THE OPEN UNIVERSITY OF SRI LANKA

B Sc Degree/ Stand Alone courses in Science

LEVEL 5 - ASSIGNMENT TEST III 2015/2016

CMU 3233– POLYMER CHEMISTRY

DURATION : One Hour

DATE : 04th November 2016 TIME : 4.15 p.m. to 5.15 p.m.

This Assignment test paper consists of two parts, A and B. Part A consists of 10 MCQ and part B consists of two structured type questions. You need to hand over only part B with the MCQ answer sheet.

- Answer all questions
- Choose the most correct answer to each question and mark a cross" X" over the answer on the given answer sheet.
- Use a PEN (not a pencil) in answering.
- Any answer with more than one cross will not be counted.
- Marks will be deducted for each incorrect answer (1/6×3 = 0.5 per incorrect answer).
- The use of a non – programmable electronic calculator is permitted.
- Logarithm tables will be provided.

Avogadro constant, (L)	$= 6.022\times10^{23}$ mol^{-1}
Plank constant, (h)	$= 6.63 \times 10^{-34}$ Js
Velocity of light, (c)	$= 3 \times 10^{8}$ ms^{-1}
Standard atmospheric pressure, (π)	$= 10^{5}$ Pa(Nm^{-2})
Gas Constant (R)	$= 8.314$ J mol^{-1} K^{-1}
Faraday constant (F)	$= 96{,}500$ C mol^{-1}
Log_e (x)	$= 2.303\ \text{Log}_{10}$ (x)

PART A – Answer all questions. (30 marks)

01). In the polymerization of hexamethylene diamine with adipic acid, the percent conversion of adipic acid is 0.90. The degree of polymerization is

1. 50 2. 30 3. 40 4. 10 5. 20

02). In Carother's equation, when p reaches one,

a) the degree of polymerization reaches infinity.
b) the polymer produced are very tough. c) high molecular mass polymers are produced.

The correct statement/s is/are,

1. a only. 2. b only. 3. c only. 4. a and c only. 5. a, b and c only.

03). The order of free radical polymerization with respect to monomer concentration (with four assumptions) is

1. zero order 2. first order. 3. zero or first order
4. second order. 5. first or second order.

04). Rate equation for anionic polymerization of styrene is

1. $\frac{-d[M]}{dt} = \frac{k_i k_p [I][M^2]}{k_{tr}[NH_3]}$ 2. $\frac{-d[M]}{dt} = \frac{k_{tr}[NH_3]}{k_p[I][M]}$ 3. $\frac{-d[M]}{dt} = \frac{k_i[M]^2}{k_p[NH_3]}$

4. $\frac{-d[M]}{dt} = \frac{k_p[NH_3]}{k_i[I]}$ 5. $\frac{-d[M]}{dt} = \frac{k_{tr}[I]^2[M]}{k_i\|NH_3\|}$

05). Which statement is **true** about free radical polymerization?

a) The rate of reaction increases with increase of temperature.
b) The rate of reaction decreases with increase of temperature.
c) The chain length increases with increase of temperature.
d) The chain length decreases with increase of temperature.

The correct statement/s is/are,

1. a only. 2. b and c only. 3. a and d only. 4. b and d only. 5. a and c only

Questions **5** and **6** are based on the following information.

Table below shows some preliminary observations made on two polymers **A** and **B.**

Polymer	Appearance	Colour	Heat test	Rigidity
Polymer **A**	Transparent	colourless	melts	rigid
Polymer **B**	Translucent	white	melts	flexible

06). Which one of the following statements is correct regarding above polymers A and B?

1. Polymer A is a thermoplastic material whereas the polymer B is a thermoset material.
2. Polymer B should have a higher elastic modulus than that of polymer A.
3. Polymer A is a crystalline material.
4. Both polymers are thermoset materials.
5. Both polymers are thermoplastic materials.

07). Which one of the following statement is true regarding glass transition temperatures ($\mathbf{T_g}$) of polymers A and B?

1. T_g of the polymer A is above the room temperature and should be higher than that of polymer B.
2. $\mathbf{T_g}$ of the polymer B is above the room temperature and should be higher than that of polymer A.
3. $\mathbf{T_g}$ of the polymer A should be lower than the room temperature.
4. $\mathbf{T_g}$ of the polymer B should be higher than the room temperature.
5. It is impossible to predict or compare glass transition temperatures of above polymers from the information provided.

