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

Polymer Science 2025/26

Exercise 5 – Solution

1. The melting temperature of polytetrafluoroethylene (PTFE) has been measured as a function of the lamellar thickness *l*, controlled via different crystallization conditions. The data are summarized in the table below. Determine the thermodynamic melting temperature T_{m0} of PTFE? Calculate the fold-surface free energy σ_e, given that the volumetric melting enthalpy is given as Δh_v = 226 J/cm³?

l **(nm)**	***T*****m** **(°C)**
250	330.0
294	331.0
333	331.5
400	331.5
357	332.0
222	330.0
217	329.6
181	329.0
175	329.0
143	328.0
125	327.0
127	327.5
118	327.0
108	326.0

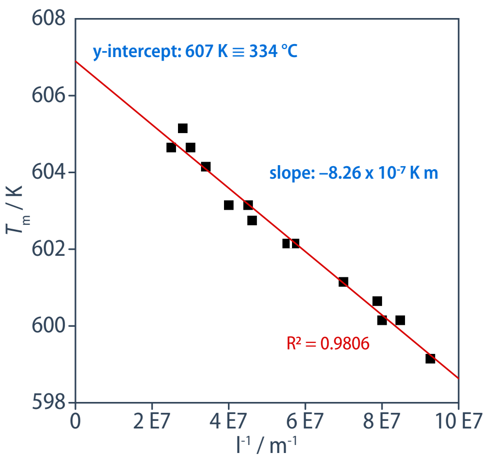
The Thomson-Gibbs relation for the melting of lamellar crystals (in SI units) is:

$$\boldsymbol{T_{\mathrm{m}} = T_{\mathrm{m0}}\left(1 - \frac{2\sigma_{\mathrm{e}}}{l\Delta H}\right)}$$

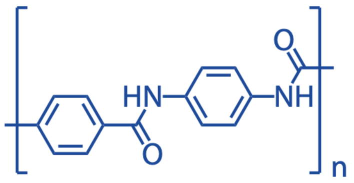
From a linear regression of T_{m} versus $1/l$ (with T_{m} in K and l in m) the thermodynamic melting temperature is determined from the intercept as $T_{\mathrm{m0}} \approx 607\ \mathrm{K} \equiv 334\ °\mathrm{C}$.

From the slope, σ_{e} can be determined:

$$\sigma_{\mathrm{e}} = -\frac{-8.26 \cdot 10^{-7}\,\mathrm{K\,m}\,\Delta H}{2T_{\mathrm{m0}}} = \frac{8.26 \cdot 10^{-7}\,\mathrm{K\,m}\ \cdot 226\ \cdot 10^{6}\,\mathrm{J\,m^{-3}}}{2 \cdot 607\ \mathrm{K}} \approx 0.154\ \mathrm{Jm^{-2}}$$



2. Kevlar™ (poly(*p*-phenylene terephthalamide)) is a high-performance polymer used in bulletproof vests and composites. Explain why Kevlar™ cannot be processed from its melt state. Draw its chemical structure and include a discussion of its melting temperature in your answer. The only way to process Kevlar™ into fibers involves its dissolution in sulfuric acid. What is the purpose of sulfuric acid?

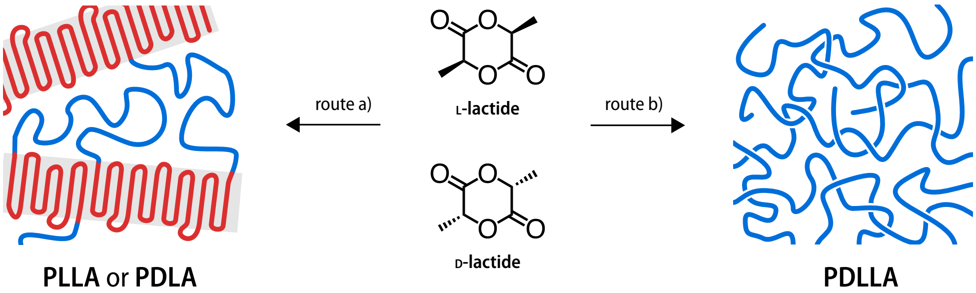


Kevlar™ has a rigid, rod-like backbone due to aromatic rings and restricted rotation at the amide group, which gives the chains very high stiffness. In addition, strong interchain hydrogen bonds between the amide groups further stabilize the crystalline structure. Together, these effects raise the melting temperature to such an extent that Kevlar™ decomposes before melting, making melt processing impossible.

