Midterm

Wednesday, February 24, 2021 6:02 PM

JOHNS HOPKINS
WHITING SCHOOL
of ENGINEERING

Department of Materials Science and Engineering

EN. 510.316 Biomaterials I

Spring 2021 | Midterm Exam I

2/24/2021 6:00 - 8:00p.m.

Name: _____

Q1 [45]	Q2 [15]	Q3 [15]	Q4 [10]	Q5 [15]	Total [100]

Instructions:

- This is an open-book exam. | Answer ALL questions. | You should work on this exam independently. No consultation or discussion is allowed!
- If you do not have a printer, write the answers to Q1 on a separate sheet of paper neatly. Mark your answers to each question neatly. For example, 1.1 A; 1.2 B; 1.3 C 1.4 D, etc.
- Write answers to Q2 to Q5 on separate sheets of papers. Turn all answer sheets in on BlackBoard.

1. Multiple Choices. Choose ALL correct answer(s) to each of the following question. **There could be more than one correct answer to each question.** Please select the answer(s) on the answer sheet below. (45' total, 3' per question)

Use #2 Pencil or pen; Fill the circle completely. INSTRUCTIONS: Example: A○ B● C○

SECTION 1

1	A○	B○	C○	D○	9	A○	B○	C○	D○
2	A○	B○	C○	D○	10	A○	B○	C○	D○
3	A○	B○	C○	D○	11	A○	B○	C○	D○
4	A○	B○	C○	D○	12	A○	B○	C○	D○
5	A○	B○	C○	D○	13	A○	B○	C○	D○
6	A○	B○	C○	D○	14	A○	B○	C○	D○
7	A○	B○	C○	D○	15	A○	B○	C○	D○
8	A○	B○	C○	D○					

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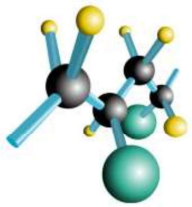
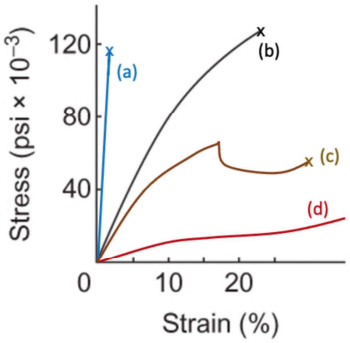
1. Choose one answer to each of the following questions.
(3 points for each question, 45 points)

[ ] 1.1 A poly(vinyl chloride) (PVC) sample was synthesized using anionic polymerization. In this PVC sample, a representative neighbouring unit has a configuration as shown to the right. Which of the following describes the neighbouring repeating units (diad) configuration shown and corresponding tacticity of the polymer?



(a) Racemic diad; atactic polymer
(b) Racemic diad; syndiotactic polymer
(c) Meso diad; isotactic polymer
(d) Meso diad; syndiotactic polymer

[ ] 1.2 Consider four polymer samples: syndiotactic polystyrene (~200,000 Da); low density polyethylene (~200,000 Da), lightly vulcanized natural rubber, and Bakelite. Their stress-strain curves were collected and plotted as shown below. Which one of the four curves reflects the tensile property of syndiotactic polystyrene?



[ ] 1.3 Which of the following is the most important consideration in designing a gecko feet-inspired adhesive?

(a) Formation of soft micropillar arrays allows the adhesive to interpenetrate with the target substrate and form strong covalent bonds;
(b) Hygroscopic (hydrophilic) structures naturally present in gecko feet can remove interfacial water to increase wet adhesion strength;
(c) Formation of stiff microspatulae using a brittle polymer allows the adhesive to maintain integrity under high levels of deformation;
(d) Increasing microscale surface contact area from micropatterned arrays can exploit non-covalent van der Waals interaction forces and create a higher overall adhesion strength.

[ ] 1.4 Which of the following statements is most accurate to describe the effect of chain transfer reagent on the number average degree of polymerization initiated by a free radical?

(a) Chain transfer to monomer increases the molecular weight of the polymer;
(b) The addition of chain transfer agent does not influence the polymerization rate when the chain transfer occurs to the solvent;
(c) The average degree of polymerization increases when chain transfer occurs to the solvent molecules;
(d) The presence of chain transfer agent generally decreases the average degree of polymerization.