08). IR/FTIR is a valuable tool in polymer characterizations in many ways. Select the correct statement/s from the following about the IR spectra of Poly Propylene (PP) and Poly Ethylene (PE).

1. PP and PE can be qualitatively distinguished from their IR spectra.
2. It is possible to determine the presence of any crystallinity in PE from IR spectrum of PE.
3. Tacticity of a given PP sample may be determined using IR spectrum of PP.
4. All of the above statements 1,2, and 3 are correct.
5. All of the above statements 1,2, and 3 are incorrect.

09). A thermogram obtained from a DSC experiment for a sample of polyamide-6 showed an exothermic peak (upward peak) at lower temperature range (30-35 C^0) followed by an endothermic peak (downward peak) at a higher temperature range (50-55 C^0). The enthalpy of fusion of the sample was found to be 168 J/g. Literature values indicated that the 100% crystalline sample of polyamide-6 has heat of fusion of 188 J/g. Which of the following statement is correct regarding degree of crystallinity of the polyamide-6 sample?

1. The degree of crystallinity of the sample of polyamide-6 is 89.4%.
2. The degree of crystallinity of the sample of polyamide-6 is 112%.
3. The degree of crystallinity of the sample of polyamide-6 cannot be calculated from the given data, and enthalpy of crystallization is needed to calculate it.
4. Given polyamide-6 sample should be 100% amorphous as it has lower enthalpy of fusion compared to 100% crystalline sample.
5. All of the above statements are incorrect.

10). "Perfectly elastic materials obey (**a**) ---------- law and can be represented by a (**b**) ---------- model in which stored energy is (**c**) ----------." In the above statement, pick the correct set of words that are in **correct** order to fill the blanks in

1. (**a**) Newton's law, (**b**) spring, (**c**) recoverable.
2. (**a**) Newton's law, (**b**) dashpot (**c**) recoverable.
3. (**a**) Hook's , (**b**) spring, (**c**) recoverable.
4. (**a**) Hook's, (**b**) dashpot (**c**) recoverable.
5. (**a**) Newton's law, (**b**) dashpot (**c**) irrecoverable.

THE OPEN UNIVERSITY OF SRI LANKA
B.Sc DEGREE/STAND ALONE COURSE IN SCIENCE - LEVEL 5
Assignment Test III – 2015/2016
CMU 3233 – POLYMER CHEMISTRY

MCQ ANSWER SHEET: Mark a cross (x) over the most suitable answer.

Index No. | |

		Marks
Unanswered		
Correct Answers		
Wrong Answers		
Total		

1.	1	2	3	4	5	2.	1	2	3	4	5	3.	1	2	3	4	5
4.	1	2	3	4	5	5.	1	2	3	4	5	6.	1	2	3	4	5
7.	1	2	3	4	5	8.	1	2	3	4	5	9.	1	2	3	4	5
10.	1	2	3	4	5												

PART B – Answer all questions only in the space provided. Attached sheets will not be graded. (70 marks)

01 (a) i. Write down Carother's equation for a 1:1 bi functional reaction mixture and define terms.

(03 marks)

ii. Calculate the percentage conversion of polyethylene by assuming the molecular weight of polyethylene sample is 56,0000 g/mol.

(05 marks)

(b) i. List down the assumptions used in the derivation of rate equation in free radical polymerization by giving reasons.

(08 marks)

ii. "Average molar mass in polymers formed by free radical polymerization is higher than those formed by anionic polymerization". Justify the statement.

(05 marks)

(c) i. Write down modified Carothers' equation and define the terms.