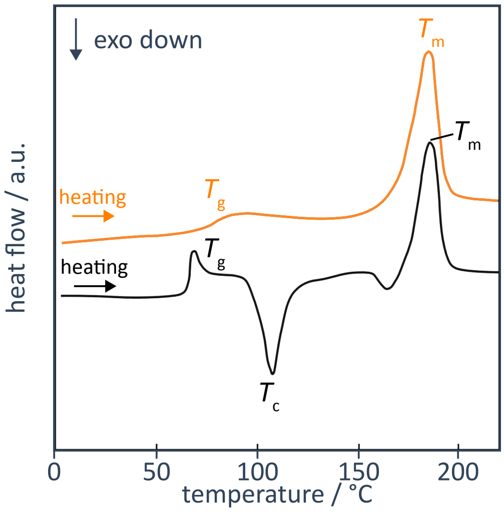
Concentrated sulfuric acid disrupts the hydrogen-bond network by protonating and solvating the amide groups, which enables solution processing into highly oriented fibers.

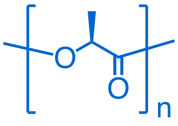
3. Poly(lactic acid) (PLA) is a widely used biodegradable polyester and an example of a glassy, semicrystalline polymer (T_{g} ca. 60 °C). Its ability to crystallize depends strongly on the stereochemistry of the repeat unit:

a) Explain why stereochemically pure PLA prepared from only L-lactide (PLLA) or only D-lactide (PDLA) is semicrystalline (route a), whereas PLA prepared from a racemic mixture of L-lactide and D-lactide (PDLLA) is typically amorphous (route b). In your answer, draw the chemical structure of the resulting polymers and indicate the stereocenter configuration. Note that the polymerization proceeds via a ring-opening polymerization (see the reading recommendation for a detailed explanation).

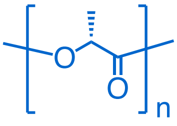


b) Like polycarbonate (PC), PLLA crystallizes slowly. Under typical processing (fast cooling) fully amorphous, glassy materials are often obtained. Two DSC heating trances (same heating rate) are shown below. Explain the structural difference between the two PLLA samples that produce these traces.

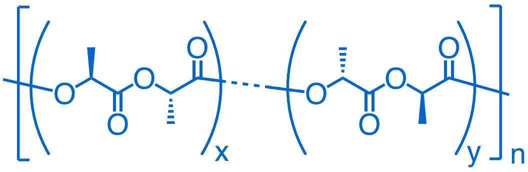




PLLA



PDLA



PDLLA

a) PLLA/PDLA: all stereocenters have the same configuration (only S from L-lactide or only R from D-lactide). Both are isotactic, with stereoregular chains. The regular backbone structure allows periodic packing into crystalline lamellae. They are semi-crystalline materials.

PDLLA polymerized from a racemic mixture has a random sequence of R,R and S,S stereocenters. This irregularity resembles an atactic polymer, so the backbone cannot pack periodically into a crystalline lattice. The material remains amorphous.

b) Upper DSC trace: the sample was already semicrystalline before the DSC run (it crystallized during prior slow cooling/annealing). The DSC heating trace only shows the glass transition of the amorphous fraction (ca. 60 °C), followed by melting of the pre-existing crystals (ca. 180 °C).

Lower DSC trace: the sample was rapidly cooled and remained amorphous. On heating, the material shows additional "cold crystallization" (exothermic peak). The crystals formed during this process then melt at ~180 °C. Cold crystallization thus indicates an initially amorphous (or very low-crystallinity) sample.

4. Which of the following polymers are capable of crystallizing?

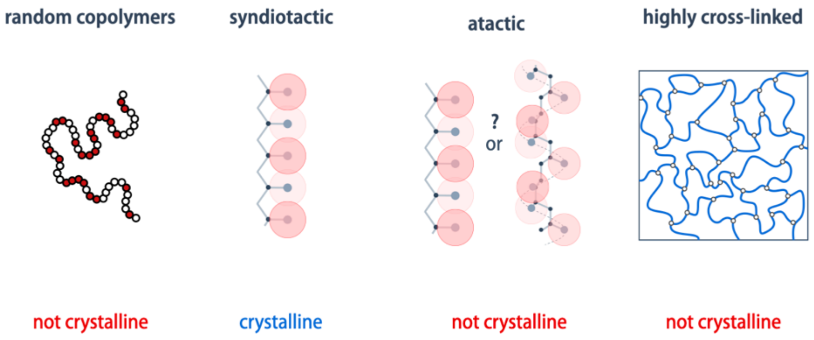
a) poly(ethylene-co-propylene);
b) syndiotactic polyvinyl chloride;
c) atactic polystyrene;
d) epoxy resin made from bisphenol A diglycidyl ether and diethylenetriamine.

a) random copolymers generally do not crystallize unless the comonomer content is very low.

b) syndiotactic PVC has a regular stereochemistry and can crystallize.

c) atactic polymers lack regularity and therefore do not crystallize.

d) thermosets are highly crosslinked networks and are amorphous, glassy.



