# Exam RPK Course Module A
1 July 2022

**Below you find seven questions related to the different topics of Module A.
You are supposed to answer five questions of your choice.**

Question 1   Step-growth polymerization (Heuts)

Poly(butylene terephthalate) (PBT) is a semi-crystalline engineering plastic that is produced from the monomers terephthalic acid (TPA, m_{TPA} = 166 g/mol) and butane diol (BD, m_{BD} = 90 g/mol):
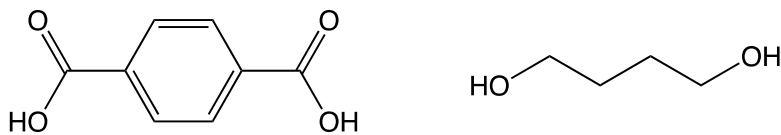

PBT is characterized by very fast crystallization rates which makes injection molding a very suitable processing technique for this plastic. The glass transition temperature of PBT $T_g \approx 60°C$ and the melting temperature $T_m \approx 220°C$. Since the molar mass between entanglements in PBT is very high, commercial PBT is hardly entangled and therefore it behaves like a true visco-elastic liquid above the melting point.

a. A sample of PBT is now synthesized from 670.00 g TPA and 360.00 g of BD in the melt under constant removal of the condensation product. After a certain reaction time the polymerization is stopped and the number of residual acid groups in the sample is titrated. The sample is found to contain 0.2323 mol of COOH groups. Determine the number-average molar mass M_n of this sample. You may ignore the contributions of the end-groups.   (8)

b. Suppose that the polymerization of part b were carried out <u>without</u> complete removal of the condensation product. Calculate the maximum amount of condensation product that is allowed to remain in the reaction mixture to achieve the M_n of part b. The equilibrium constant for this polycondensation K = 1. If you did not manage to get an answer in part b, you may assume that the conversion p of the hydroxyl groups is 0.9600 (note that this is an arbitrarily picked value!).   (7)

c. Commercially, PBT is produced in a continuous process with several different reactors in series. The reactor configurations (stirrers etc.) change along the process. <u>Briefly</u> explain why this is necessary.   (5)

Question 2 Biopolymers (Van Hest)

The blue mussel prepares a composite protein-based fiber which allows it to stick well to the substrate (see figure). The fiber is composed of two proteins, which form a gradient within the fiber. The protein which is enriched further away from the mussel (the distal position) is a pentablock structure in which the central collagen domain is flanked by two silk-like domains. The other protein, which is enriched closer to the mussel, is similar regarding structure, but has elastin-like domains instead of the silk ones.
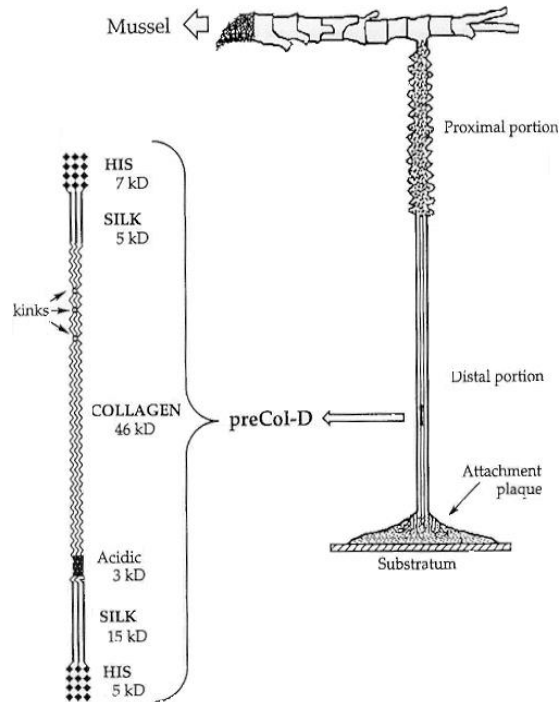

a)   What is the consensus peptide sequence found in silk, which provides stiffness to silk fibers, and what is the secondary structure formed by this peptide repeat?   (4)

b)   Based on the composition of these peptides and the gradient structure of the peptide fiber, what kind of mechanical features do you expect these fibers exhibit?   (4)

c)   Intrigued by the unique properties of the pentablock polypeptide depicted in the figure, a materials scientists tries to reconstruct this polypeptide by protein engineering. This turns out to be difficult. Which domain(s) turn(s) out to be most difficult to create? Explain your answer.   (6)

d)   Provide an alternative synthetic scheme how you could synthesize the abovementioned pentablock copolypeptide.   (6)