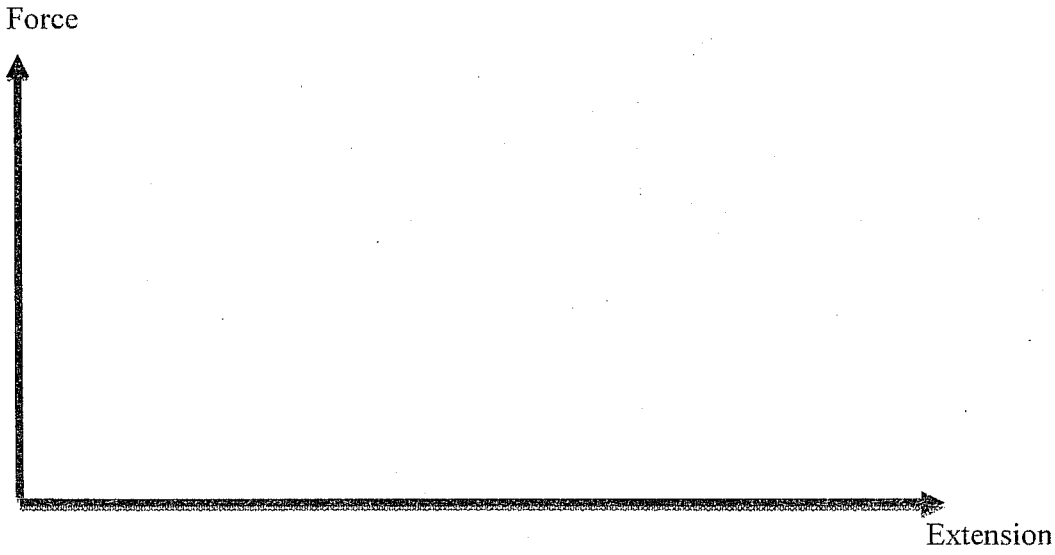
(03 marks)

ii. When 10% more of adipic acid is used in the preparation of nylon 6,6 with hexamethylene diammine, the percent conversion is found to be 95%. Calculate the degree of polymerization?

(06 marks)

02 (a). General Purpose Polystyrene (GPPS) is a hard and brittle material whereas High Density Polyethylene (HDPE) is soft and tough material. Tensile testing was carried out on both GPPS and HDPE with standard dump-bell specimens with same test area dimensions of 10mm width and 4 mm thickness. The initial gauge length was set for 100 mm.

i. Sketch the Force-Extension variation of both GPPS and HDPE on the same graph below clearly assigning curves for those two materials. (04 marks)



ii. Briefly illustrate how you can calculate elastic moduli of GPPS and HDPE using the above graph.

(04 marks)

iii. Calculate the elastic modulus of HDPE in MPa using the following data of force and extension. Name the assumption made for the calculation.

Force (N)	Extension (mm)
25	0.018
75	0.064

(05 marks)

iv. List down four other material parameters that can be obtained from a similar graph as above.

(04 marks)

v. Give three other factors which affect the stress-strain behavior of polymers.

(03 marks)

b). The Fox equation is used to calculate the glass transition temperature of random copolymers. The relevant equation for the binary random copolymer is given below.

$$1/(T_g)AB = W_A/(T_g)A + W_B/(T_g)B$$

i. Define the terms in the above equation.

(05 marks)

ii. Use the above equation to calculate the glass transition temperature of a copolymer made with 200 g of HDPE (T_g= -90 °C) and 400g of PP (T_g= -15°C).

(05 marks)

C) i. **Define** creep and stress relaxation as applied to an amorphous polymer.

(04 marks)

ii. **Define** the term Melt Flow Index (MFI) as applied to a thermoplastic polymer. **Name** two other parameters which could be calculated using MFI data in order to observe the low behavior of a material.

(06 marks)

Registration Number:.....

Name:.....

Address:.....

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THE OPEN UNIVERSITY OF SRI LANKA
B Sc Degree/ Stand Alone courses in Science
CMU3233 (Polymer Chemistry)
ASSIGNMENT TEST III (2015/2016)
Answer Guide

Part A

01) 4	02) 5	03) 2	04) 1	05) 3
06) 5	07) 1	08) 4	09) 3	10) 3

Part B

01. (a) i. $\bar{X}_n = \frac{1}{(1-p)}$ where $\bar{X}_n$ is the degree of polymerization, p is the percentage conversion

ii. $\bar{X}_n = \frac{1}{(1-p)}$ here, $\bar{X}_n = \frac{\bar{M}_n}{M}$ So, $\bar{X}_n = \frac{56{,}000 g/mol}{28 g/mol} = 2000$

$2000 = \frac{1}{(1-p)}$ So, p = 0.9995

Percentage conversion is **99.95%**.

(b) i. 1. To reduce the number of rate constants, the rates of reaction of the polymer radicals in the propagation steps are independent of their chain lengths.

2. Since there are intermediate products in the propagation step, rate of production of radicals in the initiation step is balanced by the rate of termination.

3. Several steps are involved in the propagation and each radical consume monomer for the production of next radical, the consumption of monomer in the initiation step is negligible compared to the consumption of monomer in the propagation steps.