5. Since the density, ρ, of crystalline polyethylene (PE) is 1000 kgm^{-3}, and that of amorphous PE is 865 kgm^{-3}, calculate the degree of crystallinity by weight:

   (i) a low density PE (LDPE), ρ = 910 kgm^{-3};

   (ii) a high density PE (HDPE), ρ = 975 kgm^{-3}

   What is the origin of this difference?

   The sample density is a two-phase mixture of crystalline and amorphous regions:

   $$\rho = X_v \rho_c + (1 - X_v)\rho_a \quad ,$$

   where X_v is the degree of crystallinity by volume. Solving for X_v:

   $$X_v = \frac{\rho - \rho_a}{(\rho_c - \rho_a)} \quad ,$$

   The crystalline region takes up a volume of $V_c = X_v V$, so its mass is $m_c = \rho_c V_c$. The amorphous region occupies a volume $V_a = (1 - X_v)V$, so its mass is $m_a = \rho_a(1 - X_v)$. The total mass is hence: $m = m_c + m_a = \rho_c X_v V + \rho_a(1 - X_v)V$.

   The degree of crystallinity by weight (fraction of the mass that is crystalline) is

   $$X_w = \frac{m_c}{m} = \frac{\rho_c X_v V}{\rho_c X_v V + \rho_a(1 - X_v)V} = \frac{\rho_c X_v}{\rho_c X_v + \rho_a(1 - X_v)} \quad .$$

   For LDPE, $X_v \approx 33\%$ and $X_w \approx 36\%$.

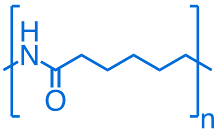
   For HDPE, $X_v \approx 81\%$ and $X_w \approx 84\%$.

   LDPE contains many short-chain branches that disrupt chain packing and reduce crystallinity. HDPE is largely linear and packs efficiently into lamellae, which results in a much higher degree of crystallinity (see Slide 191).

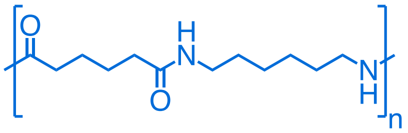
6. Polyamides can be synthesized in different ways, which determines the nomenclature of Nylons™.

   - The condensation of a diamine and a diacid produces polymers named *Nylon X,Y* (or *PA X,Y*), where X and Y are the numbers of methylene (–CH_2–) units in the diamine and diacid, respectively.
   - The condensation of an unsymmetric α,ω-amino acid (containing both amine and carboxylic acid groups in one molecule) yields *Nylon X* (or *PA X*), where X is the number of methylene units in the monomer.

a) Draw the chemical structures of Nylon 6,6 and of Nylon 6.



Nylon 6



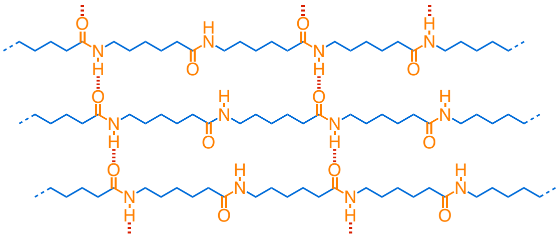
Nylon 6,6

b) The melting temperature of Nylon 6 is compared to that of *n*-Nylon homologues on Slide 188. Why does the melting temperature generally decrease with increasing *n*?

