

2016

M.Sc. Part-II Examination

CHEMISTRY

PAPER—VIII

Full Marks : 75 / 100

Time : 3 / 4 Hours

The figures in the right-hand margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

{ Physical + Organic }

New Syllabus

F.M. - 100

Time : 4 Hrs.

Answer Q. No. 1 and any five from the rest.

1. Answer any ten questions :

10×2 $\frac{1}{2}$

- (i) State the differences between 'monomer' and 'mer' with suitable examples.

(Turn Over)

- (ii) Write down the structures of the repeat unit of the following polymers :
- (a) Polymethyl methacrylate.
- (b) Polyhexamethylenedipamide.
- (iii) Draw the specific volume (\bar{V}) vs. temperature (T) graphs for purely amorphous and crystalline polymers.
- (iv) Calculate the average functionality of a mixture of 1.95 moles of glycerol and 3.15 moles of adipic acid.
- (v) The number average degree of polymerisation (\bar{X}_n) of a sample of polystyrene is 800 ; calculate its number average molecular weight, \bar{M}_n .
- (vi) An absolute value of molecular weight cannot be assigned to any polymer mass. — Explain.
- (vii) Write down the names of two amorphous polymers, two crystalline polymers and a semicrystalline polymer.
- (viii) The simultaneous polymerisation of a mixture of two vinyl monomers does not always lead to the formation of a copolymer — Explain.

- (ix) Give examples of a fire resistant rubber, a solvent resistant rubber and a rubber having low gas permeability.
- (x) Show the structures of isotactic, syndiotactic and atactic polypropylene.
- (xi) Name the vulcanising agents used to vulcanise natural rubber, neoprene rubber and polyurethane rubber.
- (xii) Name two accelerators and one accelerator activator used in the compounding of rubber.
- (xiii) Name the monomers used to synthesize polycarbonates and write down the reaction between the monomers which lead to the synthesis of polycarbonate.
2. (a) Classify polymers on the basis of :
- (i) Origin ;
- (ii) Morphology ; and
- (iii) Line structure. 3×2
- (b) Discuss the following properties of polymers :
- (i) Molecular weight distribution and polydispersity index.

- (ii) Thermal transitions.
- (iii) Mechanical strength as a function of molecular weight. $2\frac{1}{2} + 2\frac{1}{2} + 2$
- (c) Account for the very high melt and solution viscosity of polymers. 2
3. (a) Write down the mechanism of free radical polymerisation of styrene (vinyl benzene) with azobisisobutyronitrile (AIBN) as initiator. 5
- (b) Write down the relationship between kinetic chain length $\bar{\nu}$ and number average degree of polymerisation (\bar{X}_n). 2
- (c) For a free radical polymerisation where termination takes place via normal bimolecular path and also through chain transfer reactions establish the Mayo equation. 6
- (d) State the differences in the nature of dead polymer molecules formed through coupling and through disproportionation. 2

4. (a) Write down the mechanism of cationic polymerisation of isobutylene with $\text{BF}_3\text{-H}_2\text{O}$ combination as initiator. 5
- (b) Deduce a mathematical expression showing the importance of stoichiometric imbalance of functional groups in controlling the molecular weight of polymer in condensation polymerisation. 6
- (c) Distinguish between addition and condensation polymerisation. 4
5. (a) Write down the expressions for weight average molecular weight, \bar{M}_w and viscosity average molecular weight, \bar{M}_v . Under what condition \bar{M}_w and \bar{M}_v become equal. 1+1+1
- (b) Write down the Mark-Houwink equation and explain the terms involved in the equation. 1+2
- (c) Ethylene glycol and adipic acid are polymerised in the molar ratio of 1.00 : 1.01. Calculate the number average degree of polymerisation (\bar{X}_n) of the polymer formed at the extent of reaction 0.8. 3

(d) Deduce a rate expression for the self-catalysed polyesterification reaction. 5

(e) Give an example of an inhibitor. 1

6. (a) Deduce the binary copolymer composition equation in terms of mole fractions of monomers in copolymer and monomer feed and monomer reactivity ratios. 10

(b) State three important differences between suspension and emulsion polymerisation. 3

(c) Write down the values of the product $r_1 r_2$ for the following copolymerisation processes :

(i) Ideal copolymerisation ; and

(ii) Alternate copolymerisation. 2

7. (a) What do you mean by compounding of rubber ? Write a short note on the principal additives of rubber. 2+8

(b) Discuss the important properties and uses of polychloroprene rubber. 4

(c) What is novolac ? 1

8. (a) Name the raw materials used to synthesize nylon 66. How are the monomers synthesized ? Describe the manufacturing process of nylon 66. 2+2+5

(b) Mention the important properties and uses of polyvinylchloride. 4

(c) Name two catalysts used to synthesize isotactic polypropylene. 2

9. Write short notes on any *three* of the following : 3×5

(a) Manufacture of styrene-butadiene rubber.

