Samples questions on 'Polymer Chemistry'

Symbols carry usual meanings

Module 1: Lecture 1 - 3

1. For a *polydisperse* polymer sample rank the M_n, M_w, M_z, and M_v according to their values.

   In 10 g of a polystyrene sample (*Mn* 30,000; *Mw* 60,000), you add 1 g of a mono-disperse polystyrene sample of (i) $M_w = M_n = 10,000$ (ii) $M_w = M_n = 30,000$ (iii) $M_w = M_n = 45,000$ (iv) $M_w = M_n = 60,000$ (v) $M_w = M_n = 80,000$. What would be the M_w and M_n for new mixed samples – lower or higher than the first sample? Between M_w and M_n which one will change more (in terms of %)?

2. A 1 L of polymer solution contains 10 g of a polymer. A non-solvent was added to the solution in steps and different fractions of polymer samples were precipited out in each step of non-solvent addition. The polymer fractions were washed, dried, weighed, and subjected to M_n determination. Assuming that for each fraction $M_n = M_w$ calculate the M_n, M_w, and PDI of the original polymer sample that was dissolved at the beginning.

Fraction No.	Weight (g)	M_n (= M_w) (g mol^{-1})
1	1.0	2,000
2	5.0	20,000
3	20.0	50,000
4	5.0	100,000
5	1.0	500,000

3. What is the no. average degree of polymerization (DP) of each of the following polymers with M_n 254,000?
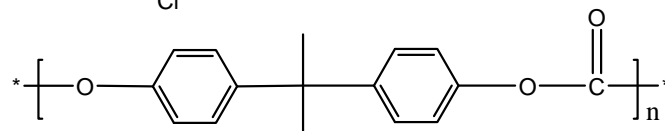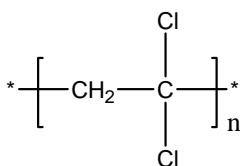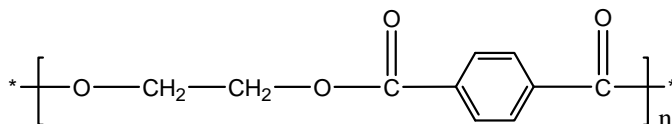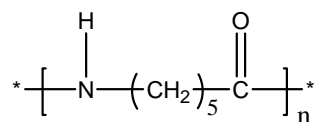
4. Draw the repeat unit of the polymer that would be obtained in the polymerization of the following monomers. Also write names of the following polymers and classify them whether they are condensation or addition polymers, formed by chain or step or ring opening polymerization.
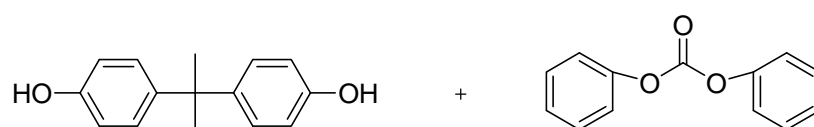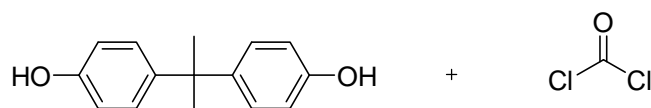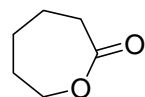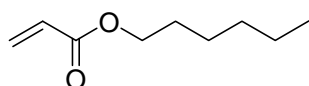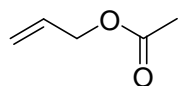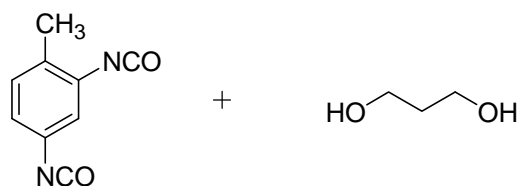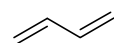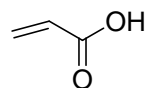
5. In 10 g of a polystyrene sample (M_n 30,000; M_w 60,000), you add 1 g of polystyrene sample with (i) M_n 20,000, PDI=2; (ii) M_n 40,000, PDI=2. Will the % change, (+ve or –ve), of M_w and M_n be same in (i) or (ii)? Justify your answer.

