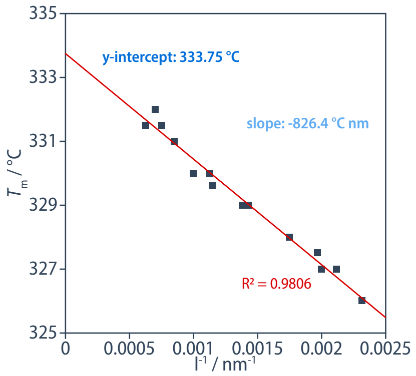
School of Engineering
Institute of Materials
Laboratory of Macromolecular
and Organic Materials

Polymer Science 2024

Exercise 5 – Solution

1. The melting temperature of a polytetrafluoroethylene has been measured as a function of the lamellar thickness, *l* (which was achieved by varying the crystallization conditions). The results obtained are shown in the table below. What is the thermodynamic melting point, T_{m0}, of this polymer? What is the energy of the folding surface, σ_e, if the volume melting enthalpy is given as ΔH = 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



$$T_m = T_{m0}(1 - \frac{2\sigma_e}{l\Delta H})$$

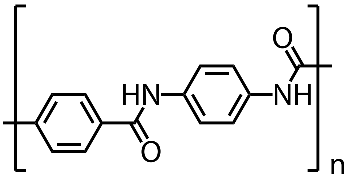
$$T_{m0} \approx 333.8\,^{\circ}C$$

$$-826.4\,^{\circ}C\ nm \equiv -8.3 \cdot 10^{-5}\ K\ cm$$

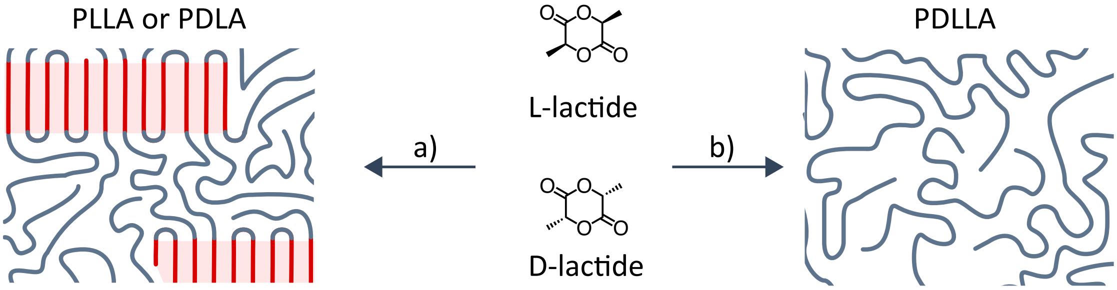
$$\sigma_e = \frac{8.3 \cdot 10^{-5}\Delta H}{2T_{m0}} = 1.55 \cdot 10^{-5}\ \frac{J}{cm^2}$$

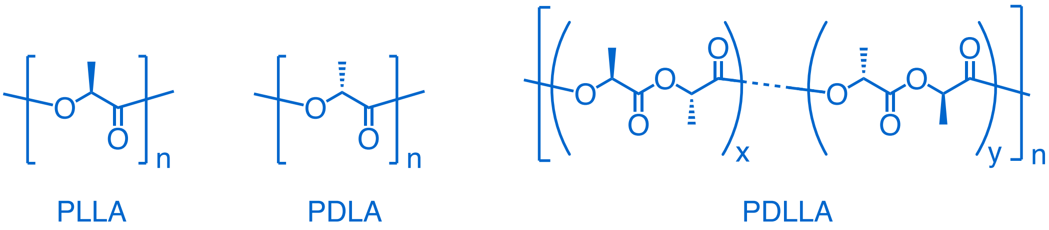
2. Why can Kevlar™ not be processed from its melt state (the only way to transform Kevlar™ involve its dissolution in sulfuric acid)? Draw its chemical structure and include a discussion of its melting temperature in your answer.

   Rigid structure + hydrogen bonds (see PAs) raise the T_m (explain why!). Kevlar's T_m is so high, that you can't melt it for processing, because it will degrade first. All that remains is to dissolve it in concentrated sulfuric acid, which can compete for the hydrogen bonding interactions, thus facilitating processing.



