



THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. DEGREE/STAND ALONE COURSES IN SCIENCE – LEVEL 5
FINAL EXAMINATION -2009/2010
CHU3238/CHE5238 – POLYMER CHEMISTRY – I
DURATION : THREE (03) HOURS

Date : 18th June 2010

Time : 9.30 a.m. 11.30 a.m.

- Answer all 50 questions
- Choose the most correct answer to each question and mark this answer with an "X" on the answer script
- Use a **PEN** (not a pencil) in answering.
- Any question with more than one answer will be counted as **incorrect answer**.
- **1/6th marks** will be deducted for each incorrect answer.
- The use of a **non-programmable** electronic calculator is permitted.
- Logarithm tables and graph paper will be provided.

Gas Constant (R)	=	8.314 JK ⁻¹ mol ⁻¹
Avogadro Constant (L)	=	6.023 x 10 ²³ mol ⁻¹
Planck Constant (h)	=	6.63 x 10 ⁻³⁴ Js
Velocity of light (C)	=	3.0 x 10 ⁸ ms ⁻¹
Atmospheric Pressure (π)	=	10 ⁵ Pa(Nm ⁻²)
Faraday constant (F)	=	96,500 C mol ⁻¹
Log _e (X)	=	2,303 log ₁₀ (X)

01. Which monomer can be easily polymerized by using KNH_2 as an initiator.
- $CH_2 = CH_2$
 - $CH_2 = C(CN)(COOC_2H_5)$
 - $CH_2 = CHCN$
 - $CH_2 = C(CH_3)_2$
 - $CH_2 = CHCl$
02. Polymers differ from simple organic molecules by not having fixed (definite)
- melting point
 - boiling point
 - dissolution
 - molar mass
 - all of the above
- What is the most probable answer?
03. Polymer physical properties are dependent on
- degree of crystallinity
 - amorphous nature
 - T_g
 - size
 - none of the above
- What is the irrelevant statement?
04. Molar mass of polyester during polymerisation can be controlled by mixing
- Acetic acid
 - Alcohol
 - Different ratios of the two monomers
 - Stoichiometric ratios of the monomers
 - inhibitor
- What is the wrong answer?
05. What is the most favourable mode of addition in the polymerisation of styrene by I^\cdot radical
- Head to Head
 - Head to tail
 - Tail to head
 - tail to tail
 - none of the above.
06. Name the probable mechanism involved in the termination process of the polymerisations of propylene by cationic initiator.
- combination
 - Disproportionation
 - Solvent transfer
 - Monomer transfer
 - rearrangement
07. Which of the following does not form polymer with toluene di isocyanate
- $HO - CH_2 - CH_2 - OH$
 - H_2O
 - CO_2
 - $(CH_2)_4 HOOC(CH_2)_4 COOH$
 - $H_2N - (CH_2)_6 - NH_2$

08. When 100 molecules of dimethyl terephthalate is condensed with equal number of glycol molecules, mass of the byproduct formed is
 i. 3168 ii. 1782 iii. 6368
 iv. 3568 v. 6000gm
09. When natural rubber is fully hydrogenated, the resulting polymer appears as
 i. random ethylene and isoprene
 ii. alternate ethylene and isoprene
 iii. alternate ethylene and propylene
 iv. block ethylene and propylene
 v. alternate copolymer ethylene and isoprene
10. Name the wrong observation, when a rigidform sample was exposed to sun light for a lengthy period.
 i. yellow discolouration ii. No colour change
 iii. molar mass change iv. Hardness change
 vi. solubility change
11. The most effective way of deteriorating tyre in service is by
 i. O_3 ii. $O_2 + \text{heat}$ iii. $O_2 + \text{light}$
 iv. $O_3 + \text{mechanical stress}$ v. $O_3 + \text{light}$
12. Which one is the most heat resistant polymer among the followings?
 i. $\left[O - CH_2 - CH_2 - O - C(=O) - \text{C}_6\text{H}_4 - C(=O) \right]_n$ ii. $\left(CH_2 - \overset{\text{OH}}{\underset{|}{CH}} \right)_n$
 iii. $\left(CH_2 - \overset{\text{Cl}}{\underset{|}{CH}} \right)_n$ iv. $\left(O - \text{C}_6\text{H}_4 - \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}} - \text{C}_6\text{H}_4 - O - C(=O) \right)_n$
 v. $\left(HN - (CH_2)_6 - NH - C(=O) - (CH_2)_4 - C(=O) \right)_n$
13. Which one is the most impact resistant polymer in Q 12?
 i. ii. iii. iv. or v.
14. Which polymer is insoluble in methyl ethyl ketone?
 i. phenol - formaldehyde resin
 ii. chloroform rubber
 iii. nitro cellulose
 iv. nitrile rubber
 v. natural rubber

