Sample exam questions Soft Matter MSE-425

Question 1: Intermolecular forces (2 points)

a) Why is the viscosity of hexane lower than that of water?
b) Why is the melting temperature of pentanol lower than that of hexanol?

Question 2: Phase diagram (5 points)

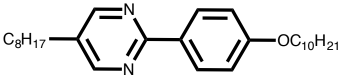
You have a blend composed of two different types of polymers. The first type of polymer is composed of 100 repeat units, the second type of polymer is composed of 1000 repeat units. You mix them in the absence of any solvent at 200°C and cool this mixture down to 25°C.

a) What is the critical composition of this mixture, where you always get spinodal decomposition if $T < T_c$?
b) What is the critical interaction parameter for this mixture?
c) If the interaction parameter of this mixture can be described as $\chi = \frac{200K}{T}$, does this mixture phase separate at 25°C?

Question 3: Liquid crystals (5 points)

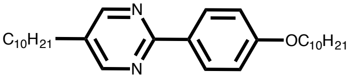
a) Why are all the transition temperatures of mesogen A lower than those of mesogen B?

Mesogen A



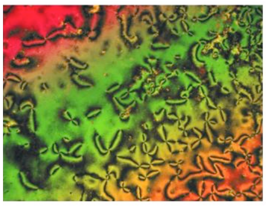
T_m = 32°C, T_{SC} = 60°C,
T_{SA} = 65°C, T_N = 70°C

Mesogen B



T_m = 36°C, T_{SC} = 73°C,
T_{SA} = 77°C

b) You are asked to design a quarter wavelength plate with mesogen A (Δn = 0.314) for a laser with λ = 488 nm. How thick would you make this plate? How thick would the plate be if you used mesogen B (Δn = 0.396) instead?
c) What is the phase of the liquid crystal shown in the image acquired with polarized light microscopy? Based on what features can you identify this phase?



Question 4: Gibbs adsorption isotherm (5 points)

a) You have a trough filled with water and you slowly add a water soluble surfactant into the aqueous phase. Draw the surface tension of this system as a function of the surfactant concentration. In this graph, indicate the CMC.

b) You are working with sodium dodecyl sulfate (SDS) which has a CMC of 8.2 mM at 25°C. You are asked to replace SDS by a molecule that has a lower CMC. What would you change on the molecular structure to decrease the CMC and why?

Question 5: Micelles (5 points)

a) The critical micelle concentration of sodium octyl sulfate ($CH_3(CH_2)_7SO_4Na$) at 25°C is 0.13 M. What is the excess free energy in k_BT?

b) The area of the headgroup of sodium octyl sulfate is 60 $Å^2$. What shape do these micelles have and why?

c) What is the maximum packing density of these surfactants at the air-liquid interface?

d) The CMC of sodium dodecyl sulfate (SDS, $CH_3(CH_2)_{11}SO_4Na$) at room temperature is 8.2 mM. Why is this CMC so much lower than that of octyl sulfate?

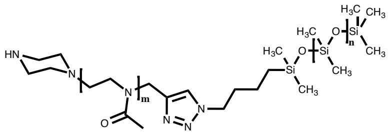
Question 6: Vesicles (5 points)

a) What is the difference between a micelle and a vesicle? Draw the structure of a micelle and a vesicle.

b) Why is the mean lifetime of a molecule in a micelle much shorter than that of a molecule in a vesicle?

c) You are asked to produce polymersomes from poly(2-methyl-2-oxazoline) (*PMOxa*)-poly(dimethyl siloxane) (PMOxa-PDMS). What molecular weight of PMOxa would you chose to ensure that the block-copolymers assemble into vesicles and why?

Given variables: You perform the experiment at 25°C in water.
Assume the length of a MOxa repeat unit to be 0.5 nm and the molecular weight of a single repeat unit is 83 g/mol.
The radius of gyration, R_g of PDMS is 1 nm. Assume PDMS and PMOxa to behave like ideal chains.



Chemical structure of a PMOxa-PDMS block copolymer

Question 7: Polymers (5 points)

a) For a linear polyethylene molecule –(-CH_2-CH_2-)- of a molar mass of 128241 g/mol calculate

   I. The length of a repeat unit
   II. The contour length
   III. The root mean square end-to-end distance.
   IV. The radius of gyration

Assume the bond length of C-C to be 0.154 nm and the valence angles 109.5°.

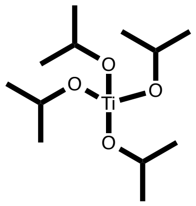
b) You disperse PMOxa in water, which is a good solvent for this polymer. You gradually increase the PMOxa concentration and measure the storage modulus *G'* and the loss modulus *G"* of this solution. At low concentration, *G"* >> *G'*. Once the concentration is increased to 8 mol/l, *G"* ≈ *G'*. What is the molecular weight of the PMOxa in your solution?