6. Write characteristics of *chain growth* and *step growth* polymerization with respect to the following features if the reaction is stopped before completion (say at 80% Conversion) – (i) MW as a function of conversion (show schematically); (ii) Composition of reaction medium.

7. Given A and B are two monomers, write generic structures of Random, Alternating, Block, Graft, Start copolymers.

8. Draw schematically how the stress vs. strain plots would look like for following polymer samples when the stress is applied in the longitudinal direction – fibre, flexible plastics, rigid plastics, and elastomers.

Module 2: Lecture 4 - 8

9. Calculate the Mn of a mixture of adipic acid and hexamethylene diamine for extent of reaction (p) of 0.995. Molar ratio of adipic acid to hexamethylene diamine taken in the feed is 0.95 : 1.0. Assume no side reactions.

10. The following data were obtained during externally catalyzed condensation of 12-hydroxyl stearic acid (MW ~ 300) at 433.5 K. [COOH] was determined for each sample by titrating with ethanolic sodium hydroxide. How long it would take to build a Mn of 30000?

t (h)	[COOH] (mol dm^{-3}]
0	3.10
2.0	0.48
3.0	0.34

11. A high molecular weight copolyester was synthesized by reacting the two diacids with a diol. The composition of the monomer mixture was HOOC-R^1-COOH **:** HOOC-R^2-COOH **:** HO-R-OH = 1 **:** 1 **:** 2 (by mole); reactivity of R^1-COOH group towards R-OH is higher compare to the reactivity of R^2-COOH group towards R-OH. Estimate the composition (mole ratio) of R^1, R^2, R in the final copolymer? Justify your answer in brief by assuming that it has the most probable distribution of molar mass.

12. Everything else remaining same, in which of the following two cases the chances of forming *cyclic products* is more for a *step-growth polymerization* process: – conc. of monomer is 2 M, and 0.5 M. Explain briefly.

13. Show that the time required for reaching p = 0.98 to p = 0.99 is very close to the time to reach p = 0.98 from the start of polymerization for the external acid-catalyzed polymerization of an equimolar mixture of a diol and a diacid. (p is the fraction of functional group reacted in the polymerization).

14. A polyamide was prepared by bulk polymerization of hexamethylene diamine (11.525 g) with adipic acid (14.6 g) at 300 °C. Analysis of the whole reaction product showed that it contained 2.0×10^{-3} mol of carboxylic acid groups. Evaluate the number-average molar mass, M_n, of the polyamide, and also estimate its weight-average molar mass, M_w, by assuming that it has the most probable distribution of molar mass.

15. When an equilibrium step- growth polymerization is 99% complete what fraction of the reaction mixture is still monomer? (a) on a mole basis? (b) on a weight basis?

16. In the polymerization of $H_2N(CH_2)_5COOH$ to form Nylon-6, what weight fraction of the reaction mixture has the following structure when 99% of the functional groups have reacted?
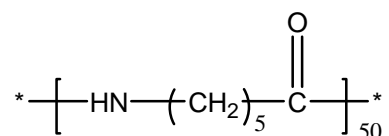
17. Can the following polyester recipe be carried to "complete" conversion without gelling?

    Pentaerythritol (1.2 mol), phthalic anhydride (0.5 mol) and tricarballyic acid (0.49 mol).

18. When caprolactam is polymerized into 6-nylon, 5 wt. % of the monomer is left unchanged, and remaining 95 % is converted to polymer having the Flory distribution of molecular weight and $X_w = 500$. Later the mixture was extracted by that removed all species up through that with x = 5. Calculate X_n for the following:

    a.   The polymer with $X_w = 600$.
    b.   The mixture of 10 % monomer and 90 % polymer.

19. Discuss the possibility of cyclization in the polymerization of

$$H_2N-(CH_2)_n-COOH$$

$$HOOC-(CH_2)_n-COOH \quad + \quad HO-(CH_2)_2-OH$$
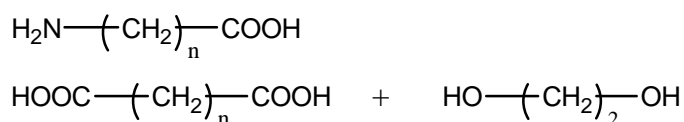
    For the cases where n has values from 2 to 12? At what stage(s) in the reaction is cyclization possible? What factors determine whether cyclization or linear polymerization is the predominant reaction?