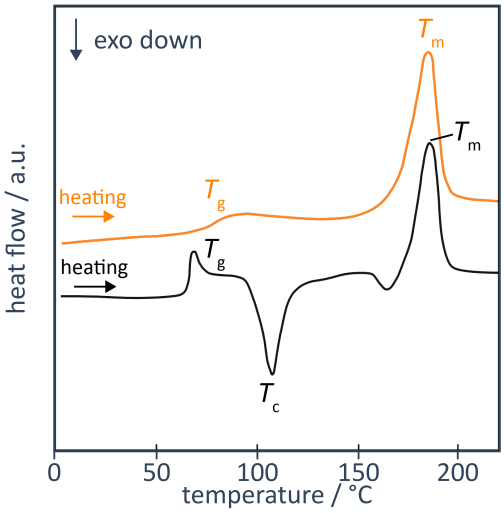
3. Poly(lactic acid) (PLA) is one of the mostly demanded biodegradable polyesters, and an example of a glassy semi-crystalline polymer (T_g ca. 60 °C). However, whether the polymer crystallizes depends on the stereoconfiguration of its repeating unit. Stereochemically pure PLA from either L- or D-lactide (referred to as PLLA or PDLA, respectively) is indeed semi-crystalline (route a), whereas the polymerization of a mixture of L- and D-lactide results in an amorphous grade (PDLLA) (route b). Why is this the case? Draw the chemical structure of the resulting polymers! Note that the polymerization proceeds via a ring-opening polymerization (see the reading recommendation for a detailed explanation).





Only if the distribution of stereocenters along the polymer backbone is regular, the polymer is isotactic and can crystallize. A mixture of L- (which is S,S-configured at its stereocenters) and D-lactide (R,R-configured stereocenters) used during the polymerization leads to a random distribution of (pairs of) S- and R-configured stereocenters along the backbone. It is atactic.

Like for polycarbonate (PC), also the crystallization of PLLA is a slow process so that under usual processing conditions (for instance, cooling rates applied in injection molding) often a glassy, amorphous material is obtained. Below are shown the DSC thermograms (heating curves) of two different grades of PLLA. How do these PLLA grades differ in structure?



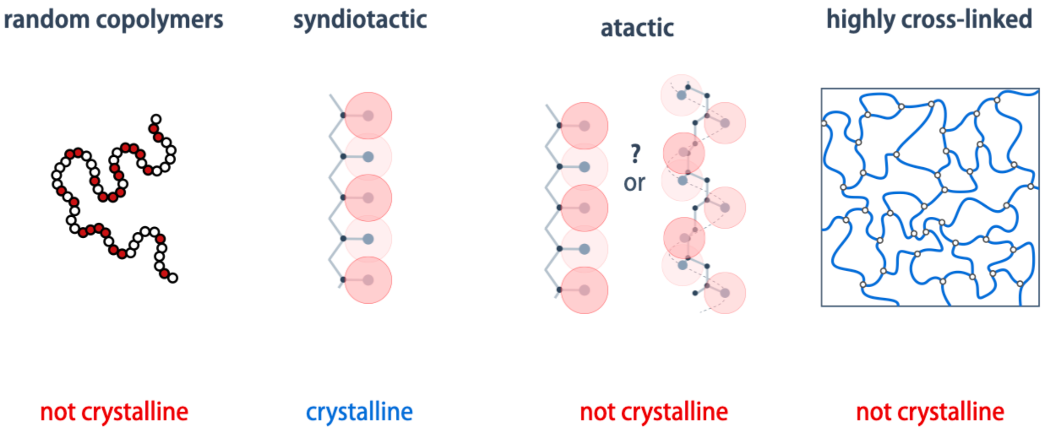
The upper heating curve shows the familiar thermogram of a glassy semi-crystalline polymer with a glass transition at around 60 °C and a melting temperature at ca. 180 °C.

The lower heating curve corresponds to an amorphous sample that may have been obtained upon fast cooling so that the polymer could not crystallize. Upon heating with a moderate heating rate, however, an additional crystallization transition at ca. 110 °C (commonly referred to as *cold crystallization*) can be observed, which is occasionally the case for semi-crystalline materials with low degrees of crystallinity once the glass transition temperature was exceeded. The crystals formed during this process melt then at the usual melting temperature of 180 °C. Note that for clarity, the two curves are vertically shifted with respect to each other.

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) a random copolymer does not crystallize, b) a homopolymer of regular configuration crystallizes; c) a homopolymer of irregular configuration does not crystallize; d) thermosets are usually amorphous and 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}

   degree of crystallinity by volume: X_v

   $\rho = X_v \rho_c + (1 - X_v)\rho_a$ **LDPE:** $X_v = 33\,\%$ **HDPE:** $X_v = 81\,\%$

   degree of crystallinity by weight: X_p

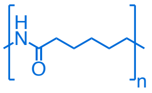
   $X_p = \dfrac{X_v \rho_c}{X_v \rho_c + (1 - X_v)\rho_a}$ **LDPE:** $X_p = 36\,\%$ **HDPE:** $X_p = 83\,\%$

   The difference is associated with the high degree of branching in case of LDPE, which limits its ability to crystallize (see Slide 178).