[ ] 1.5 Which of the following statements is TRUE for the polymer with this label?

(a) This polymer is typically synthesized in a reaction under high pressure and temperature; and initiated by free radicals.
(b) It is typically synthesized by coordination polymerization.
(c) This polymer typically contains short-chain branches with 4, 5, or 6 carbons, as a result of extensive chain transfer.
(d) This polymer has an isotactic structure leading to high crystallinity.

[ ] 1.6 Which of the following sequence isomer connections is **most likely** observed in polystyrene chain prepared by free radical polymerization?

(a) Head-to-Tail; because the steric hindrance of the aromatic ring biases the sequence isomerism.
(b) Head-to-Head/Tail-to-Tail; because the hydrophobic interactions of similar hydrocarbon groups causes intermolecular attraction.
(c) Both Head-to-Head/Tail-to-Tail and Head-to-Tail; because there is no preference for sequence isomers in polystyrene.
(d) Either Head-to-Head/Tail-to-Tail or Head-to-Tail; because sequence isomerism can be controlled under this polymerization scheme.

[ ] 1.7 According to the **Schulz-Flory Distribution** for an A-B type step growth polymerization, which of the following equations correctly describes number average chain length $\overline{x_n}$ at an extent of reaction p?

(a) $\overline{x_n} = \sum(1-p)p^{x-1}$
(b) $\overline{x_n} = \sum(1-p)xp^{x-1}$
(c) $\overline{x_n} = \sum(1-p)^2x^2p^{x-1}$
(d) $\overline{x_n} = \sum(1-p)x^{p-1}$

[ ] 1.8 Four different polystyrene samples, all with an average molecular weight of 200,000, were analyzed on a gel permeation chromatography (GPC) system. Which of the following samples will have the largest elution volume?

	(a)	(b)	(c)	(d)
Sample Description	Linear	Star copolymer with 10 equal length arms	Star copolymer with 4 equal length arms	Branched

[ ] 1.9 Which of the following statements is TRUE about the Tromsdorff Effect?

(a) It occurs as a result of restriction of Brownian motion, thereby reducing collision speed of the formed (i.e. "dead") polymer chains;
(b) It occurs as a result of auto-acceleration in the chain initiation reaction;
(c) It occurs when the relative rate of chain termination reaction decreases dramatically due to the limited collisions between the extending polymer chains;
(d) It occurs when the free radical concentration increases as chain transfer intensifies.

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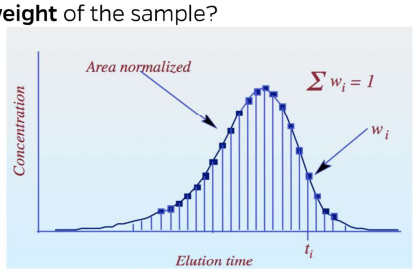
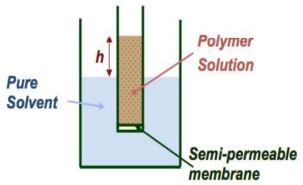
[ ] 1.10 The following GPC trace was obtained for an unknown polymer sample. The slices represent different fractions of the polymer sample. For each fraction of the sample (slice of the graph), the corresponding molecular weight (M_i) can be calculated from the standard curve collected in a separate run. The corresponding weight fraction w_i for each slice of the sample can also be calculated. Which of the following expression correctly calculates the **number average molecular weight** of the sample?

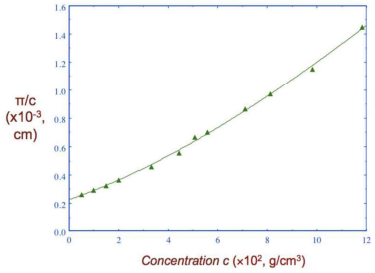


(a) $\sum M_i/w_i$ (b) $\sum w_i M_i$

(c) $1/\sum w_i/M_i$ (d) $\sum w_i/\sum M_i$

[ ] 1.11 Osmotic pressure measurements were conducted on a series of solutions of an unknown polymer sample at different concentrations using the setup shown below (left panel). A graph is then generated to illustrate the relationship between (π/c) and sample concentration (c) as shown below (right). Which of the following statements is TRUE?