(b) Synthesis of a fibre forming polyester.

(c) Viscose rayon.

(d) Manufacture of smoked sheet rubber from natural rubber latex.

(e) Chlorosulfonated polyethylene (hypalon).

(f) Vulcanisation of rubber.

(g) Manufacture of novolac resin.

Old Syllabus

F.M. - 75

Time : 3 Hrs.

Answer any five questions.

1. (a) Discuss the following properties of polymers :
- Molecular weight distribution and polydispersity index. 2
 - Thermal transitions. $2\frac{1}{2} + 2\frac{1}{2}$
- (b) Distinguish between 'monomer' and 'mer' with suitable examples. 2
- (c) Classify polymers on the basis of : 3×2
- Origin ;
 - Morphology ; and
 - Line structure.
- (d) Account for the very high melt and solution viscosity of polymers. 2
2. (a) Discuss the mechanism of free radical polymerisation of styrene with benzoyl peroxide as the initiator. 5

- (b) Write down the relationship between kinetic chain length (ν) and number average degree of polymerisation (\bar{X}_n). 2
- (c) For a free radical polymerisation where termination takes place via normal bimolecular path and also through chain transfer reactions establish the Mayo equation. 6
- (d) State the differences in the nature of dead polymer molecules formed through coupling and through disproportionation. 2
3. (a) Write down the mechanism of cationic polymerisation of isobutylene with $\text{BF}_3\text{-H}_2\text{O}$ combination as initiator. 5
- (b) Deduce a mathematical expression showing the importance of stoichiometric imbalance of functional groups in controlling the molecular weight of polymer in condensation polymerisation. 6
- (c) Distinguish between addition and condensation polymerisation. 4

4. (a) Write down the expressions for weight average molecular weight, \bar{M}_w and viscosity average molecular weight, \bar{M}_v .
1+1
- (b) The number average degree of polymerisation (\bar{X}_n) of a sample of polystyrene is 700 ; calculate its number average molecular weight, (\bar{M}_n). 2
- (c) Calculate the average functionality of a mixture of 1.95 moles of glycerol and 3.15 moles of adipic acid. 2
- (d) Ethylene glycol and adipic acid are polymerised in the molar ratio of 1.00 : 1.01. Calculate the number average degree of polymerisation (\bar{X}_n) of the polymer formed at the extent of reaction (p) 0.8. 4
- (e) Deduce a rate expression for the self-catalysed polyesterification reaction. 5
5. (a) Derive the binary copolymer composition equation in terms of molefractions of monomers in copolymer and monomer feed and monomer reactivity ratios. 10

- (b) Write down the merits and demerits of emulsion polymerisation. 3
- (c) Draw the 'F₁' vs 'f₁' graphs for ideal copolymerisation. 2
6. (a) What do you mean by compounding of rubber ? Write a short note on the principal additives of rubber. 2+8
- (b) Discuss the important properties and uses of butyl rubber. 4
- (c) Name one accelerator used in the vulcanisation of rubber. 1
7. (a) Name the monomers used to synthesize nylon 66. How are the monomers prepared ? Describe the manufacturing process of nylon 66. 2+2+5
- (b) Compare the properties of isotactic and atactic polypropylene. 3
- (c) Name the monomers used to synthesize polycarbonates and write down the reaction between the monomers that lead to the formation of polycarbonate. 1+2

8. Write short notes on any *three* of the following : 3×5

(a) Manufacture of styrene-butadiene rubber.

(b) Carother's equation.

(c) Synthesis of a fibre forming polyester.

(d) Determination of viscosity average molecular weight

(\overline{M}_v) of polymers.

(e) Manufacture of smoked sheet rubber from natural rubber latex.

(f) Preparation and properties of viscose rayon.