4. The consumption of initiator remains constant since initiator is used as a catalyst and small amount is needed for the initiation.

ii. In free radical polymerization, X_f (Degree of polymerization) α [M] $[I_2]$
In anionic polymerization, X_a (Degree of polymerization) α [M] and α 1/transfer agent

So, $X_f > X_a$, that means molar mass formed by free radical polymerization is higher.

(c) i. $\bar{X}_n = \frac{1+r}{1+r-2rp}$ $\bar{X}_n$=degree of polymerization; R = stoichiometric ratio;

P = extend of reaction or percentage conversion of monomer

ii.

$\bar{X}_n = \frac{1+r}{1+r-2rp}$

here, $r = \frac{100\% \text{ of hexamethylene diammine}}{110\% \text{ of adipic acid}}$

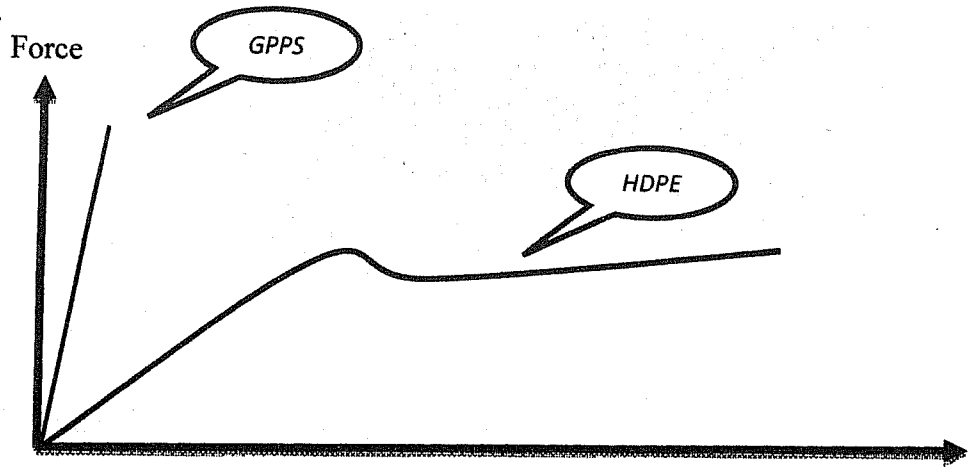
$\therefore r = \frac{100}{110} = 0.91$ and p = 0.95

$\bar{X}_n = \frac{1+0.91}{1+0.91-2\,(0.91)\,(0.95)}$

$= 10.61$

02.

(a) i.



ii. Calculate the slope of the initial straight line parts of the curve **and**
Elastic modulus = Slope X initial gauge length/ Cross sectional area **or**
Elastic modulus = Stress/Strain = (Force/area)/(Extension/Original length)
= (Force/Extension) X (Original length/area)
= Slope x Original length/area

iii. Calculate the slope from given data :
Slope = 50/0.046 = 1087 N/mm
Elastic modulus = Slope x Original length/area
= (1087 x100)/ (10x4) =**2717 MPa** (Units are important).
Assumption: Given force/extension values lies in the initial straight line part of the curve

iv. Tensile strength, Total elongation, Elongation at break, Yield point, Yield force, Extension at yield, Toughness, Force at break.

v. Temperature, Strain rate/ rate of loading, Previous loading history, Time length application of load.

b). i. $(T_g)_{AB}$ =Glass transition temperature of the binary copolymer (in K).
W_A and W_B are weight fractions of polymer A and B respectively.
$(T_g)_A$ and $(T_g)_B$ are glass transition temperatures (in kelvin) of individual polymers A and B respectively.

ii. Weight fraction of HDPE = 1/3
T_g of HDPE = -90+273 = 183 K

Weight fraction of PP = 2/3
T_g of PP = -15 + 273 =258 K

Substitute the values in the given equation and simplify.
The T_g of the copolymer **is 227 K or -46 °C**

c). i. Creep: Delayed strain response at **constant stress.**
Stress relaxation: Subsequent decay of stress at **constant strain.**

ii. **Mass** of a polymer in **grams** flowing in **10 minutes** time through a capillary of a given diameter and length under the influence of a **prescribed gravimetric pressure at specific temperature.**

Shear stress and shear rate are the other two parameters that can be calculated with MFI data.