(a) The intercept of the graph is $RT/\overline{M_w}$;

(b) The slope of the graph is $RT/\overline{M_w}$;

(c) The Y-axis of the graph is $\rho gh/c$;

(d) The intercept gives the intrinsic viscosity of the solution.

[ ] 1.12 In a step-growth polymerization between monomers A-A and B-B where a polymerization reaction with equal molar concentrations of the two monomers was planned, a 1% excess of A-A was added by mistake. What is the effect of this mishap on the maximum average degree of polymerization that can be achieved?

(a) Dropping from 10,000 to 9,900 (by 1%);
(b) Dropping from 201 to 199 (by 1%);
(c) Dropping from infinity to 1,999;
(d) Dropping from infinity to 199.

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[ ] 1.13 The Mark-Houwink-Sakurada (MHS) Equation describes the relationship of the average molecular weight and the intrinsic viscosity of a dilute solution of a given polymer. Which of the following statements is **TRUE**?

(a) The intrinsic viscosity of the polymer solution is only dependent upon the polymer average molecular weight;
(b) The intrinsic viscosity of the polymer solution is independent of the solvent used for the measurements;
(c) The intrinsic viscosity of the polymer solution is independent of polymer concentration;
(d) The intrinsic viscosity of the polymer solution, similar to the average molecular weight of the polymer, is independent of the temperature at which the measurements are made.

[ ] 1.14 Which of the following statements is TRUE when comparing free radical chain addition polymerization and step growth polymerization?

(a) In chain growth polymerization, no monomer can be detected when polymerization reaches completion ($t = \infty$);
(b) In step growth polymerization, molecular weight distribution widens with time, *i.e.*, the polydispersity increases when the extent of reaction p increases;
(c) In step growth polymerization, high molecular weight can be achieved as long as the molar ratio of the complementary reactive groups to controlled to 1:1, regardless of the concentration of the monomers and the extend of reaction;
(d) High molecular weight polymers can be achieved for step growth polymerization by mixing monofunctional and bifunctional monomers, as long as the total complementary reactive groups are maintained at 1:1 molar ratio.

[ ] 1.15 Which of the following viscosities measures the contribution of polymer to viscosity of a sample solution; AND is independent of polymer concentration?

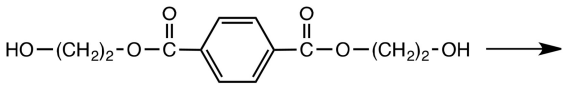
(a) Relative viscosity
(b) Specific viscosity
(c) Inherent viscosity
(d) Intrinsic viscosity

2. Fill in the blanks or give brief answers to the questions below. (15 points)

(a) 

is used as a material for producing vascular grafts.

Its full name is _____.

(Monomer) 

_____ (give the polymer structure)

This is a _____ (choose from step or chain)-growth polymerization.

(b) Synthesis of Nylon-6,8 (give structures for both monomer(s) and the polymer):

⟶

_____

This is a _____ (choose from step or chain)-growth polymerization.

(c) 

is the symbol for _____ (full name). Give the structures of its monomer and the polymer below:

⟶

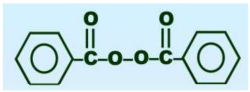
_____

This is a _____ (choose from step or chain)-growth polymerization.
Briefly explain why this polymer could not be synthesized by free radical polymerization:

What types of all possible isomers that you could find in this polymer structure? Give all the possible configurations (isomers) in each category (no need to draw the structures or illustrations):

(a) 

can be processed into various forms of products. Use the monomer and polymer structures to write the reaction equation(s) for all three steps of polymerization (ignore chain transfer reactions), when it is initiated by benzoyl peroxide (BPO, below):



(i). Chain_____ (complete the name of this step and write the reaction equation(s)):

(ii). Chain_____(complete the name of the step and write the reaction equation(s)):

(iii). Chain termination reactions: (**show the joint chain structures**)

