

Polymer Science 2024

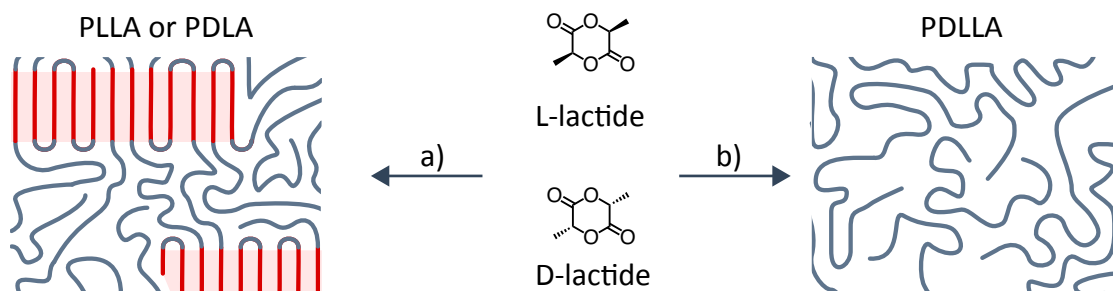
Exercise 5

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 $\Delta H = 226 \text{ J/cm}^3$?

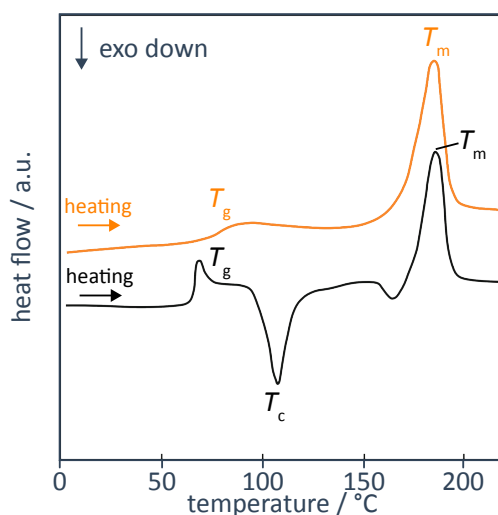
$l \text{ (nm)}$	$T_m \text{ (}^\circ\text{C)}$
250	330.0
294	331.0
333	331.5
400	331.5
357	332.0
222	330.0
217	329.6
181	329.0
175	329.0
143	328.0
125	327.0
127	327.5
118	327.0
108	326.0

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



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 did these PLLA grades differ in structure prior to the measurement?



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), $\rho = 910 \text{ kgm}^{-3}$;
- (ii) a high density PE (HDPE), $\rho = 975 \text{ kgm}^{-3}$
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.

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.

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

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'.)