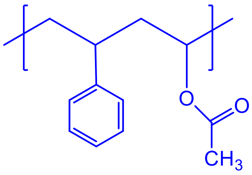
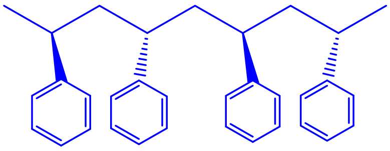
Properties of Polymers   Midterm Exam Solutions   May 2019

1. [2 + 2 + 3 x 3 pts] **Answer the following questions.**

(a) Draw the structure of poly(styrene-*alt*-vinyl acetate).

(b) Draw the structure of syndiotactic polystyrene.





(c) Why is (atactic or syndiotactic) polystyrene insoluble in methanol, while styrene is soluble?

Since the entropy change ΔS for the dissolution of a polymer in methanol is small, the $T\Delta S$ term is outweighed by the enthalpy change. The ΔS for monomer/solvent solution is much larger than corresponding polymer/solvent solution.

(d) Why is syndiotactic polystyrene insoluble in xylene, while atactic polystyrene is soluble?

For semicrystalline polymers like sPS to be soluble in solvents there need extra (positive) heat or enthalpy of solution for destruction of crystals, which outweighs the $T\Delta S$ term.

(e) What would you do to dissolve syndiotactic polystyrene in xylene? Explain your answer.

Raise the temperature to make $T\Delta S$ term larger than enthalpy term.

Using a solvent to introduce specific interaction like H-bonding can be an answer. However, there's no moiety for H-bond in polystyrene. minus one point.

2. [3 x 3 points] **Answer the following questions.**

(a) Is the solvent in an ideal solution always a good solvent? Why or why not?

Yes. [1 pt] For ideal solution, $\Delta H = 0$ and $T\Delta S > 0$, which gives $\Delta G < 0$, and the solvent dissolve the solute.

(b) Actually, a polymer solution cannot be an ideal solution. Why?

One requirement for an ideal solution is that the size of solvent and solute is the same, which is not possible for a polymer solution. Polymers are much bigger than solvents.

(c) A polymer solution can behave as an ideal solution, though. How?

At a certain temperature in a certain solvent, which is called a theta condition, the excess enthalpy change and the excess $T\Delta S$ term cancels each other, and the free energy change of mixing deviated from ideal free energy change of mixing becomes zero.

3. [3 x 3 points] **For polyethylene chains with the molar mass of 140000, the bond angle of 110°, and the bond length of 0.15 nm, answer the following questions.**

(a) If the chains take the most preferred conformation for all of their bonds, what would be the root-mean-square end-to-end distance?

$(10000)(.15\text{ nm})(\sin 55°) = 1230\text{ nm}$. It actually is a contour length.

(b) If the chains are freely rotating, what would be the root-mean-square end-to-end distance of the chain?

$(\sqrt{2})(\sqrt{10000})(.15\text{ nm}) = 21.2\text{ nm}$.

(c) If the characteristic ratio determined by SANS at 140 °C was 6.8, what would be the unperturbed root-mean-square radius of gyration?

$(\sqrt{6})(\sqrt{6.8})(\sqrt{10000})(.15\text{ nm}) = 95.8\text{ nm}$.

4. [2 + 2 + 3 + 3 points] **For DSV and GPC for measuring molar mass of polymers, answer the following questions.**

(a) Spell out DSV and GPC.

dilute solution viscometry, gel permeation chromatography

(b) Both of DSV and GPC are 'relative' methods. Why are they 'relative?'

The quantity measured by these methods is the volume of polymer chain in the solution, which is dependent on the temperature and the type of solvent.

(c) What is the equation used in DSV practice to get molar mass from your raw data? Write the name of the equation, and describe the equation in one sentence.

Mark-Houwink-Sakurada [MHS] equation. The equation relates the intrinsic viscosity of a polymer solution to its (viscosity-average) molar mass.

(d) What is the concept (or observation) used in DSV practice to get molar mass from your raw data? Describe it in one sentence.

universal calibration (curve). In the same environment [solvent/temperature] of GPC, the species eluted at the same elution volume has the same hydrodynamic volume. OR Many polymers fall on the same curve on the [η]M vs elution volume curve.