15. A Crystalline and an amorphous polymer (same repeating unit) can be distinguished from each other by
- solubility
 - plasticizing effect
 - density
 - hardness
 - none of the above
- what is the wrong answer?
16. Polymer $\text{-(CH}_2\text{-}\underset{\text{X}}{\text{CH}}\text{)}_n$ has high T_g when X is
- OH
 - CN
 - C₆H₅
 - C₂H₅
 - Cl
17. Teflon $\text{-(CF}_2\text{-CF}_2\text{)}_n$ is used as a heat resistant coating material due to its
- inorganic nature
 - high fractional coefficient
 - helix structure arrangement
 - crystallinity
 - all of the above
- What is the most relevant statement?
18. Phthalates are used as plasticizers for PVC because they have
- high volatility
 - same polarity
 - similar density
 - similar solubility
 - lower volatility
- what is the wrong statement?
19. The volumes of five polyethylene samples of the same mass are given below.
- $\frac{10}{0.917}$
 - $\frac{10}{0.932}$
 - $\frac{10}{0.945}$
 - $\frac{10}{0.952}$
 - $\frac{10}{0.98}$
- Which sample has the lowest degree of crystallinity?
20. Assume combination as the only termination process in the polymersation of propylene ($\text{CH}_2 = \text{CH CH}_3$) and the kinetic chain length is x , the number average molar mass \overline{M}_n is
- 21x
 - 14x
 - 42x
 - 84x
 - 28x
21. If disproportionation is the prominent termination process in the polymerisation of ethylene and kinetic chain length is v , then \overline{M}_n is
- 14v
 - 9v
 - 28v
 - 56v
 - 42v

22. What is the wrong assumption stated in the derivation of rate equation for free radical polymensation is
- monomer concentration in the initiation step is negligible.
 - activity of all polymer radicals are equal
 - rate of initiation is equal to rate of termination.
 - Steady state assumption
 - Rate of initiation is equal to rate of propagation
23. Rate equation for cationic polymerisation is
- 1st order w. r. t. monomer concentration
 - 2nd order w.r.t. monomer concentration
 - 0th order w.r.t. monomer concentration
 - 1st order w.r.t. catalyst concentration
 - Is independent of catalyst concentration
- What is the correct statement?
24. A mixture of 3 different polymers formed when monomer $\text{CH}_2 = \text{CHX} - \text{CH} = \text{CH}_2$ is polymerized if X is
- H
 - CH_3
 - Cl
 - C_2H_5
 - OH
25. In butadiene polymensation syndiotactic polymer is produced by
- 1, 2 addition
 - 1, 4 addition
 - 1, 4 addition cis structure
 - 1,4 addition trans structure
 - None of the above
26. Which one of the following catalysts is most suitable to produce a living polymer from $\text{CH}_2 = \text{CH-CN}$
- benzoyl peroxide
 - $\text{Al}(\text{CH}_3)_3/\text{TiCl}_3$
 - $\text{BF}_3/\text{H}_2\text{O}$
 - HCl
 - KNH_2
27. Lowest activation energy complex is formed by
- rubber + sulphur
 - rubber + sulphur + accelerator
 - rubber + sulphur + accelerator + ZnO
 - rubber + sulphur + accelerator + ZnO + stearic acid
 - rubber + sulphur + accelerator + ZnO + antioxidant

28. Disadvantage of solution polymerisation is
 i. expensive process
 ii. results low molar mass
 iii. recovery of solvent is expensive
 iv. cannot be used as it is in application
 v. termination occurs through solvent transfer
 what is the wrong answer?
29. What is the percentage conversion of the monomer caprolactum required to produce nylon 6, its degree of polymerisation being 10,000?
 i. 99% ii. 99.90% iii. 99.990%
 iv. 99.9990% v. 99.91%
30. What is the molar mass (g/mol) of the polymer, if the % conversion is 99.90 in Q. 29?
 i. 11,300 ii. 113,000 iii. 22,600
 iv. 226,000 v. 5650
31. A polymer will dissolve in a given solvent at a given temperature if
 i. ΔH is +ve and $> T\Delta S$ (> greater than)
 ii. ΔH is -ve and $> T\Delta S$
 iii. $\Delta H = 0$
 iv. ΔH is +ve and less than $T\Delta S$
 v. ΔH is -ve and less than $T\Delta S$
 What is the wrong statement?
32. Exothermic nature of free radical polymerisation is due to conversion of
 i. σ to σ^* bond
 ii. σ to π bond
 iii. π to π bond
 iv. π to σ bond
 v. π to π^* bond
33. Number of NMR peaks possible for the polymer $-\text{CH}_2-\text{C}(\text{CH}_3)_2-$ is
 i. 1 ii. 2 iii. 3 iv. 4 v. zero
34. Number of vibrational degree of freedom in polystyrene is
 i. 0 ii. 21 iii. 42 iv. 6 v. 12
35. With the increase of molar mass and crystallinity
 i. elasticity increases
 ii. hardness increases
 iii. solubility decreases
 iv. heat resistivity decreases
 v. air permeability increases
 What is the incorrect statement?

