Solutions to sample exam questions Soft Matter (MSE425)

Question 1: Intermolecular forces (2 points)

a) Hexane: only **VdW forces**, or **no H-bonds**. (1/2 point)
Water: Can form **H-bonds**: stronger intermolecular force (1/2 point)

b) T_m hexanol: -53 °C to -41°C, T_m pentanol: -78°C Pentanol has 5 C atoms, hexanol 6 C atoms. Hence **pentanol** is **shorter (or less C atoms)**, (1/2 point) and thus has **weaker VdW** interactions than hexanol. (1/2 point)

Question 2: Phase diagram (5 points)

a) $\frac{\Delta G}{RT} = \frac{(1-\phi)}{N_1} ln(1-\phi) + \frac{\phi}{N_2} ln\phi + \chi\phi(1-\phi)$

$$\phi_c = \frac{1}{1+\sqrt{\frac{N_2}{N_2}}}$$

$\phi_c = 0.24$ (1 point)

b) $\chi_c = \frac{1}{2N_2}\left(1+\sqrt{\frac{N_2}{N_1}}\right)^1$ (1 point), $\chi_c = 0.00866$ or 0.0087 (1 point)

c) $\chi = 0.67$ (1 point)

$\chi = 0.67 > \chi_c$-> **yes**, the two polymers will phase separate (1 point)

Question 3: Liquid crystals (5 points)

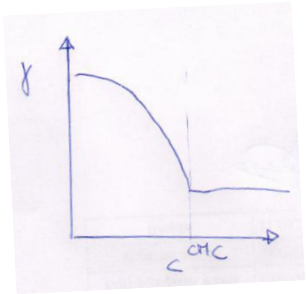
a) Mesogen A has a **shorter aliphatic chain** (1/2 point) -> **weaker VdW interactions** (1/2 point)-> lower transition temperature

b) $\delta = \frac{2\pi}{\lambda}\Delta nd$ -> Mesogen A: d = 389 nm (1 point),
Mesogen B: d = 308 nm (1 point)

c) **Nematic (1 point)**: **Two brush schlieren** texture (1 point)

Question 4: Gibbs adsorption isotherm (5 points)

a)



Axis correct: ½ point
Initial decrease in gamma: 1 point
Constant gamma at c>CMC: 1 pint
CMC indicated correctly: ½ point

c) A molecule with a **longer aliphatic chain or bulkier monomer with larger r (1 point)**. $CMC \approx e^{-\alpha} \approx e^{-\frac{1\pi rl}{k_B T}}$ (1 point).

Question 5: Micelles **(5 points)**

a) $CMC \approx e^{-\frac{\Delta E}{k_B T}}$ (1/2 point) Excess free energy = 2.04 k_BT or 2 k_BT. (1/2 point).

b) $\alpha = \frac{v}{a_0 l_c}$

v = 0.2157 nm^3 (1 point), l = 0.913 nm, α = 0.39 (1/2 point) -> slightly elliptical (or cylindrical) micelle (1 point)

c) maximum packing density = 1/0.6 nm^2 = 1.667 nm^2. (1 point)

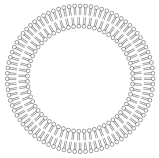
d) SDS: **longer aliphatic chain** (1/2 point)-> smaller CMC (lower solubility in water) $CMC \approx e^{-\alpha} \approx e^{-\frac{1\pi rl}{k_B T}}$ (1/2 point)

Question 6: Vesicles **(5 points)**

a) *Micelle:* **Amphiphilic molecules** that are arranged into a sphere. Micelles are **monolayers** of self-assembled molecules that form a sphere (1/2 point).

 (1/2 point)

Vesicle: **Bilayer of amphiphilic molecules (1/2 point)**. Much larger than micelles.

 (1/2 point)

b) Micelles are formed if the ratio of the hydrophilic headgroup area : cross-section of the hydrophobic part, α, is < 1/3 whereas vesicles from if α is approximately unity. Hence, molecules that form micelles typically have a higher solubility and thus a **higher CMC (1/2 point)**. **The mean lifetime of a molecule is inversely proportional to the CMC (1/2 point)** -> the mean lifetime of molecules in vesicles is longer as their CMC is lower.

c) For vesicles to form: α = 1 (1/2 point)

R_g PDMS= R_g PMOxa. (1/2 point)

$N = \frac{6R_g^2}{l^2} = 24$ (1/2 point)

$M_w = 24 * 83\ Da = 1992\ Da$ (1/2 point)

***Question 7: Polymers* (5 points)**

a) *I) N = (128241-2)/28 = 4580. a = 2*sin(109-5/2)*0.154 nm = 0.25 nm (1/2 point)*

II) L_{cont} *= Na (1/4 point) = 1145 nm (1/2 point)*

III) $\langle r^2 \rangle_0 = Na^2 \left(\frac{1+cos\theta}{1-cos\theta}\right)$ *(1/4 point) r = 24 nm (1/4 point)*