20. For each of the following reactions system indicate whether the product is a linear, branched, cross-linked, or hyper branched polymer.

    a. $A_2 + B_2$ b. AB_2 c. AB_3 d. $A_2 + B3$ e. $AB_2 + B_3$ f. $AB + B_3$

21. The polymerization between equimolar amounts of a di-ol and di-acid proceeds with an equilibrium constant of 100. What will be the expected degree of polymerization and extent of reaction if the reaction is carried out in a closed system without removal of by-product water? To what level must $[H_2O]$ be lowered in order to obtain a degree of polymerization of 100 if the initial concentration of carboxyl groups is 1 M?

Module 3: Lecture 9 - 16

22. For a monomer of general structure $CH_2=CHX$, complete the following table. Put '+' if the monomer can be polymerized by the method mentioned at the top of the column, and '-' if polymerization by the method is not feasible. Briefly justify your answer.

X	Free radical	Anionic	Cationic
-CN			
-Ph			
-OCH$_3$			
-OCOCH$_3$			

23. Derive an expression for the rate of polymerization in a radical polymerization reaction. Assume steady state, termination of reaction is only by bimolecular reaction between propagating species, equal reactivity of different propagating chains.

24. A typical *radical polymerization* is being carried out with the following assumptions: initiation by thermal dissociation of initiator, steady state and equal reactivity of propagating radicals, termination of reaction is only by bimolecular coupling, and no chain transfer. What will happen to the polymer MW and Rp if one increases: (i) initiator conc. (ii) monomer conc. Justify your answer.

25. Arrange in increasing order of Xn of polymers obtained by polymerization of styrene initiated by thermal decomposition of benzoyl peroxide at 80°C in the following solvents – benzene, 1-butanethiol, isopropylbenzene, carbon tetrachloride. Assume chain transfer only to solvent. Briefly explain your answer.

26. Assuming that in free radical polymerization the rate constant can be replaced by the appropriate Arrhenius expressions:

$K_d = A_d \exp(-E_d/\mathbf{R}T)$; $K_p = A_p \exp(-E_p/\mathbf{R}T)$; $K_t = A_t \exp(-E_t/\mathbf{R}T)$

Calculate the changes in the rate of polymerization and the degree of polymerization caused by increasing the temperature of polymerization of styrene in benzene initiated by AIBN from 60°C to 70 °C given that: $E_p = 34$ kJ mol^{-1}; $E_t = 10$ kJ mol^{-1}; $E_d = 126$ kJ mol^{-1}. State any assumption made by you.

27. Mention two advantages and two disadvantages of solution polymerization over bulk polymerization.

28. Write the main ingredients required in an *emulsion polymerization*. Mention one disadvantage and one advantage of *emulsion* polymerization over *dispersion* polymerization. How can one increase Rp without compromising on molecular weight in an *emulsion* polymerization?

29. Explain briefly "*autoacceleration*" in *radical* polymerization? Why does it happen?

30. Write the constitutional isomers of polyisoprene possible when it is synthesized from isoprene by radical chain polymerization process. Comment on the relative proportion of these isomers at the end of polymerization reaction done at various temperatures.

31. In a typical free-radical polymerization rank the following according to their values –

    (a) R_i, R_p, R_t

    (b) k_d, k_p, k_t

32. Styrene was polymerized by heating to 100 °C (self initiated). Styrene was taken from four different bottles for four reactions. The following data were obtained from the experiments. Comment on the difference in the monomer bottles. Assume all other conditions remained same.
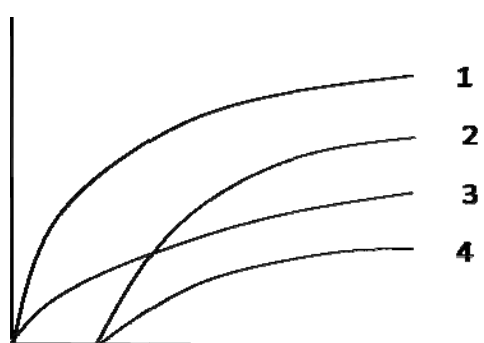
Module 4: Lecture 17 - 24

33. Define of living polymerization. Mention two benefits of living polymerization in general over conventional non-living polymerizations. Mention two techniques of living radical polymerization. Give an example of block copolymer that is usually synthesized by living anionic polymerization.

