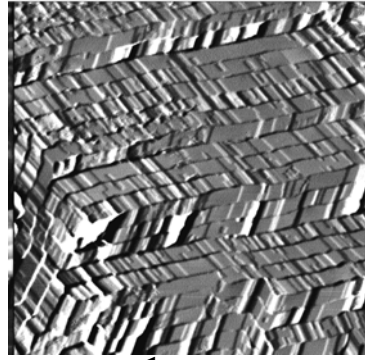
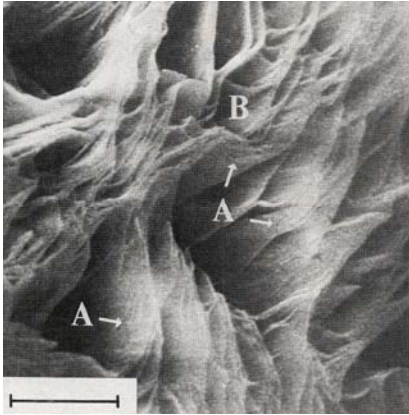


Figure 10 AFM image of fracture surface of the same sample as in previous figure. Ridges, one or several molecules thick, show direction of chain tilt.



Polymer in the form of crystals grown from dilute solution is useless in terms of mechanical properties. Since there are *no* tie molecules joining the crystals, the material is brittle. It is the presence of *tie molecules* in melt-crystallized polymer that gives it *ductility*. On large deformation, above the yield point, melt-crystallized polymer lamellae transform to microfibrils (see further below). Ductility, of course, presupposes that the polymer is near or above the glass transition temperature T_g . Semicrystalline polymers with flexible chains like polyethylene, polypropylene and nylons have T_g below room temperature, while more rigid polymers, like poly(ethylene terephthalate) (PET, Mylar® or Terylene®) have their T_g above room temperature (hence, at room temperature, you can draw a PE carrier bag but not a PET Coca-Cola bottle).

Figure 11 This scanning electron microscope (SEM) image of the surface of melt-crystallized polyethylene was taken after the low molecular weight fraction had been removed by extraction in hot solvent (xylene). The remaining lamellar crystals, which grew first during solidification, contain mainly the high MW fraction. Without extraction no surface features would be visible by SEM.

WHY ARE POLYMER CRYSTALS THIN LAMELLAE?

This morphology maximizes the fold surface, which has the highest energy.

Thermodynamically, the lowest energy shape of a crystal of finite volume is that with minimum surface energy:

$$\sum A_i \sigma_i = \min$$

(A_i = area of a crystal face, σ_i = surface free energy of that face)

Since in polymers $\sigma_e \gg \sigma$ (extra energy of folds), crystals elongated in the chain direction are expected (Figure 12), i.e. the exact opposite of the thin lamellae observed.

Crucially, lamellar crystals are favoured by *growth and nucleation*. **Thinnest crystals grow fastest**. Crystals grow **as thin as possible**. The lower limit of l is l_{min} , i.e. the thickness of crystals whose $T_m = T_c$.

There are 2 reasons for thinner crystals growing faster:

1. If l is large - *long* chain segment must become straight. Many bonds must all be in the correct conformation (e.g. *trans*) at the same time. Probability of this decreases exponentially with increasing l . E.g. neglecting the energy difference between *trans* and *gauche* states in PE, the probability of a C-C bond being *trans* is $P_1 = 1/3$. Probability that 2 bonds are *trans* at the same time is $P_2 = 1/3 * 1/3 = 1/9$. Probability of a 100 bond chain segment straightening spontaneously (stem length in a solution-grown crystal) is $P_{100} = 1/3^{100}$. P_{100} is 0 for practical purposes, hence 1000 atom thick polymer crystals do not form (except in special circumstances).
2. Once a folded-chain crystal had formed, there is little chance of its growing in the chain direction. Only lateral growth takes place, by new chain stems (stem = straight portion of chain traversing the crystal) depositing on side surfaces (Figure 13). The lamellae may sometimes thicken slowly on annealing near T_m .