Question 3 Radical polymerization (Haddleton/Heuts)

Monomers A ($m_{0,A}$ = 100 g/mol, $T_{g,pA}$ = 40°C) and B ($m_{0,B}$ = 130 g/mol, $T_{g,pB}$ = 110°C) undergo a free-radical copolymerization with the following reactivity ratios: r_A = 0.1 and r_B = 0.8.

a. Determine the glass transition temperature of the instantaneously formed copolymer at very low conversion ($x < 0.01$) when 50 g of A is reacted with 50 g of B in a batch process. (7)

b. Describe as accurately as possible the composition of the polymer product in your reactor when you stop the batch process of part a at 100% monomer conversion. (7)

c. Describe as accurately as possible the composition of the polymer product in your reactor at 100% monomer conversion when you carried out the batch process of part a in the presence of a RAFT agent. (6)


RAFT agent
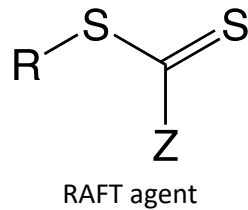
Question 4   Π conjugated polymers (Vanderzande)

The properties of most conjugated polymers containing ring systems in the monomeric unit can be understood by considering two geometries for the ground state, e.g. an aromatic and a quinoid geometry.

a. Where are these two geometries from a conceptional point of view coming from using a basic concept from solid state physics? (5)

b. In the general case described above, typically one lattice is more stable energetically than the other. What is the origin of the energy difference? (5)

c. Furthermore, the bandgap of the two alternative lattices tends to be different. For a typical case which of the two lattices will have the larger bandgap? (5)

d. Suppose you know the bandgap of two conjugated homopolymers and you are planning to study alternating copolymers of these monomeric building blocks. Is it possible to estimate upfront the to-be-expected bandgap? (5)

Question 5   Metal catalyzed polymerizations (Duchateau)

a)   Which of these catalysts will produce syndiotactic polypropylene and which one isotactic polypropylene, and explain why?   (10)
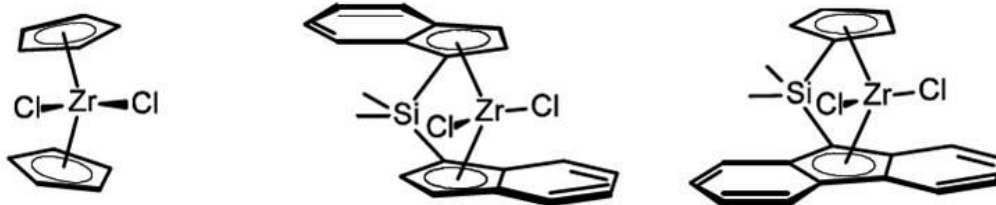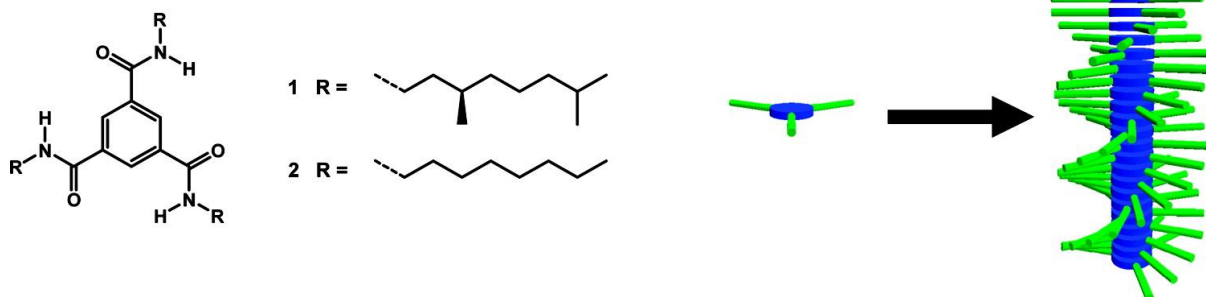

