

2021

CHEMISTRY — HONOURS

Paper: DSE-B-3
(Polymer Chemistry)

Full Marks : 50

The figures in the margin indicate full marks.

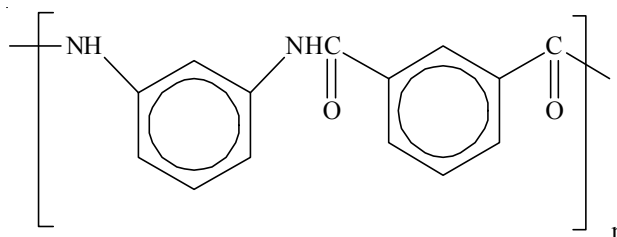
*Candidates are required to give their answers in their own words
as far as practicable.*

Answer **question no. 1** and **any eight** from the rest.

1. Answer **any ten** questions:

1×10

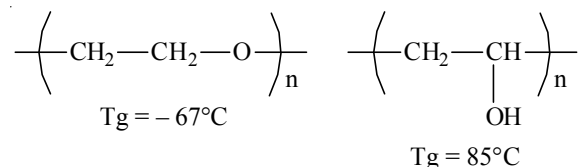
- (a) What will be the values of the reactivity ratios r_A and r_B of two monomers A and B respectively, so that they can form alternate copolymers?
- (b) What will be the degree of polymerization of a poly(methyl methacrylate) sample having number average molecular weight of $1,50,000 \text{ g mol}^{-1}$? (Show all calculations)
[Given: Chemical formula : $(\text{C}_5\text{H}_8\text{O}_2)_n$]
- (c) What is the functionality of allyl alcohol ($\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$) for condensation reaction with terephthalic acid? Explain.
- (d) Name the following condensation polymer according to the common nomenclature,



- (e) Which of the following polymers lacks the ability to exhibit tacticity?
- Polypropylene
 - Polystyrene
 - Polyisobutylene.
- (f) What is the solubility parameter of a polymer having cohesive energy density (E_{coh}) 43870 J mol^{-1} and molar volume (v) $136 \text{ cm}^3 \text{ mol}^{-1}$?

Please Turn Over

- (g) Which monomer is used in the synthesis of poly(vinyl alcohol)? Write down the corresponding reaction.
- (h) Find the rate of initiation (in mol L⁻¹S⁻¹) of a polymerization reaction using a peroxide initiator with a half life of 0.1sec and efficiency of 70%, if the concentration of the initiator is 0.05 mol L⁻¹.
- (i) Account for the differences in glass transition temperature for the following pair of isomeric polymer:

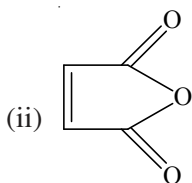
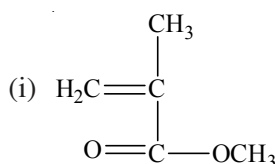


- (j) How can you express the specific viscosity of a polymer solution (η_{sp}) in terms of η and η_0 , where η represents the viscosity of polymer solution and η_0 represents the viscosity of pure solvent?
- (k) Which of the following monomers cannot be polymerized by anionic polymerization?
- Styrene
 - Ethyl Vinyl Ether
 - Butadiene
 - Methyl methacrylate.

Explain your answer.

- (l) What is the difference between an alternating copolymer and a block polymer?

2. (a) What is the functionality of the following monomers in reaction with adipic acid, HOOC(CH₂)₄COOH?

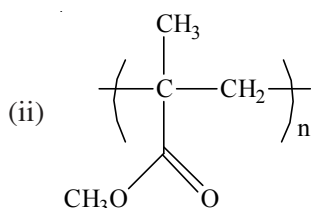
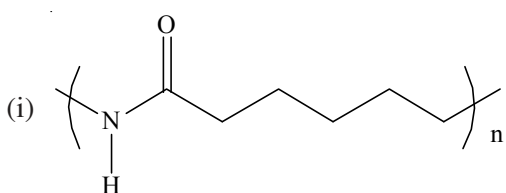


Explain your results.