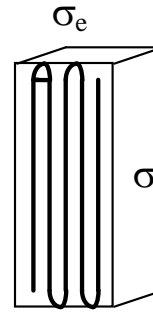


Figure 12
Equilibrium
shape of a
polymer
crystal

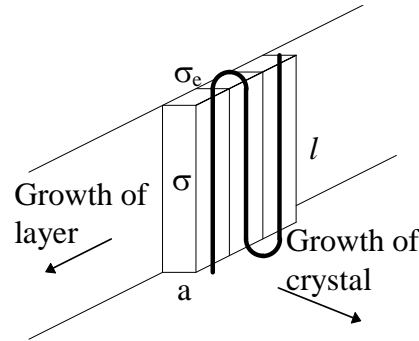


Figure 13 A polymer crystal lamella grows by deposition of layers of chain stems on side surfaces.

At any given crystallization temperature T_c the crystal thickness l will be slightly larger than l_{min} . This is because crystallization requires a finite negative *driving force* (driving force = $G_c - G_l$ is the difference in free energies of the crystal and the liquid at a given T). For crystals of thickness l_{min} , $G_c - G_l = 0$ at T_c by definition, since $T_m = T_c$.

How does crystal thickness depend on crystallization temperature? An approximate answer is found by determining how l_{min} depends on T_c . To find out, we must answer the inverse question: how does T_m depend on l ?

MELTING TEMPERATURE OF LAMELLAR POLYMER CRYSTALS

Start from:

General change in Gibbs free energy

$$dG = Vdp - SdT$$

At $p=const.$ all free energies decrease with T .

Slope $dG/dT = -S$ (entropy of the given phase) (see Figure 14)

G_c = Gibbs free energy of crystal of ∞ thickness

G_l = Gibbs free energy of liquid (melt)

At the equilibrium melting point T_m^0 : $G_c = G_l$.

Free e. of crystal of thickness l (per unit volume):

$$G_c' = G_{bulk} + G_{surface} = G_c^0 + \Delta G$$

$$\Delta G = A\sigma_e \quad A = \text{surface area}$$

σ_e = fold surface free energy

$$\Delta G = (2/l)\sigma_e \quad (\text{see Figure 15})$$

Real (depressed) melting temperature $T_m' = T_m - \Delta T$ is defined by the geometry of G/T diagram (Figure 14):

$$\begin{aligned} bc &= \Delta G \\ ac &= \Delta T S_l \\ ab &= \Delta T S_c \end{aligned}$$

$$\Rightarrow \Delta G = G_c' - G_c^0 = ac - ab = \Delta T(S_l - S_c) = \Delta T \Delta S_f$$

(ΔS_f = entropy of fusion)

Thus **melting point depression** ΔT is:

$$\Delta T = \frac{\Delta G}{\Delta S_f} = \frac{2\sigma_e}{l\Delta S_f} = \frac{2\sigma_e T_m^0}{l\Delta H_f} \quad (1)$$

(since $\Delta S_f = \Delta H_f/T$, where ΔH_f = heat of fusion)

→ Melting point depression is **inversely proportional to crystal thickness**.

Thin crystals: high free energy = low stability = low T_m

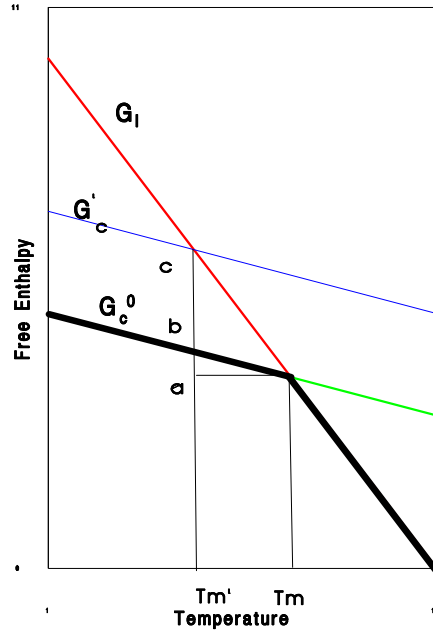
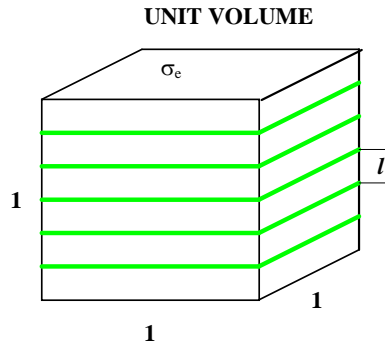