34. Show the possible propagation steps of polymerization of styrene initiated by Na + naphthalene.

35. Mention two possible termination steps of polymerization of isobutylene by initiating system $BF_3 + H_2O$.

36. A *living anionic polymerization* (without any side reaction) of 1 M acrylonitrile was initiated by 0.01M C_4H_9Li (butyl lithium). After all the acrylonitrile was polymerized, 1 M methylmethacrylate (MMA) was added maintaining the perfect inert atmosphere. When all the MMA was consumed, little amount of water added to quench the living chain ends. (i) Write the structure of the final polymer produced including the end groups. (ii) What is the Mn of the final polymer?

37. How are *ionic chain polymerizations* different to *radical chain polymerization* in regard to solvent polarity and inherent termination steps?

38. Write three mechanistic features for propagation step in Ziegler-Natta polymerization.

39. Consider the following *reactivity ratios* for the copolymerization of three monomer pairs:

Case	r_1 (for M_1)	r_2 (for M_1)
(i)	0.0	0.0
(ii)	2.0	0.5
(ii)	0.7	0.3
(iv)	1.0	1.0

Specify the *type of copolymer (random/alt/block)*. Which of the two *monomers* (M_1 or M_2) would be present in higher mole fraction in each case? Assume polymer sample is isolated at low conversion, feed ratio of $M_1:M_2$ =1:1.

40. Show the possible stereochemical forms of polymers derived from monomers of the type $CH_2=CXY$. Mention in which condition it is possible to synthesize these different stereochemical forms.

41. Write the chemical structure and names of the polymers produced by ring-opening polymerization of the following monomers –
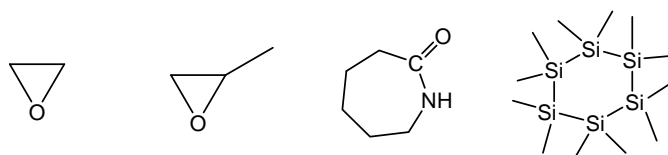
Discuss the effect of ring size on the tendency of a cyclic monomer toward ring-opening polymerization.

Module 5: Lecture 25 - 30

42. Write the expressions of root-mean-square end-to-end distance for a volumeless polymer chain in the following cases – a) freely-jointed and freely-rotated; b) with restrictions in both bond angle and rotation around single bond; c) free-jointed but restricted rotation.

Also write the expression for case b) when polymer chain is a true chain with definite volume (this is case d). Rank the values of rms end-to end distance for the above four cases.

Mention two conditions when the values in cases b) and d) become equal.

43. In reference to above question, how will the magnitude of (c) differ (more/less/equal) from (b) in following cases: pure amorphous polymer; polymer in a good solvent; polymer in a theta solvent; polymer in a non-solvent.

44. For the same polymer chain what would happen to the value of contour length, $<r^2>_o^{1/2}$ and $<r^2>^{1/2}$ on increasing the temperature assuming all other parameters remain same. Explain your answer in brief.

45. Why do we need to add an expansion factor over unperturbed dimension to get a true dimension of polymer chain?

46. Write the Flory-Huggins equation for Gibbs free energy of mixing of a polymer solution describing all the terms. Write two limitations of this with brief explanation.

47. From Flory-Huggins equation it can be shown that for the formation of a solution from a monodisperse polymer the partial molar Gibbs free energy of mixing, $\overline{\Delta G_1}$ for solvent is given by

$$\overline{\Delta G_1} = RT \left[\ln(1 - \phi_2) + (1 - \frac{1}{r})\phi_2 + \chi\phi_2^2 \right]$$

where ϕ_2 is the volume fraction of polymer, r is the ratio of the molar volume of the polymer to that of the solvent, and χ is the polymer-solvent interaction parameter. Show that the solution behaves like an ideal solution when the value of χ equals to 0.5.

