

**BMEN 343: Introduction to Biomaterials**

**EXAM 1**

**2 October 2009**

**KEY**

**Name:** \_\_\_\_\_

**Signature:** \_\_\_\_\_

**ID #:** \_\_\_\_\_

*"On my honor, as an Aggie, I have neither given nor received unauthorized aid on this academic work."*

Page 1: Cover

Pages 2-8: Problems

Page 9: Equation Sheet (may be "torn" from exam – if so, do not hand back in)

Page 10: Periodic Table (may be "torn" from exam – if so, do not hand back in)

**YOU MAY USE A CALCULATOR**

**Problem 1: True or False****/32 points**

- T **F** The bonding exhibited by SiC would be stronger (i.e. higher in energy, kJ/mol) than bonding exhibited by MgO.  
**False:** ionic character of MgO bonds much higher due to large differences in electronegativity.
- T **F** Graphite is amorphous.  
**False:** Graphite is an “allotrope” or “polymorph” of elemental C; allotropes or polymorphs are the different crystal structures formed by some substance are thus crystalline by definition. Graphite has a distinct crystal structure consisting of layers of hexagonally arranged C atoms.
- T **F** As molecular weight of polypropylene (PP) increases, the magnitude of dipole-dipole forces increases.  
**False:** dipole-dipole F's not present (London forces would increase with MW).
- T** F Spherulites are semi-crystalline.  
**True**
- T** F C-O bonds are directional.  
**True**
- T **F** The number of atoms in a BCC unit cell is 4.  
**False:** FCC = 4 atoms, BCC = 2 atoms
- T **F** BCC is more densely packed than FCC.  
**False:** For FCC, APF = 0.74 (close packed) whereas BCC APF = 0.68 (not close packed).
- T** F Isotactic polypropylene (PP) is more crystalline than atactic PP.  
**True**
- T **F** Covalently (i.e. chemically) crosslinked poly(methyl methacrylate) (PMMA) can be melted and re-shaped without thermal decomposition.  
**False:** If it's crosslinked it's a thermosett and not able to be melted & re-shaped.
- T** F For a cation having a coordination number (CN) of 8, the coordination geometry is cubic.  
**True:** for CN = 8 (cubic geometry)
- T **F** The glass transition temperature ( $T_g$ ) of a semi-crystalline polymer originates from the lamellae.  
**False:** amorphous tie chains
- T** F A  $\text{Si}^{4+}$  ion is smaller than a neutral Si atom.  
**True**
- T **F** A key compositional feature of “bioactive” glasses and/or glass ceramics is low CaO content.  
**False:** high
- T **F** In the zinc blende (ZnS) crystal structure, the coordination numbers of anions and cations are both 8.  
**False:** CN = 4 (ZnS); CN = 8 (CsCl)
- T** F Linear polyethylene (PE) with a  $M_n = 100,000$  g/mol would be expected to be more crystalline than linear PE with a  $M_n = 500,000$  g/mol.  
**True:** Crystallinity increases with lower  $M_n$ .
- T **F** A bioactive glass-ceramic exhibits a glass transition temperature ( $T_g$ ).  
**False:** Polycrystalline – no longer amorphous

**Problem 2: Brief answer**

**/12oints**

a. **(4 pts)** Provide a formal definition of  $T_g$  (glass transition temperature) of a polymer. (Describe what is actually happening to the polymer chain, not just what physical changes are observed).

A temperature at which (or above which) there is an increase in segmental mobility (2 pts) of the polymer backbone (2 pts).

Note: Because asked for formal definition, “glassy/rigid to rubbery/flexible transition” is not okay—**1 pt** only if that is all you write.

b. **(3 pts)** Provide a definition for a ceramic.

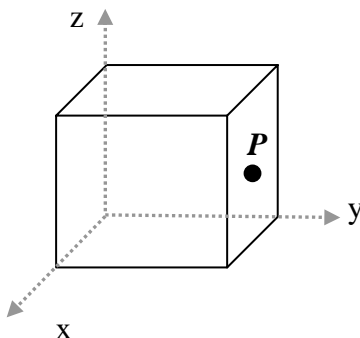
A compound consisting of 2 or more **elements** where at least one is not a metal.

c. **(2 pts)** What mineral forms at the surface of bioactive glasses when placed in the body? Provide the formula or full name (not just abbreviation).

$\text{Ca}_5(\text{PO}_4)_3\text{OH}$  or carbonated hydroxyapatite (HCA)

(only 1 point for CORRECT abbreviation)

d. **(3 pts)** What are the *point coordinates* for the point “P” in the cubic unit cell below. (Note: “P” is at the face center of the right side of the cube).



