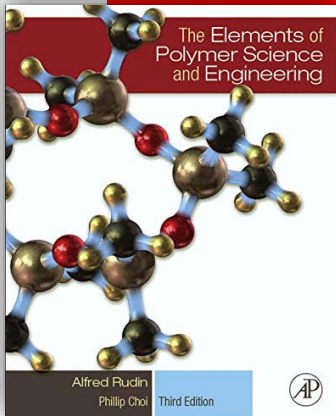


Montogue



Quiz MST02

Reviewed Solutions to *The Elements of Polymer Science and Engineering, 3rd Ed.*, by Rudin and Choi

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PROBLEM DISTRIBUTION

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PROBLEMS

■ Chapter 2 – Basic Principles of Polymer Molecular Weights

Problem 2.1 (2nd edition: 2.1)

If equal weights of polymer A and polymer B are mixed, calculate the weight-average molecular weight \bar{M}_w and the number-average molecular weight \bar{M}_n of the mixture.

Polymer A	$\bar{M}_n = 35,000$	$\bar{M}_w = 90,000$
Polymer B	$\bar{M}_n = 150,000$	$\bar{M}_w = 300,000$

Problem 2.2 (2nd edition: 2.2)

Calcium stearate ($\text{Ca}(\text{OOC}(\text{CH}_2)_{16}\text{CH}_3)_2$) is sometimes used as a lubricant in the processing of poly(vinyl chloride). A sample of PVC compound containing 2 wt% calcium stearate was found to have $\bar{M}_n = 25,000$. What is \bar{M}_n of the balance of the PVC compound?

Problem 2.3 (2nd edition: 2.3)

If equal weights of “monodisperse” polymers with molecular weights of 5000 and 50,000 are mixed, what is \bar{M}_z of the mixture?

Problem 2.4 (2nd edition: 2.4)

Calculate the number-average molecular weight \bar{M}_n and the weight-average molecular weight \bar{M}_w for a sample of polystyrene with the following composition (i = degree of polymerization; % is by weight). Calculate the variance of the number distribution of molecular weights.

i	20	25	30	35	40	45	50	60	80	>80
wt%	30	20	15	11	8	6	4	3	3	0

Problem 2.6 (Not on 2nd edition)

Given that homopolymers formed by the following monomers (a – e) have the molecular mass distribution shown to the side, Calculate the number average molecular weight \bar{M}_n and the corresponding degree of polymerization of each polymer.

w_i	M_i
0.05	10,000
0.25	50,000
0.20	80,000
0.20	100,000
0.15	150,000
0.10	200,000
0.05	500,000

- (a) $\text{CH}_2=\text{CH}(\text{CH}_3)$
- (b) $\text{CH}_2=\text{CHCl}$
- (c) $\text{CF}_2=\text{CF}_2$
- (d) $\text{CH}_2=\text{CH}(\text{OH})$
- (e) $\text{CH}_2=\text{CH}_2$

Problem 2.7 (Not on 2nd edition)

If 200 g of polymer A, 300 g of polymer B, 500 g of polymer C, and 100 g of polymer D are mixed, calculate the number-average molecular weight \bar{M}_n and the weight-average molecular weight \bar{M}_w of the blend.

- Polymer A: $M_n = 45,000$; $M_w = 65,000$
- Polymer B: $M_n = 100,000$; $M_w = 200,000$
- Polymer C: $M_n = 80,000$; $M_w = 85,000$
- Polymer D: $M_n = 300,000$; $M_w = 900,000$

What are the polydispersity index and the standard deviation of the number distribution of molecular weight of the mixture?

Problem 2.11 (2nd edition: 2.8)

The degree of polymerization of a certain oligomer sample is described by the distribution function

$$w_i = K(i^3 - i^2 + 1)$$

where w_i is the weight fraction of polymer with degree of polymerization i and i can take any value between 1 and 10, inclusively.

- (a) Calculate the number average degree of polymerization.
- (b) What is the standard deviation of the weight distribution?
- (c) Calculate the z average degree of polymerization.
- (d) If the formula weight of the repeating unit in this oligomer is $100 \text{ g}\cdot\text{mol}^{-1}$, what is \bar{M}_z of the polymer?

Chapter 3 – Practical Aspects of Molecular Weight Measurements

Problem 3.1 (2nd edition: 3.1)

Two “monodisperse” polystyrenes are mixed in equal quantities by weight. One polymer has a molecular weight of 39,000 and the other has a molecular weight of 292,000. What is the intrinsic viscosity of the blend in benzene at 25°C? The Mark-Houwink-Sakurada constants for polystyrene/benzene are $K = 9.18 \times 10^{-5} \text{ dL/g}$ and $a = 0.74$.

Problem 3.2 (2nd edition: 3.2)

The following are data from osmotic pressure measurements on a solution of a polyester in chloroform (HCCl_3) at 20°C. The results are in terms of centimeters of solvent. The density of chloroform is $1.48 \text{ g}\cdot\text{cm}^{-3}$. Find \bar{M}_n .

Concentration (g/dL)	h (cm HCCl_3)
0.57	2.829
0.28	1.008
0.17	0.521
0.10	0.275

Problem 3.5 (2nd edition: 3.3)

The relative flow times (t/t_0) of a poly(methyl methacrylate) polymer in chloroform are given below.

- (a) Determine $[\eta]$ by plotting η_{sp}/c and η_{inh} against c .
- (b) Find \bar{M}_v for this polymer, given $[\eta] = 3.4 \times 10^{-5} \bar{M}_v^{0.80} \text{ (dL/g)}$.