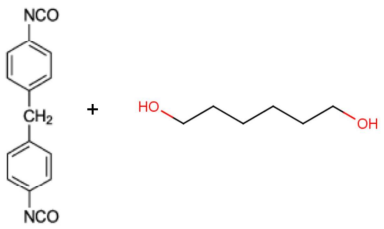
_____(give the name) termination:

Combination termination:

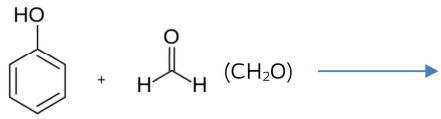
3. **Brief answer questions** (15')

(a) Briefly describe the nylon rope experiment to prepare Nylon 6,6; write the **reaction equation** and sketch out the synthesis setup. Explain the principle of this reaction.

(b) Complete the following reaction for synthesis of polyurethane; Briefly describe the method to generate the polyurethane foam sponge. How to control the foam density and pore size?



(c) Complete the equation for synthesis of Bakelite. What are the structure features of this polymer material? Sketch out a representative stress-strain curve for this polymer.



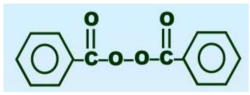
4. Nylon-6 can be synthesized by step growth polymerization using H_2N-$(CH_2)_5$-COOH as the monomer in an inert solvent. A strong acid (sulphuric acid, concentration is 0.1 M) is used as a catalyst. Given that the formula weight of the repeating unit is $M_0 = 113$, and the initial concentration of the monomer is c_0 (with proper units). (10 points)

(a) Express the relationship between the number average molecular weight ($\overline{M_n}$) and conversion of monomer (p). [No derivation is needed].

(b) What is the corresponding conversion of monomer p when $\overline{M_n}$ reaches 22,600?

(c) **Start with the reaction scheme, derive** the relationship between $\overline{M_n}$ and polymerization time t. **State the hypothesis you need to make in order to derive this kinetics.** Hint: Derive the $\overline{x_n} \sim t$ relationship first.

(d) Sketch out the relationship between $\overline{\mathbf{x_n}}$ and polymerization time $\boldsymbol{t}$. Label all axes of the figure and highlight all necessary details.

5. Polymer PMMA is initiated with benzoyl peroxide (BPO, ) to undergo bulk polymerization at 70°C. The dissociation constant of BPO at this temperature is $\boldsymbol{k_d = 2.0 \times 10^{-5} s^{-1}}$ and the efficiency of BPO as an initiator $\boldsymbol{f = 0.80}$. The initial BPO concentration $\boldsymbol{[I]_0 = 0.01\ mol \cdot L^{-1}}$, the initial monomer concentration $\boldsymbol{[M]_0 = 15\ mol \cdot L^{-1}}$, and the initial chain propagation rate $\boldsymbol{r_p = 6.4 \times 10^{-3} mol \cdot (L \cdot s)^{-1}}$. The molecular weight of the monomer MMA is 100. (15 points)

(a) **Derive** the expression for chain initiation rate of this polymerization; and calculate the chain initiation rate at the start of polymerization (t = 0).

(b) Calculate the average kinetic chain length for the initially formed polymer.

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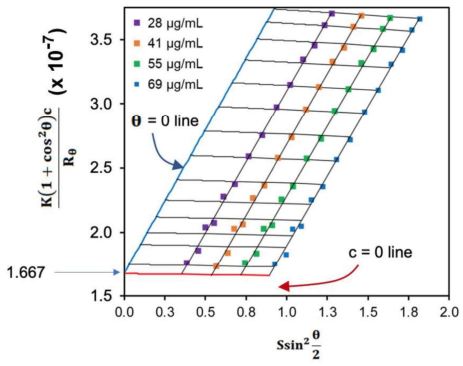
(c) A set of static light scattering measurements of this polymer sample in a solvent were conducted and the processed data are plotted in the figure to the right. In addition, a separate analysis of the sample revealed a PDI of 2.0. Calculate the Mn and Mw of this sample.



(d) Calculate the number average degree of polymerization ($\overline{x_n}$) and the chain termination parameter ξ.

(e) Calculate the molar percent of combination termination for this polymerization.

–End of exam paper–