$\frac{1}{2}$  1  $\frac{1}{2}$

**Problem 3: Brief answer**

**/7points**

a. (4pts) (i) What is the electronic configuration of  $Ti^{3+}$  (manganese)? (ii) What is the valence electronic configuration of  $Ti^{3+}$ ? (Note: For i and ii, do not use any abbreviation like “[Ar]”. You do not have to show an orbital diagram; only do so if it helps you.)

Note:

$Z = 22$  (neutral Ti) and  $22 - 3 = 19$  electrons for  $Ti^{3+}$

(1) Write electronic configuration of neutral Ti atom. Note, that although 4s fills *before* beginning to fill 3d, they switch E levels once 4s filled:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$

(2.) From a neutral Ti atom, lose two ns electrons first, then one (n-1)d electrons because removed from highest E level first.

(i) The electronic configuration =  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$  (2points)

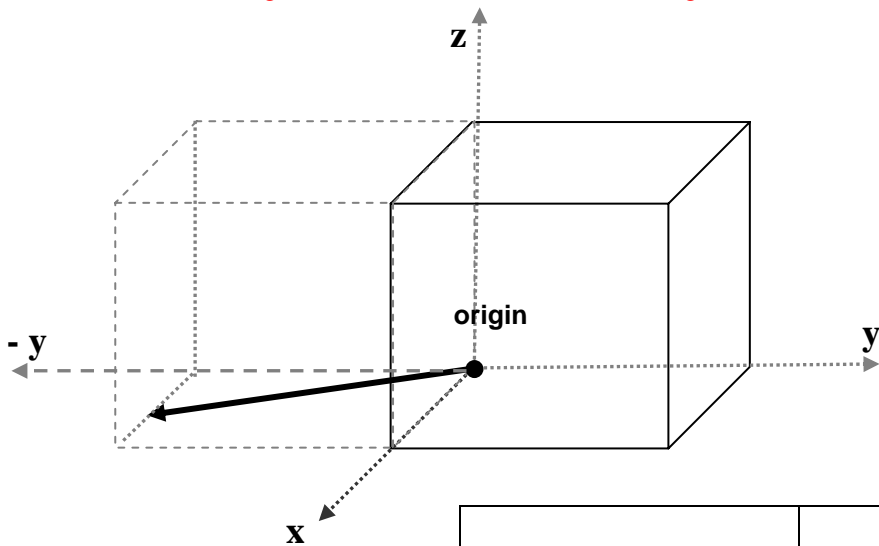
(ii) Thus, the valence electronic configuration =  $3s^2 3p^6 3d^1$  (2 points)

b (3 pts) Clearly draw a  $[1 \bar{2} 0]$  direction within a cubic unit cell. Label x, y, and z axes (and any negative axes) and origin.

Notes:

1. Not necessary to complete the table.

2. Directional indices are the (a) point coordinates where vector ends (if vector ends at a corner) or (b) point coordinates reduced to smallest integer values (if vector ends at unit cell edge).



**1 pt:** draw cube, adjacent cube, label axes, label origin  
**3 pt:** draw direction correctly—“adjacent cube” should be clearly drawn (or -2); the vector should clear hit the edge at 1/2 distance.

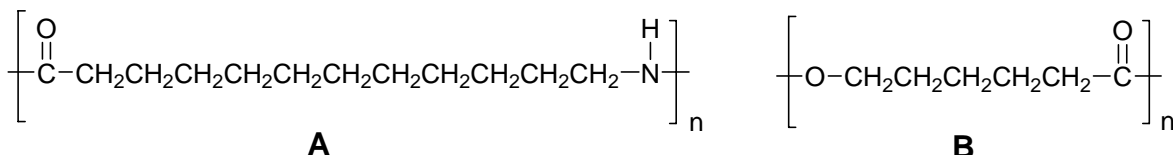
- If direction is correct, but table is incorrect, deduct one point for each incorrect entry.

	x axis	y axis	z axis
Projection	$a/2$	$-a$	0
Projection in terms of a	$1/2$	-1	0
Reduction	1	-2	0
Enclosure	$[ 1 \quad \bar{2} \quad 0 ]$		