48. Explain why thermodynamically it is always difficult to form miscible blends of two high molecular weight polymers. In what condition do two high molecular weight polymers become miscible?

49. A dilute polymer solution obeys Einstein equation for non-draining polymers. Derive Mark-Houwink equation from this.

50. Write Mark-Houwink expression. How can you determine MW of an unknown polymer sample using this equation?

51. In a single sentence define binodal compositions. On slowly adding a non-solvent to a polymer solution which fraction of the polymer sample precipitates first and why?

52. I have taken a 10% solution of a polymer and on decreasing the temperature of the solution the polymer precipitated at 15 °C, can you call 15 °C is the UCST of the polymer in that solvent?

53. What are LCST and UCST? For which type of polymer LCST and UCST exists. Explain with the help of thermodynamic parameters. Give example of one polymer in each case.

54. Two different polymers having high molecular weight were mixed and they were found to form a miscible blend. Which is more likely to be observed for this system - LCST or UCST and why?

55. What is solubility parameter? How this is determined for small organic molecules and polymers.

Module 6: Lecture 31- 34

56. Complete the table with respect to the MW obtained by the following techniques of measurement -

Technique	Absolute or Relative	M_w or M_n or M_v or M_z	Comment of applicability range
Viscosity			
GPC			
Light scattering			
Osmotic pressure			
End group by NMR			

57. State the methods you would use to determine - a) M_n for samples of PEG with values in the range of 4×10^2 to 5×10^3 g mol^{-1}, b) M_n for samples of PAN with values in the range of 5×10^4 to 2×10^5 g mol^{-1}, c) the polydispersity indices of samples of PS with molar masses in the range 10^4 to 10^6 g mol^{-1}. For each method, give the reasons for your choice, and discuss briefly possible errors in the determinations.

58. Osmotic pressure (Π) of solutions containing different concentration (c) a polymer was measured. Π/c was found to be independent of c. What would happen to the solution(s) if you add another solvent to it where the added solvent is a non-solvent for the polymer? Explain your answer in brief.

59. For a polydisperse sample, show that measurement of any colligative property would give information about M_n.

60. Explain why the value of ΔR_θ for polymer solutions depends on θ? Two polymers have same Mw but they have different shapes – Coil and rod. Will the light scattering intensity at 45° be different for the solutions containing same concentration of the two polymers?

61. You are provided with a polymer sample, a solvent for the polymer, a balance, and a multi-angle laser light scattering instrument. Describe the steps you will take to construct Zimm Plot. (Values of n_0, dn/dc, and other instrument parameters are also provided). From the Zimm Plot what are the information you can get about the polymer, polymer/solvent system and how?

62. What is the principal behind gel permeation chromatography? What are the types of detector can be use to detect polymer concentration at the end a GPC run – give two example.

63. You are given three mono-disperse polystyrene sample of same M_W (as determined by light scattering) but of different shape viz. Coil, Rod, Sphere. If these three samples are passed through GPC column under same experimental condition (column, solvent, temperature, flow-rate, detector position) what would the order of elution? Justify your answer.

64. How would intrinsic viscosity change (decrease or increase) in following cases - a) increase chain length (MW) of linear molecule, b) increase mass of chain segments, keeping chain length constant, c) increase stiffness of chain, d) add branches to chain keeping MW constant.

65. You have synthesized a polymer by chain growth mechanism and subsequently submitted for molecular weight determination. You have been provided with the following report – i) M_n measured by light scattering method is 55,000 g/mol; ii) M_n and M_w measured by GPC are 95,000 g/mol and 55,000 g/mol respectively. Identify the error(s) in the report i) and ii).

66. Why M_v measured by viscosity method is not an absolute molecular weight?

67. Why polymers made by step-growth mechanism are usually not used as GPC standard?

68. The table below gives the mean flow times (t) in a suspended-level viscometer recorded for solutions of one of the five monodisperse samples of polystyrene (sample B) at various concentrations (c) in cyclohexane at 40 °C. Under these conditions, the mean flow time (t_0) for cyclohexane is 150.0 s.

| Concentration $\times 10^3$ (g cm^{-3})	Time (s)
1.59	158.5
5.55	178.6
7.40	189.6
8.88	199.5

Determine the intrinsic viscosity of the sample. The intrinsic viscosities of the other three polystyrene samples were evaluated under the same conditions and are given in the following table together with their Mw values determined by light scattering.