Given variables: Assume all PMOxa chains have exactly the same molecular weight, they behave as ideal chains and the length of a MOxa repeat unit is 0.8 nm and the molecular weight of an MOxa repeat unit is 83 g/mol

c) You are asked to adjust the chemical composition of a water bottle that can be recycled. What type of polymer would you chose and why? What types of crosslinks does this polymer have?

Question 8: Gels (5 points)

a) You are asked to fabricate thin TiO_2 films using the sol-gel method. You start from the titanium isopropoxide precursors (see chemical structure below). Describe the different steps involved in the formation of TiO_2.



Chemical structure of a titanium isopropoxide precursor

b) At which point during the synthesis does the sol transform into a gel? How would you characterize this transition?

Question 9: Polymers at interfaces (5 points)

a) Polymers grafted from surfaces using surface-initiated polymerization can adopt different conformations. Which quantitative criterion needs to apply to consider a surface-grafted polymer to be in the "brush-regime" and in the "mushroom-regime"?

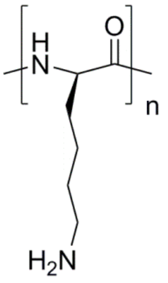
b) The radius of gyration of poly(methyl methacrylate) (PMMA) with a weight average molecular weight of 40 000 g/mol in a good solvent is 5 nm. Consider two surfaces (**sample I** and **sample II**) that present PMMA chains grown from the surface using surface-initiated atom transfer radical polymerization. The grafting density of PMMA chains on **sample I** is 0.01 chains/nm^2 and that on **sample II** is 0.70 chains/nm^2. For both samples, indicate whether the surface-grafted PMMA chains are in the brush or mushroom regime. Support your answer with a short calculation.

Question 10: Polymer mechanochemistry (5 points)

a) Ultrasound induced chain scission generally occurs near the mid-point of the polymer chain. (i) why is this the case ?; (ii) Propose a strategy to design synthetic polymers, which upon ultrasound irradiation do not undergo scission near the mid-point of the chain, but at a location closer to e.g.- one of the chain ends.

b) Consider the hypothetical ultrasound induced chain scission of the water-soluble synthetic polypeptide polylysine (structure below). Two experiments are performed under completely identical conditions: same polymer concentration and molecular weight, same ultrasound power. The two experiments only differ in the pH of the aqueous solution; **experiment I** is performed at pH 5, whereas **experiment II** is carried out at pH 12.
Does the pH of the solution have an influence of the chain scission process and if yes how (does it affect the cleavage yield)? Note: the pK of polylysine in water is ~ 10.

b)



Question 11: Emulsions (5 points)

a) Name two different ways to stabilize an emulsion. What is the underlying principle of each of these methods? Name one advantage and one disadvantage of each method.

b) What surfactant (HLB value, charge, and composition) would you use to ensure that the sauce hollandaise, which is similar to mayonnaise, does not phase separate?

c) You are asked to formulate foam that is stable for a long time. This foam is composed of an aqueous phase that contains air bubbles. It should be used for decorative purposes and ideally it should remain stable for days. You use some SiO_2 particles with a diameter of 20 nm to stabilize this foam. You optimized the formulation to maximize the foam stability. What is the energy required to remove the particles from the air-liquid interface? How does that compare to the thermal energy? Does this foam coalesce if you keep it in air for a week?

Given variables: Assume the air-liquid interfacial tension is 50 mN/m and remains unchanged throughout the optimization of your formulation.

Question 12: Particles (5 points)

You would like to design spherical gold nanoparticles with a diameter of 15 nm that you would like to use as labels for cell experiments. These experiments are conducted at 25°C in buffers containing high salt concentrations. To avoid that the gold nanoparticles aggregate, you sterically stabilize them.

a) What chemical group would you use to bind dispersants to the nanoparticle surface?

b) You use poly(ethylene glycol) (PEG) as a tail of the dispersants. What molecular weight of PEG would you use if the dispersant layer surrounding the gold nanoparticle should be approximately 5 nm thick? *Given variables:* Assume you can adsorb these dispersants at a density of 0.5 molecule/nm^2. The molecular weight of an ethylene glycol repeat unit is 44 g/mol and the length of this repeat unit is 0.34 nm.

c) By mistake, someone once uses pure PEG without any anchoring group to stabilize the gold nanoparticles. The gold nanoparticles immediately agglomerate and sediment even though they were stable before the PEG was added. Why could this be?

d) How would you characterize the size of these nanoparticles? What is the principle of this method and what happens to your measurement if you analyze aggregated nanoparticles with a broad size distribution?