5. [5 x 3 points] **There are three theories explaining the glass transition of polymers.**

(a) What are they? Name the three.

thermodynamic, kinetic, and free-volume theories

(b) How is the glass transition defined by each of the theories? Limit your answer to one sentence for each theory.

thermodynamic: Glass transition is a (pseudo-)2nd-order phase transition.

kinetic: Glass transition occurs when the experimental time is the same to the material (relaxation) time.

free-volume: Glassy state is an iso-free-volume state, and free volume expands at above Tg.

(c) Would the glass transition temperature appear at a higher or a lower temperature when you increase the heating rate of the DSC experiment? Explain your answer using one of the theories above.

higher. [1 pt] According to the kinetic theory, higher heating rate or smaller experimental time results in higher Deborah number, more solid-like, and higher Tg.

(d) Would the glass transition temperature appear at a higher or a lower temperature when you increase the crosslinking density of the same polymer? Explain your answer using one of the theories above.

higher. [1 pt] According to the free-volume theory, higher crosslinking density results in lower free volume, more difficult segmental motion, and higher Tg.

(e) Would the glass transition temperature appear at a higher or a lower temperature when you 'age' the polymer sample? Explain your answer using one of the theories above.

higher. [1 pt] According to the free-volume theory, aging results in lower free volume, more difficult segmental motion, and higher Tg.

You don't agree? Ask for the comment in the class.

6. [10 x 2 points] **Fill the blanks in the description of polymer crystals below.**

By slowly lowering the temperature of a polyethylene solution, the plate-like single crystal, called (a) lamella is formed. The unit cell crystallographic structure the crystal is (b) orthorhombic or orthogonal, in which the c-axis [chain axis] is perpendicular to the a-b plane.

The crystal grows by crystallization of the chains on (c) 110 plane (which is called fold-plane; write down the Miller index), and folding at (d) 001 plane (which is fold surface; write down the Miller index). By the discovery of this polyethylene single crystal, the idea of folded-chain model, in contrast to the earlier (e) fringed-micelle model, of polymer semicrystalline state was developed.

By lowering the temperature of a polyethylene melt, a ball-like crystal, called (f) spherulite, is formed. This type of crystal formed in thin film shows characteristic (g) Maltese cross pattern under polarized light. Examining this type of crystal formed in the bulk, the crystal is actually (a), and the chain axis is (h) ~~radial~~ or tangential (choose one) to the ball. The mode of re-entry to (a) is (i) switchboard or random rather than adjacent, and the region between (a)s contains (j) tie-molecule(s) that holds the (a)s together.

7. [5 x 3 points] **Consider the three crystallizable polymers; Polymer 1 with T_g of –50 °C, Polymer 2 with T_g of 10 °C, and Polymer 3 with T_g of 100 °C.**

(a) Estimate or guess the melting temperature of Polymer 1, 2, and 3.

applying the 2/3 rule: 60 °C, 150 °C, and 290 °C, respectively

(b) After the polymers were cooled to room temperature from their melt state, it was found that Polymer A had very low degree of crystallinity and Polymer B showed continuous after-shrinkage for weeks. Match the polymers 1, 2, and 3 to A, B, and C.

1-C, 2-B, 3-A or A-3, B-2, C-1

(c) Explain your answer to (b).

The crystallinity of Polymer 3 should be very low, since it would not have enough time to crystallize. Between Polymer 1 and 2, the rate of crystallization of Polymer 2 should be lower, since its Tg is just below the crystallization temperature [room temperature]. At the room temperature the crystallization proceeds slowly for weeks.

(d) If you want to get the product of Polymer A with a higher crystallinity, what would you do? Explain.

Heat to a temperature higher than the Tg [100 °C], hold for a while, and cool the polymer to the room temperature. It is an annealing treatment.

(e) If the Avrami exponents for the crystallization of Polymer B and C are the same, which polymer would have larger crystals? Explain.

When the nucleation behavior is the same (either thermal or athermal) Polymer C (or Polymer 1) would have larger crystals, since the crystallization temperature [room temperature] is farther from Tg.

8. [3 x 3 points] **TPU and TPO are two examples of TPE.**

(a) Spell out TPU, TPO, and TPE.

thermoplastic polyurethane, thermoplastic polyolefin, thermoplastic elastomer

(b) Define TPE in one sentence.

TPE is the processable elastomer that is physically crosslinked

(c) What is the difference in the structure of crosslinking point between TPU and TPO?

Urethane hard segment is the crosslinking point in TPU, while crystal(lite) is the one in TPO.