Sample	Mw (g mol^{-1})	[η] (cm^3 g^{-1})
A	370,00	15.8
B	102,000	-
C	269,000	42.6
D	690,000	68.1

Using these data together with the calculated values of intrinsic viscosity of sample B, evaluate the constants of the Mark-Houwink equation for polystyrene in cyclohexane at 40 °C.

69. The chemical structure of a copolymer is given below. Quantitative ^{1}H and ^{13}C NMR spectra are available for the copolymer. How can you use the NMR spectra to derive at the following information about the copolymer: Composition of the two monomers in the copolymer (x:y); nature of the copolymer (alt/ran/block), and value of n.
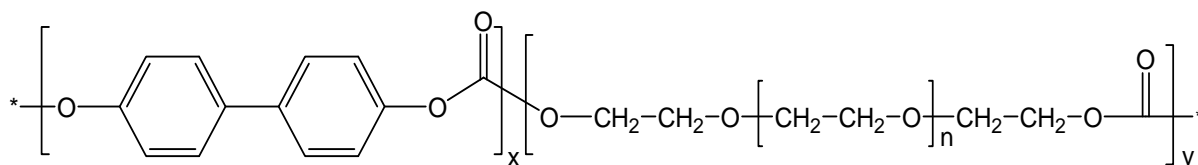

Module 6: Lecture 35 - 41

70. A polymer is being cooled from a temperature above T_m to a temperature below T_m. What are the possible states possible just below the T_m – a) 100% crystalline solid; b) polymer remains in melt form; c) part of it is melt and part is crystalline solid. Explain your answer in brief.

71. The RMS end-to-end distance of three polymers in their respective theta solvent follows the following order PolyA > PolyB > PolyC. Assuming that solubility parameters of the polymers are similar what could be the possible rank of the three polymers according to their T_g. Explain your answer in brief.

72. Same number of moles of two monomers (A and B) was mixed and polymerized and the product was analysed after completion of reaction. Two Tg was obtained for the reaction product. Which ones from the below cases are feasible – a) immiscible blend of Poly A +

Poly B, b) Poly A - *block* - Poly B, c) miscible blend of Poly A + Poly B, d) poly (A-*ran*-B), poly(A-*alt*-B)

73. Draw schematically modulus (or logarithm of it) vs. temperature curve to show the four (or five) different regions of viscoelasticity that an amorphous polymer experience when heated from a temperature below T_g.

74. What are two main factors which helps crystallization of polymers? Briefly explain.

75. A copolymer was synthesized by reacting equimolar mixture of monomer A (mol. weight. 100 g/mol) and monomer B (mol. wt. 150g/mol). The T_g s of homopolymers of A and B are 100 °C and 200 °C respectively. What would be the T_g of the copolymer if it was a) a completely random copolymer and b) a pure block copolymer.

76. Which of the polymers in each pair is expected to have higher T_g and why?

 (i) polyethylene and polypropylene, (ii) poly(but-1-ene) and poly(but-2-ene),

 (iii)

$R = -CH_3$ and $R = -CH_2CH_2CH_3$
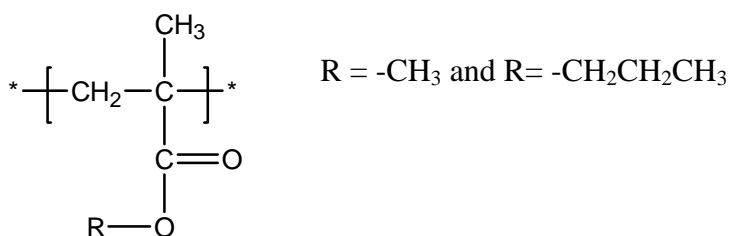
77. Draw schematically stress-strain curve(s) to show the following – elastic elongation, tensile strength, yield stress, ultimate strength, elongation at break, toughness.

78. State some of the mechanisms with examples by which additives work as fire retardant in polymer.