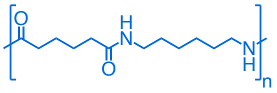
6. Polyamides can be synthesized in different ways, which in turn determines the nomenclature of Nylons™. The polymerization of a stoichiometric mixture of diamines and diacids results in Nylons that are named in the form *Nylon X,Y* (or *polyamide X,Y* or *PA X,Y*), where X, Y are the number of catenary carbons in each monomer used in the

synthesis. Nylons can also be synthesized by the polymerization of α,ω-amino acids, i.e. from a single monomer comprising both an amino and a carboxylic acid group. Then, they are named *Nylon X* (or *polyamide X* or *PA X*), where X is the number of catenary carbons in this single monomer used.

With this information at hand, draw the chemical structures of Nylon 6,6 and of Nylon 6.



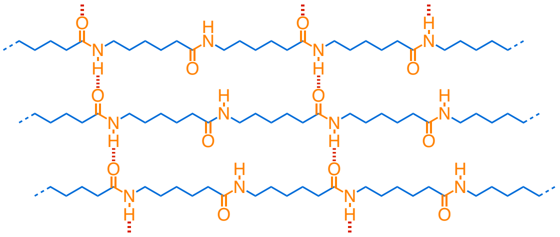
Nylon 6



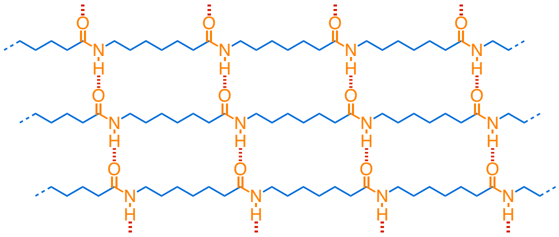
Nylon 6,6

The melting temperature of Nylon 6 is compared to the melting temperature of other *n*-Nylon-Homologues on Slide 174. Why do their melting points decrease as *n* is increased? If you look a little more carefully, you note a so-called odd-even effect, that is a variation in the melting temperatures between even-numbered and odd-numbered *n*-Nylons. Try rationalizing this phenomenon by comparing Nylon 6 with Nylon 7. In your answer sketch their inter-chain interactions in the crystalline state by assuming that both polymers crystallize from an all-*trans* conformation.

Nylon 6



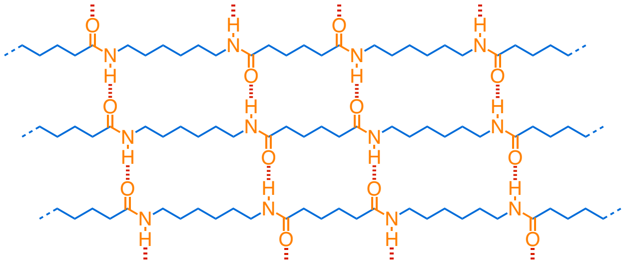
Nylon 7



In an all-*trans* conformation, hydrogen-bonding between the amide groups is efficient only in *n*-Nylons based on an odd number of catenary carbon atoms (note, however, that I have assumed here a linear geometry for the hydrogen bond, which doesn't need to be the case). The melting temperature is therefore higher for Nylon 7 even though the concentration of amide groups is less than in Nylon 6 (see Slides 173 and 174).

Is the melting temperature of Nylon 6,6 higher or lower than that of Nylon 6?

Nylon 6,6



Using the same approach, complete hydrogen-bonding arrays can only be formulated for Nylon 6,6. Hence, we expect a higher melting temperature for Nylon 6,6 compared to Nylon 6, which is indeed the case (T_m ≈ 270 °C vs. T_m ≈ 215 °C).

Note that this picture is a simplified one. The assumption of all-*trans* conformations (related to long-chain polyesters and polyethylene) in crystalline polyamide chains is not fulfilled, as the vast majority of amide groups is actually found to be arranged in hydrogen bonds (up to 100%). To generate these high degrees of hydrogen bonding, slightly twisted chain arrangements are adopted, if all-*trans* conformations hinder hydrogen-bond formation to a relevant extent. Accordingly, the observed odd–even oscillations are a direct consequence of different crystal modifications. Hence, polyamide chains crystallize from the melt such that as many hydrogen bonds as possible form (even in the melt, a significant number of hydrogen bonds remains present). For even-numbered *n*-Nylons this means, however, incompatibility with a perfect all-*trans* conformation.

Reading suggestions:

- Lecture Notes of Chapters 3.3.
- P. Van Wouwe, M. Dusselier, E. Vanleeuw, B. Sels, *ChemSusChem* **2016**, *9*, 907–921.

(You can download the latter document from the Moodle-folder ’Reading Recommendation’.)