36. Concentrated natural rubber latex
- contains 60% of dry rubber
 - stabilized by adding ammonia
 - is coagulated by adding Ca^{2+} ions
 - is coagulated by adding acetic acid
 - yellow colour is due to Mg^{2+} ions
- What is the wrong statement?
37. Field latex (natural rubber)
- iso-electric point is pH 4.5
 - is auto coagulated by bacteria
 - viscosity decreases due to presence of rubber bound aldehyde
 - can be concentrated by dichloro decantation process
 - Yellow color can be removed by bleaching
- What is the wrong statement?
38. Accelerators are used in rubber formation
- to reduce the vulcanizing time
 - to reduce the activation energy
 - to increase rate of vulcanisation
 - to form sulphur intermediate compounds.
 - to vulcanize at room temperature.
- What is the irrelevant statement?
39. Rate of vulcanization is increased
- by adding accelerator only
 - by adding ZnO only
 - by adding stearic acid only
 - by adding ZnO + stearic acid only.
 - by adding accelerator + ZnO + stearic acid
- What is the most correct answer?
40. The glass transition temperature of five different polymer samples are
- | | | |
|--------------------------|--------------------------|---------------------------|
| i. -10°C | ii. 20°C | iii. 27°C |
| iv. 35°C | v. 100°C | |
- What is the most flexible polymer?
41. Which one of the polymers in Q 40 has high modulus?
42. Five polymer samples A, B, C, D and E of density 0.90, 0.92, 0.95, 0.97, 0.99 respectively, when sudden cooled after melting, found to be having the same density. Which one of the above polymers has high elasticity?
- | | | | | |
|------|-------|--------|-------|------|
| i. A | ii. B | iii. C | iv. D | v. E |
|------|-------|--------|-------|------|

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43. Which one of the polymers in Q.42, has poor air permeability.
44. Polydispersity factor of five polymer samples of the same repeat unit are
 i. 3.5 ii. 3.0 iii. 4.0 iv. 2.0 v. 1.2
 Assuming \overline{M}_n of all the samples are the same; which one is having the highest \overline{M}_w ?
45. Highest polydispersity factor of the above Q 44 is the polymer synthesised by
 i. free radical emulsion polymerisation
 ii. free radical suspension polymerisation
 iii. free radical solution polymerisation
 iv. free radical bulk polymerisation
 v. condensation polymerisation
46. If \overline{M}_n is the molar mass of unvulcanised rubber after vulcanization,
 i. molar mass increases
 ii. viscosity increases
 iii. viscosity decreases
 iv. molar mass and viscosity decreases
 v. molar mass and viscosity increases.
 What is most relevant answer?
47. If \overline{M}_n is 10^5 g/mol and after vulcanization only disulphides are formed, then the molar mass of the rubber is
 i. 100032 ii. 100064 iii. 100016
 iv. 100048 v. 100096
48. What is the minimum quantity of pure phenol required to produce phenol - formaldehyde thermoset from 550 (g) of 40% formaldehyde?
 i. 94 ii. 47 iii. 141
 iv. 188 v. 160gm
49. Average molar mass of a polymer sample determined by light scattering is 27000 g/mol. If the polydispersity factor of the polymer sample is 1.8, what is the molar mass of the polymer determined by osmometry?
 i. 18000 ii. 15000 iii. 12000
 iv. 21000 v. 24000
50. Molar masses of five polymer samples determined by osmometry are
 i. 18000 ii. 15000 iii. 12000
 iv. 21000 v. 24000
 Assume molar masses of the polymer samples determined by light scattering is 27000 g/mol. Which of the above samples shows a narrow distribution curve?

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CHU3238/CHE5238 – POLYMER CHEMISTRY – II
DURATION : THREE (03) HOURS

Date : 18th June 2010

Time : 1.30 p.m. 4.30 p.m.