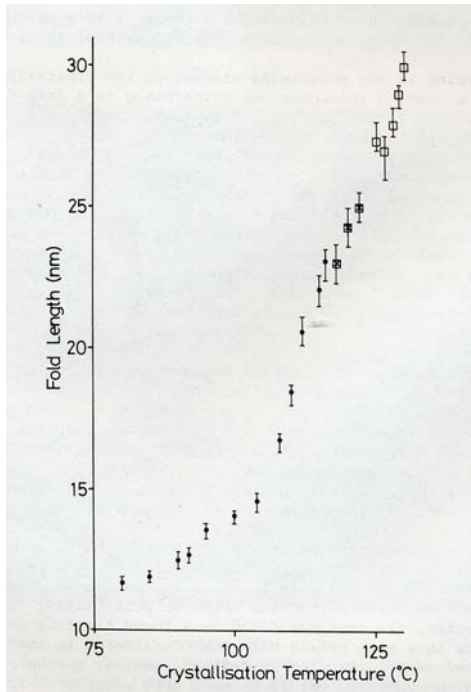
Figure 14 Gibbs free energy vs. temperature



No. of layers = $1/l$
 Total area of layers (both surfaces)
 $A = 2/l$
 Total surface free energy per unit volume of polymer
 $= A\sigma_e = 2\sigma_e/l$

Figure 15 Why $A = 2/l$.

Comment [G1]: Problem:
 The extrapolated equilibrium melting temperature of polyethylene is 142°C. Calculate the melting point of 20 nm thick lamellar crystals in melt-quenched linear polyethylene. Heat of fusion of fully crystalline PE is 293 J/g, fold surface free energy is 0.1 Jm⁻² and density of PE crystals is 1gcm⁻³. (Answer: 128°C)
 Hint: Remember that ΔH_f in Eq. (1) is per unit volume. SI units!



DEPENDENCE OF LAMELLAR THICKNESS ON CRYSTALLIZATION TEMPERATURE

For a given supercooling $\Delta T = T_m^0 - T_c$, the minimum allowed l is l_{min} .

Hence:

$$l \geq l_{min}$$

From (1):

$$l_{min} = \frac{2\sigma_e T_m^0}{\Delta H_f \Delta T}$$

Thus $l \propto 1/\Delta T$. Lamellar thickness is proportional to the supercooling. Experimental data for polyethylene are shown in Figure 16.

Figure 16 Lamellar thickness as a function of T_c for linear polyethylene. Experimental data for melt-crystallization (high T_c) and solution-crystallization (low T_c) are combined. $T_m^0 = 142^\circ\text{C}$.

DEPENDENCE OF CRYSTALLIZATION RATE ON TEMPERATURE

Close to T_m^0 :

- * Only thick crystals can grow.
- * Growth is slow.

With increasing ΔT crystal growth rate increases exponentially for 2 reasons:

1. The driving force $|G_c - G_l|$ increases;
2. Thinner crystals can grow.

However, at still lower temperatures, close to glass transition (T_g), melt viscosity increases dramatically and crystallisation rate gradually decreases to 0.

Typical crystallization rate vs. T_c for polymers - Figure 17.

Few polymers display the whole rate vs. T curve (e.g. aromatic stiffer-chain polymers like poly(ethylene terephthalate) (PET) or poly(ether ether ketone) (PEEK)). Flexible polymers like PE or PP crystallize rapidly, so that large supercooling cannot be reached before crystallization is complete. PET and PEEK can be quenched from the melt into the glassy state, bypassing crystallization altogether. Crystallization can then be turned on by annealing above T_g ("cold crystallization"). Determining the onset of cold crystallization is one method of determining T_g .

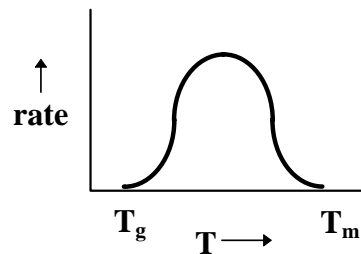


Figure 17 Typical bell-shaped curve describing crystallization rate of a polymer vs. crystallization temperature