- (b) Derive Carothers expression relating average functionality, extent of reaction and average degree of polymerization for polycondensation reaction carried out for a time period t. 2+3

3. (a) If a polymer sample contains an equal number of moles of species with degree of polymerization $x = 1, 2, 3, 4, 5, 6, 7, 8, 9$ and 10 . What are the number average and weight average degrees of polymerization?
- (b) Define degree of crystallinity of a polymer. Derive an equation relating the degree of crystallinity of a semicrystalline polymer to the sample density and densities of the crystalline and amorphous components. 2+3
4. (a) Discuss the effect of polymer molecular weight on the glass transition temperature.
- (b) In an externally added acid catalysed polyesterification, the conversion increased from 98% to 99% in 82 minutes. Calculate an estimate of time that was needed to reach the 98% conversion. Consider the reaction as acid catalysed polyesterification of a diacid and adiol. 2+3
5. (a) What is the polydispersity index of a polymer sample containing 200 molecules each of molecular weight $10,000 \text{ g mol}^{-1}$, 300 molecules each of molecular weight $30,000 \text{ g mol}^{-1}$ and 500 molecules each of molecular weight $50,000 \text{ g mol}^{-1}$?
- (b) How can you prepare polyurethanes commercially? Explain why the melting point of polyurethane is much less than that of the corresponding polyamide. 2+3
6. (a) How can you classify polymers on the basis of their,
- (i) Thermal response
- (ii) Tacticity?
- (b) Viscosity measurements were found for a set of PMMA solutions of different concentrations in toluene at 298K. The plot of reduced viscosity against concentration (c) of the PMMA solutions produced an intercept of $21.0 \text{ cm}^3 \text{ g}^{-1}$ on the ordinate at $c = 0$. What is the value of the viscosity average molecular weight of PMMA in toluene at 298K?
- Given: Mark-Houwink constant, $K = 7.5 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$ and $a = 0.72$ for PMMA in toluene at 298K. 2+3
7. (a) 1.0 g of a polybutadiene sample with carboxylic acid groups at both the ends requires 2.5 ml of 0.1 (M) KOH for complete neutralisation. What is the number average molecular weight of the polymer?
- (b) Explain the relationship between the following properties regarding the structure of the polymer:
- (i) Solubility
- (ii) Crystallinity
- (iii) Glass transition temperature. 2+3
8. (a) For the synthesis of polyester 1.5 mol of pentaerythritol (tetraol) was reacted with 1.0 mol of a tricarboxylic acid. What is the extent of reaction when the number average degree of polymerization approaches infinity?
- (b) What are polycarbonates? How can you prepare a polycarbonate using bisphenol-A with diphenylcarbonate? 2+3

9. (a) How can you prepare phenol-formaldehyde resins? Write down all necessary chemical reactions.
 (b) The glass transition temperature (T_g) of homopolymers A and B are $+100^\circ\text{C}$ and -70°C respectively. What is the T_g of a random copolymer of A and B having 40% weight of A and 60% weight of B?
 2+3
10. (a) Discuss various types of van der Waals interactions among polymer molecules.
 (b) Write down the overall scheme for free radical polymerization and hence show that the rate of polymerization depends directly on the monomer concentration and on the square root of the rate of initiation.
 2+3
11. (a) Write down the IUPAC nomenclature of the following polymers:



- (b) Explain the free volume theory in connection with the glass transition temperature of a polymer. Write down the WLF equation explaining the terms involved.
 2+3
12. Derive the following expressions for the entropy of mixing of a polymer solution when n_2 moles of polymer is added to n_1 moles of a solvent, using Flory-Huggins Model:

$$\Delta S_{\text{mix}} = -R[n_1 \ln \Phi_1 + n_2 \ln \Phi_2]$$
 where Φ_1 and Φ_2 are the volume fractions of the solvent and polymer respectively.
 5

13. (a) Which among the following are used as initiators for free radical polymerization?
 (i) K_2SO_4
 (ii) $\text{K}_2\text{S}_2\text{O}_8$
 (iii) 2, 2'-azo-bis-isobutyronitrile (AIBN)
 (iv) t-Butyl hydroperoxide + Fe^{2+}

Explain your answer.

- (b) Explain the concept of Glass transition temperature (T_g) and the melting temperature (T_m) using the temperature variation of specific volume of an amorphous, a semicrystalline and a crystalline polymer.
 2+3