Gas Constant (R)	=	$8.314 \text{ JK}^{-1} \text{ mol}^{-1}$
Avogadro Constant (L)	=	$6.023 \times 10^{23} \text{ mol}^{-1}$
Planck Constant (h)	=	$6.63 \times 10^{-34} \text{ Js}$
Velocity of light (C)	=	$3.0 \times 10^8 \text{ ms}^{-1}$
Atmospheric Pressure (π)	=	$10^5 \text{ Pa (Nm}^{-2}\text{)}$
Faraday constant (F)	=	$96,500 \text{ C mol}^{-1}$
$\text{Log}_e(X)$	=	$2,303 \log_{10} (X)$

Instructions to candidates:

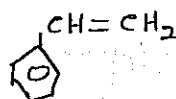
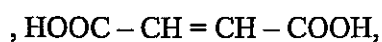
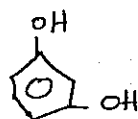
Answer any four questions out of six.

If more than four questions are answered only the first four answers will be marked.

The use of a non-programmable calculator is permitted.

01. a) What are the initiators used for the polymerization of following monomers?
 $\text{CH}_2 = \text{C}(\text{CH}_3)_2$, $\text{CH}_2 = \text{CH}(\text{CN})$, $\text{CH}_2 = \text{C}(\text{CN})(\text{COOC}_2\text{H}_5)$
- b) Give reasons for your selection.
- c) Write down the initiation step for each of the above monomers. Discuss the stability of first monomer radical formed.
- d) What are the main differences between free radical and cationic polymerization? Discuss with suitable examples.
- e) What are the advantages and disadvantages of bulk polymerization?
 (100 marks)

02. a) How many reactive sites are there in the following monomers?



Explain how to produce thermoset or thermoplastic polymers from the above three monomers separately with suitable chemicals.

- b) Write down one application for each of the thermosets or thermoplastics mentioned above.
- c) Name the catalyst used in the preparation of stereo regular poly propylene from propylene, $\text{CH}_2 = \text{CH} \text{CH}_3$
- d) Draw the structure responsible for crystallinity in polypropylene.
- e) Write brief notes on
 i. fillers ii. mechanical degradation
 iii. Ribbed smoked sheets

(100 marks)

03. a) Draw the structures of high density polyethylene and nylon 6,6. Which polymer is having more moisture absorbing property? Give reasons for your answer.
- b) i. Write down the basic principles involved in the oxidation of polymers.
 ii. What are the main factors which expedite the deterioration of polymers?

- c) Polypropylene is easily degraded by the atmosphere than polyethylene. Give reasons for this difference.
- d) What is storage hardening of field latex? Suggest methods adopted to overcome this problem.
- e) Explain why physical properties of cross linked polymers are different from their pre-polymers?

(100 marks)

- 04.
- a) What is glass transition temperature (T_g) of a polymer?
 - b) Describe a physical property used to determine T_g .
 - c)
 - i. Explain the effects of plasticizers mixing with polymers on T_g .
 - ii. What are the important properties to be considered in selecting a suitable plasticizer for a polymer?
 - d) A semi crystalline polymer sample of mass 5g was melted and by sudden cooling, it's volume was increased by 2%. When the same sample was fully crystallized, it's volume was decreased by 1%.
 - i. Calculate the degree of crystallinity.
 - ii. What are the assumptions used in the calculation?

(100 marks)

- 05.
- a) Four polymer molecules of molar masses 12,000; 24,000; 30,000 and 36,000 g/mol are mixed and their respective mole fractions in the sample are 0.2, 0.3, 0.4 and x.
 - i. Calculate \overline{M}_n and \overline{M}_w for the polymer sample. Derive all equations used in the calculation.
 - ii. Comment on the molar mass distribution curve.
 - b) Heat of dissolution (ΔH_{mixing}) is an important parameter governing solubility of polymers in solvent. Explain reasons for the above.

(100 marks)

06. a) A polyester of average molar mass of 192,000 g/mol was prepared by condensing equal concentrations of 2 mol/dm³ of phthalic anhydride and glycol (HO-CH₂-CH₂-OH) without a catalyst.
- i. How long the above reaction to be carried out to produce the required polyester.
Rate constant of the reaction is $3.5 \times 10^{-1} \text{ (mol/dm}^3\text{)}^{-2} \text{ s}^{-1}$ at mass of
C = 12.00 H = 1.00 O = 16.00
- b) If the molar ratio is changed to 1:1.05 (phthalic to glycol), what is the molar mass of the polyester? Assume same percentage conversion as in question a) i..
- c) Comment on the differences in molar mass when the molar ratios are changed from 1:1 to 1:1.05.
- (100 marks)

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