**Note: Largest # is a reduction from 1. In this case, “2” is a reduction from 1.**

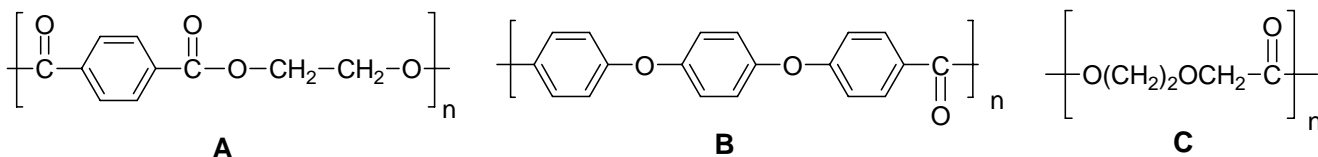
**Problem 4:****/12 points**

a. (6 pts) Consider the two polymers below. (i) Which would be predicted to exhibit higher crystallinity (A or B)? (ii) Briefly explain your answer on the basis of specific feature(s) of their molecular structure. Consider that they have similar molecular weights and are linear.

**(i) A (2 pts)**

**(ii) (a) more flexible backbone (2 pts) and (b) stronger secondary intermolecular bonding (H-bonding in addition to dipole-dipole forces) (2 pts).**

b. (6 pts) Consider the structure of linear polymers **A**, **B**, and **C**. (i) Which would be predicted to exhibit the highest  $T_g$  (**A**, **B**, or **C**)? (ii) Briefly explain your answer on the basis of specific feature(s) of molecular structure of the polymer you selected (versus that of the polymers you did not select). (iii) For **A**, **B**, and **C**: name the strongest (only) specific type of secondary intermolecular force exhibited by it and an adjacent chain and clearly circle the atoms which can participate in this type of bonding.

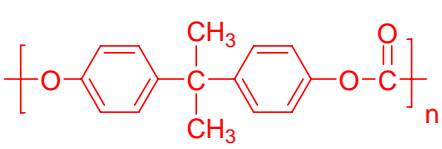
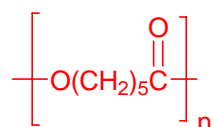
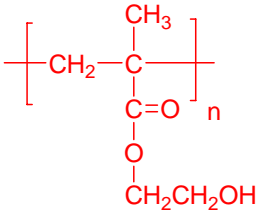
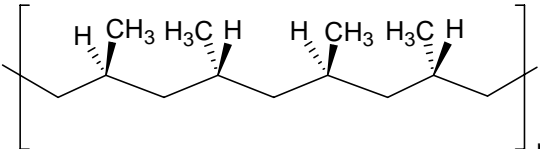
**(i) B (2 pts)****(ii) More rigid backbone (2 pts)****(iii) Dipole-dipole forces and circle C=O (2 pts)**

**Problem 5:**

**/23 points**

a. **(20 pts)** Complete all “blanks” in the following chart. When asked to give a value for  $T_g$ , select from list of possible choices:

<b><math>T_g</math> Choices:</b>	-127 °C	-41 °C	55 °C	-60 °C	105 °C	150 °C	36 °C	73 °C
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Polymer Name	Structure-draw structure if not listed	Morphology Highly crystalline*, semi-crystalline, or amorphous?	$T_g$ (°C)
Polycarbonate <b>PC</b>	 <p style="text-align: right;">2 pts</p>	amorphous	150
Polycaprolactone <b>PCL</b>	 <p style="text-align: right;">2 pts</p>	Semi-crystalline	-60
Poly(hydroxyethyl methacrylate) <b>PHEMA</b>	 <p style="text-align: right;">2 pts</p>	amorphous	55
Polypropylene <b>PP</b>	 <p>What is the tacticity? _____ <b>Syndiotactic</b></p> <p style="text-align: right;">2 pts</p>	Semi-crystalline	-8

\* “highly crystalline” = 70-90% crystalline. Select only one answer for morphology.

b. **(2 pts)** Of the four polymers listed in the above table, provide the name(s) [or abbreviation(s)] of polymer(s) which are “biodegradable” (if any).

**PCL**

**Problem 6: Calculation/Problem Solving**

**7 points**

**(7 pts)** Assume you have a polymer sample characterized by information in the table below. Calculate  $\bar{M}_n$ ,  $\bar{M}_w$ , and PDI. Put a box around each final answer.