b)   What type of polypropylene (atactic, syndiotactic or isotactic) polypropylene does the following catalyst produce, and explain why?   (10)
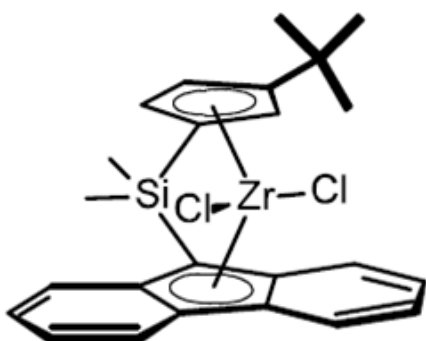
## Question 6 Supramolecular Polymers (Sijbesma)

The molecules **1** and **2** shown here aggregate in apolar solvents like hexane into supramolecular polymers in highly cooperative fashion.

a) Which interaction(s) are responsible for the aggregation? (2)

b) Consider a supramolecular polymerization via a ring-chain equilibrium with a critical concentration of 0.2 M. Draw a plot of the concentration of monomers in linear chains and the concentration of monomers in rings as a function of total concentration. Use linear axes and label both axes with concentration. Let both axes run from 0 to 1 M. (4)

The plot below depicts the weight average degree of polymerization DP_w vs a dimensionless concentration of monomer KC_t for isodesmic and cooperative polymerizations. (K = association constant; C_t = total concentration of unassociated plus associated monomer)
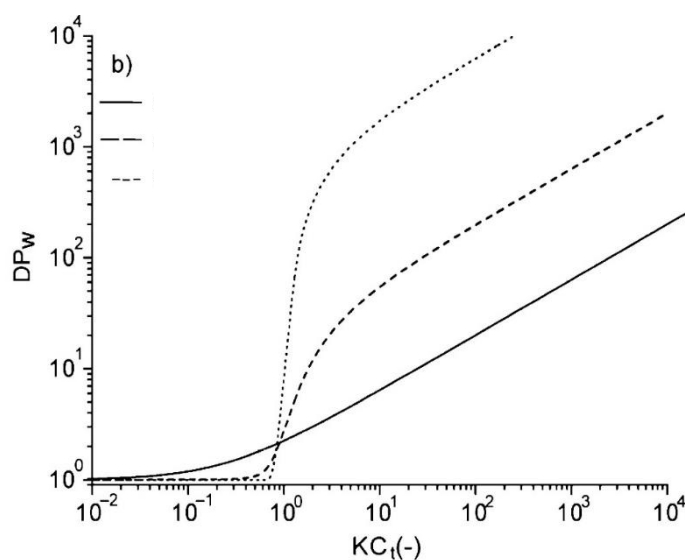
c) Which line in the plot represents non-cooperative (isodesmic) aggregation? Explain your answer. (3)

d) For an isodesmic polymerization, what is the slope of a double logarithmic plot of DP vs concentration based on the theoretical relation between the two? (2)

A certain supramolecular monomer aggregates linearly via hydrogen bonds without cooperativity and has a DP of 1000 at a monomer concentration of 1M in chloroform.

e) What is the DP at a concentration of 250 mM? (3)

f) What is the effect of performing this experiment in water on DP? And in hexane? (3)

g) What is the DP when you add 100 mM of a monofunctional monomer? (3)

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Question 7   Green/circular polymers (Tomović)

a)   How many different types of bioplastics can be distinguished? Describe the differences between these types of bioplastics. (3)

b)   What are the main processing steps involved in mechanical recycling of polymers?   (2) Explain what happens to PET, PP and PE after multiple mechanical recycling steps. Why? (3)

c)   Which method would you use for recycling of mixed plastic waste or multilayer film consisting of PE/EVOH/PET (polyethylene/ethylene vinyl alcohol/poly(ethylene terephthalate))? Explain why this method would be the best choice. (5)

d)   Provide three different methods for the closed-loop recycling via chemical depolymerization of poly(ethylene terephthalate) (PET) and draw the chemical structures of the main products. (4)

e)   Draw the chemical structures of three synthons that can be prepared beside ethylene glycol by upcycling of poly(ethylene terephthalate) (PET) using following reactants: (3)