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

Polymer Science 2025/26

Exercise 5

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/cm^3?

***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

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?

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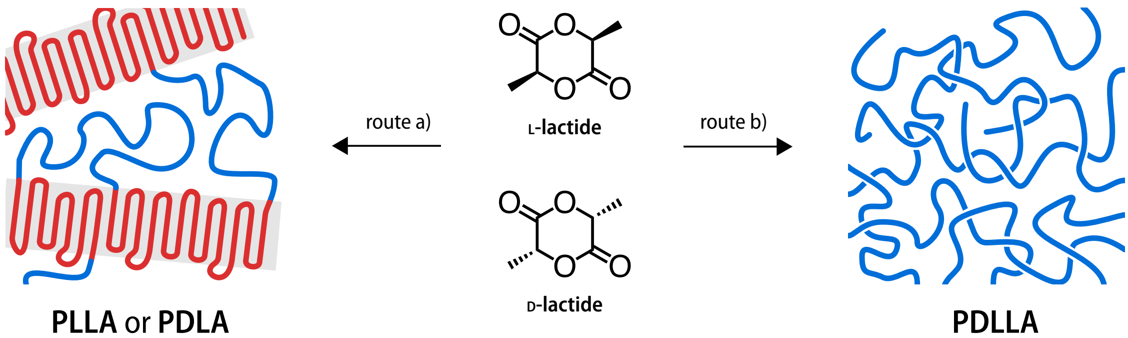
Dr. Daniel Görl
daniel.gorl@epfl.ch
lmom.epfl.ch

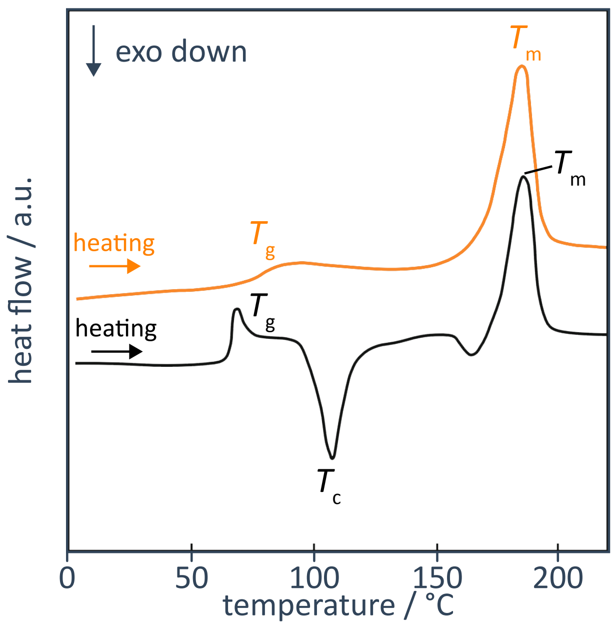
EPFL STI IMX LMOM
MXG 039, Station 12
CH-1015 Lausanne

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.



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.

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?

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.

   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*?

   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.

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

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?

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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'.)

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