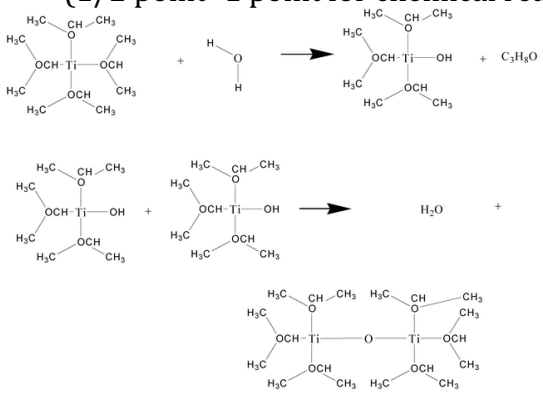
IV) $\sqrt{\langle R_g^2 \rangle} = \sqrt{\frac{\langle r^2 \rangle_0}{6}}$ *(1/4 point)* R_g *= 10 nm (1/4 point)*

b) $c_m = \frac{6^{1.5}}{l^3} N^{1-3\nu}$ -> $N^{1-3\nu} = \frac{c_m l^3}{6^{1.5}}$ -> *N = 10 (1 point) –>* M_w *= 830 Da (1 point)*

c) **Thermoplast** (1/2 point)-> can be **heated, shaped, cooled down** (1/4 point) and it keeps its shape as it is **physically crosslinked** (1/4 point). However, this is a reversible process and it can be molten again.

***Question 8: Gels* (5 points)**

a) 1. **Hydrolysis** (1/2 point+1 point for chemical reaction), 2. **Condensatio**n (1/2 point+1 point for chemical reaction), 3. Drying



Ref: Effect of hydrocarbon tail-groups of transition metal alkoxide based amphiphilic catalysts on transesterification, Gayan Nawaratna , Ronald Lacey and Sandun D. Fernando *

b) A sol transfers into a gel when a **percolating network forms (1 point)**. Characterization: With rheology (1/2 point). When a percolating network forms **G' > G'', before G'' > G'** or sol-gel transition at **G' = G''** (1/2 point)

Question 9: Polymers at interfaces (5 points)

a) (2.5 points) (i) The **brush regime** is the regime where the **average interchain distance become less than 2 x the solution radius of gyration of the polymer**. Alternatively, one can also compare the **footprint** of a surface grafted polymer (1/grafting density) with the **projected 2D area** from the solution Rg (see the answer to question b).

b) (2.5 points) (i) Sample I: 100 nm^2 per chain (0.5 points); Sample II: 1.4 nm^2 per chain (0.5 points). Rg of 5 nm corresponds to a projected 2D

footprint of (π r2) = 79 nm^2 (0.5 points). Conclusion: in sample I the chains are in the mushroom regime and in Sample II in the brush regime (1 points).

Question 10: Mechanochemistry (5 points)

a) (i) the middle of the chain is where the forces are highest (0.75 points); (ii) incorporate a mechanophore at the desired position. (0.75 points)

b) yes it does (0.5 points). At **pH 5** polylysine is **charged** and at **pH 12 uncharged** (1 points). Due to **electrostatic repulsions** (0.5 points) the **forces** acing at pH 5 are larger (0.5 points) and thus the cleavage yield at a given point of time will be **higher** (0.5 points) and/or it **takes less time** to reach 100% cleavage. (0.5 points)

Question 11: Emulsions **(5 points)**

a) Emulsions can be stabilized with **surfactants** (1/4 point) or **nanoparticles** (1/4 point).
   I. *Surfactants:* **lower interfacial tension** (1/2 point) and therefore the interfacial energy $\Delta E = \gamma A$. They have a **high mobility** and **quickly adsorb** at the liquid-liquid interface. (1/4 point if one of them is mentioned) However, their adsorption is reversible –> drops can **coalesce** if the system is not optimized (1/4 point).
   II. *Nanoparticles:* Reduce the **interfacial area** (1/2 point) and therefore the interfacial energy. If adsorbed at the liquid-liquid interface, they are strongly bound. It typically takes more than 100 k_BT to remove them -> for practical purposes irreversibly bound -> **more stable dispersion (1/4 point)**. **Slower adsorption (1/4 point)**.

b) Sauce hollandaise: **oil in water emulsion (1/2 point)**: surfactant with **HLB value between 10 and 20 (1/2 point)**. Surfactant must be food grade: **nonionic surfactant (1/2 point)**. Hydrophobic chain: aliphatic, hydrophilic for example sugar e.g. Span 80.

c) $\Delta E = \gamma \pi r^2$ -> 1.6×10^{-16} J (1/4 point)-> 3820 k_BT *(1/4 point).* Particles are for practical purposes irreversibly adsorbed at the liquid-air interface -> the foam is very stable, foam does not coalesce. (1/2 point).

Question 12: Particles **(5 points)**

Au nanoparticles:

a) Thiols (1 point)

b) $N = \frac{l_0}{l^{\frac{5}{3}}\Gamma^{\frac{1}{3}}} = 37$ or 38 (1/2 point) -> M_w = 1636 Da or 1680 Da (1/2 point)

c) PEG then acts as a **depletant** and particles agglomerate because of the **attractive depletion forces**. (1 point)

d) DLS (1/2 point): measure the **intensity of the scattered light** at **time 0 and time Δ*t* (1/4 point)**. The **correlation (1/4 point)** of the intensity

pattern is calculated and plotted as a function of Δt. This correlation function is fitted to extract a **diffusion coefficient (1/4 point)**. Using the **Stokes Einstein equation (1/4 point)**, this allows calculation of the hydrodynamic radius (diameter). The scattering intensity scales with r^6 -> you almost only see the **larger aggregates** and you overestimate the size of the particles (1/2 point)