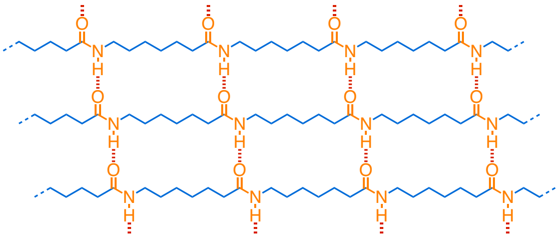
As *n* increases, the spacer length between amide groups becomes longer. The amide group concentration therefore decreases, so the density of hydrogen bonds drops. As a result, the interchain cohesive energy decreases, resulting in lower melting temperatures for longer-chain Nylons.

c) A closer look reveals an odd-even effect in the melting behavior: systematic oscillations in melting temperatures between Nylons containing an even or an odd number of methylene groups per repeat unit. Explain this phenomenon by comparing Nylon 6 and Nylon 7, and sketch their interchain hydrogen-bonding arrangements in the crystalline state assuming crystallization from all-*trans* conformation.

Nylon 6



Nylon 7



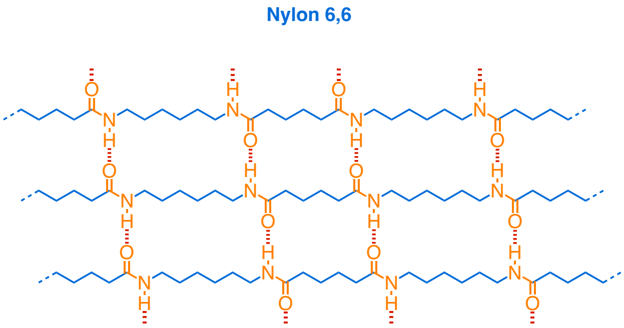
In an idealized all-*trans* conformation, hydrogen-bonding between neighboring chains can form most efficiently only when the amide groups are aligned in a favorable orientation.

For odd-numbered Nylons (e.g. Nylon 7), the amide groups on adjacent chains are aligned nearly parallel, enabling linear hydrogen bonding.

For even-numbered Nylons (e.g. Nylon 6), the groups are slightly misaligned, reducing hydrogen-bonding efficiency.

Hence, despite the lower amide concentration, Nylon 7 can exhibit a slightly higher melting temperature than Nylon 6, an example of the odd-even effect.

d) Is the melting temperature of Nylon 6,6 higher or lower than that of Nylon 6, and why?



Nylon 6,6 has a higher melting temperature than Nylon 6 ($T_m \approx 270$ °C vs. $T_m \approx 215$ °C). Its repeat unit enables complete and regular arrays of hydrogen-bonds for chains in an all-*trans* configuration within the crystalline state, resulting in stronger intermolecular cohesion.

Note: the above reasoning assumes idealized all-*trans* conformations. In reality, crystalline polyamides adopt slightly twisted chain arrangements to maximize hydrogen bonding. As a consequence, even-numbered *n*-Nylons are incompatible with a perfectly all-*trans* conformation. The observed odd-even oscillation in melting temperature therefore reflects subtle differences in crystal packing motifs rather than simple geometric constraints. Even in the melt, a significant fraction of hydrogen bonds remains present.

7. Explain why the critical lamellar thickness l^*, derived as the minimum thickness required for a stable crystal, cannot be observed experimentally. What thickness is typically observed instead, and why?

The critical lamellar thickness l^* is the thermodynamic limit for crystal stability. It is derived from the balance between the bulk free energy gain of crystallization and the surface free energy penalty associated with the fold surfaces. At l^*, the total free energy change for forming a lamellar crystal becomes zero, i.e. the crystal is just marginally stable.

However, l^* cannot be observed experimentally because crystal growth is governed by kinetics, not equilibrium thermodynamics. The associated activation barrier towards for crystal growth becomes infinitely high at $l = l^*$, meaning that lamellae of this thickness would require an infinitely long time to form. Similarly, infinitely thick lamellae, which would form only at the thermodynamic melting temperature, would also grow infinitely slowly, since the driving force for crystallization (the degree of supercooling) vanishes at equilibrium.

It is assumed that in practice, crystallization proceeds at the fastest possible growth rate, corresponding to a minimum in the kinetic barrier. The resulting lamellae therefore adopt a thickness l_{obs} slightly larger than l^{*}. This reflects an optimal compromise between the thermodynamic driving force for crystallization (which increases with supercooling, i.e. the free energy difference between melt and crystal) and kinetic constraints (the activation barrier associated with creating chain-folded and lateral surfaces). The experimentally observed lamellar thickness is thus a kinetically selected value, not the thermodynamic limit.

Reading suggestions:

- Reader on The Melting Temperature of Polymers.
- P. Van Wouwe, M. Dusselier, E. Vanleeuw, B. Sels, *ChemSusChem* **2016**, *9*, 907–921.

(You can download these documents from the Moodle-folder 'Reading Recommendation'.)