Fraction	moles	molecular weight (g/mol)
A	5	725,000
B	3	250,000
C	8	150,000

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

$$\bar{M}_n = \frac{(5\text{mols} \times 725,000\text{g/mol}) + (3\text{mols} \times 250,000\text{g/mol}) + (8\text{mols} \times 150,000\text{g/mol})}{5\text{mols} + 3\text{mols} + 8\text{mols}}$$

$$= 348,438 \text{ g/mol}$$

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

$$\bar{M}_w = \frac{[5\text{mols} \times (725,000\text{g/mol})^2] + [3\text{mols} \times (250,000\text{g/mol})^2] + [8\text{mols} \times (150,000\text{g/mol})^2]}{(5\text{mols} \times 725,000\text{g/mol}) + (3\text{mols} \times 250,000\text{g/mol}) + (8\text{mols} \times 150,000\text{g/mol})}$$

$$= 537,332 \text{ g/mol}$$

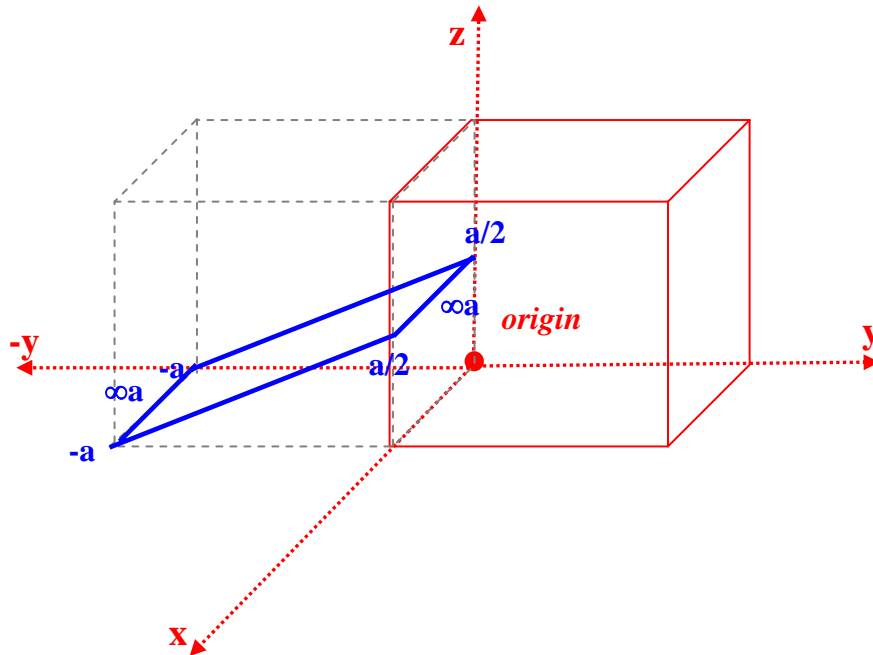
$$PDI = \frac{\bar{M}_w}{\bar{M}_n} = \frac{537,332}{348,438} = 1.54$$

**(STUDENTS TOLD THEY NEEDED TO KNOW FORMULA FOR PDI--NOT ON FORMULA SHEET).**

**Problem 7: Calculation/Problem Solving**

**/8 points**

**(8 pts) Clearly** sketch within a cubic unit cell the plane  $(0 \bar{1} 2)$ . Draw the **original unit cell** and **label**: x, y, and z axes and origin. Also, label **any adjacent unit cell** (with dashed line) for clarity (if needed), **any negative axes** (if plane extends along that direction) and **label all intercepts** on/near your drawing.



Remember that the Miller Indices are the reciprocals of the axial intercepts.

1. Complete the table to determine intercepts. (Not necessary for credit – can be helpful).
2. Find each intercept by moving **FROM THE ORIGIN** along each designated axis the appropriate distance.
3. If plane extends outside of original unit cell, be sure you clearly draw the adjacent unit cell (e.g. with a dashed line) so that your intercepts and plane drawings are clear.

	x axis	y axis	z axis
Intercepts	$\infty$	$-a$	$a/2$
Intercepts in terms of a	$\infty$	$-1$	$1/2$
Reciprocals of intercepts	$0$	$-1$	$2$
Reduction	Not necessary (lowest set of integers)		
Enclosure	$(0 \quad \bar{1} \quad 2)$		

## Equation Sheet for Exam 1

$$a = 2R\sqrt{2} \quad a = \frac{4R}{\sqrt{3}} \quad a = 2R$$

$$APF = \frac{V_s}{V_c} \quad N_A = 6.023 \times 10^{23} \text{ atoms/mol}$$

$$V_c = 16R^3\sqrt{2} \quad V_c = \frac{64R^3}{3\sqrt{3}} \quad V_c = 6R^2c\sqrt{3} \quad \rho = \frac{nA}{V_c N_A}$$

$$\%IC = \{1 - \exp[-(0.25)(X_A - X_B)^2]\} \times 100$$

$$\overline{DP} = \frac{MW_{polymer}}{MW_{mer}}$$

$$\overline{M}_n = \frac{\sum w_i}{\sum N_i} = \frac{\sum N_i M_i}{\sum N_i}$$

$$\overline{M}_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

You need to know equation for PDI