Concentration (g/dL)	t/t_0
0.20	1.290
0.40	1.632
0.60	2.026

Problem 3.7 (2nd edition: 3.5)

A polymer with true molecular weight averages $\bar{M}_n = 430,000$ and $\bar{M}_w = 1,000,000$ is contaminated with 3% by weight of an impurity with molecular weight 30,000. What effects does this contamination have on the average molecular weights determined by light scattering and membrane osmometry?

Problem 3.8 (2nd edition: 3.6)

Polyisobutene A has a molecular weight around 3000 and polyisobutene B has a molecular weight around 700,000. Which techniques would be best for direct measurement of \bar{M}_n and \bar{M}_w of each sample?

Problem 3.10 (3rd edition: 3.8)

What molecular weight measurement methods could be used practically to determine the following?

(a) \bar{M}_n of a soluble polymer from a reaction of glycol, phthalic anhydride, and acetic acid. The approximate molecular weight of this sample is known to be about 1200.

(b) \bar{M}_w of a polystyrene with molecular weight about 500,000.

(c) \bar{M}_n of high-molecular-weight styrene-methyl methacrylate copolymer with uncertain styrene content.

Problem 3.11 (3rd edition: 3.9)

In an ideal membrane osmometry experiment, a plot of π/cRT against c is a straight line with intercept $1/M$. Similarly, an ideal light-scattering experiment at zero viewing angle yields a straight line plot of Hc/τ against c with intercept $1/M$. For a given polymer sample, solvent, and temperature,

(a) Are the M values the same from osmometry and light scattering?

(b) Are the slopes of the straight-line plots the same? Explain your answer briefly.

Problem 3.13 (3rd edition: 3.11)

A dilute polymer has a turbidity of 0.0100 cm^{-1} . Assuming that the solute molecules are small compared to the wavelength of the incident light, calculate the ratio of the scattered to incident light intensities at a 90° angle to the incident beam and 20 cm from 2 mL of solution. Assume that all the solution is irradiated.

Problem 3.14 (3rd edition: 3.12)

Solution viscosities for a particular polymer and solvent are plotted in the form $(\eta - \eta_0)/(c\eta_0)$ against c where η is the viscosity of a solution of polymer with concentration $c \text{ g}\cdot\text{cm}^{-3}$ and η_0 is the solvent viscosity. The plot is a straight line with an intercept of $1.50 \text{ cm}^3\cdot\text{g}^{-1}$ and a slope of $0.9 \text{ cm}^6\cdot\text{g}^{-2}$. Give the magnitude and units of Huggins's constant for this polymer-solvent pair.

Chapter 4 – Mechanical Properties of Polymer Solids and Liquids**Problem 4.3 (2nd edition: 11.10)**

(a) Calculate the fraction of crystallinity of polyethylene samples with densities at 20°C of 926, 940, and 955 kg/m^3 . Take the specific volume of crystalline polyethylene as $0.989 \times 10^{-3} \text{ m}^3/\text{kg}$ and that of amorphous polyethylene as $1.160 \times 10^{-3} \text{ m}^3/\text{kg}$.

(b) What assumption did you make in this calculation?

Problem 4.5 (2nd edition: 11.11)

The Clausius-Clapeyron equation for the effects of pressure on an equilibrium temperature is

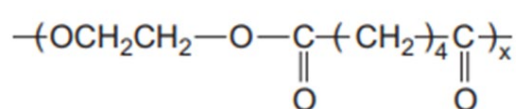
$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

where ΔH is the enthalpy change and ΔV is the volume change associated with a phase change. Calculate the melting temperature for polyethylene in an injection molding operation under a hydrostatic pressure of 80 MPa. Take $\Delta H = 7.79 \text{ kJ/mol}$ of ethylene repeat units and $T_m = 143.5^\circ\text{C}$ at 1 atm.

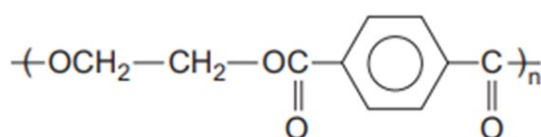
Problem 4.6 (2nd edition: 11.3)

Which of the following polymers would you expect to have a lower glass transition temperature? Which would have a higher melting point? Explain why. (Assume equal degrees of polymerization.)

(a)



(b)



Problem 4.10 (2nd edition: 11.4)

A rubber has a shear modulus of 10^7 dyn/cm² and a Poisson ratio of 0.49 at room temperature. A load of 5 kg is applied to a strip of this material which is 10 cm long, 0.5 cm wide, and 0.25 thick. How much will the specimen elongate?

Problem 4.12 (Not on 2nd edition)

An ideal rubber band is stretched to a length of 15.0 cm from its original length of 6.00 cm. It is found that the stress at this length increases by an increment of 1.5×10^5 Pa when the temperature is raised 5°C (from 27°C up to 32°C). What modulus ($E = \sigma/\epsilon$) should we expect to measure at 27°C?

Problem 4.13 (Not on 2nd edition)

About one out of every 150 chain carbon atoms is cross-linked in a typical natural rubber (*cis*-polyisoprene) compound with good properties. The density of such a vulcanizate is 0.97 g·cm⁻³ at 25°C. The gas constant $R = 8.3 \times 10^7$ ergs·mol⁻¹·K⁻¹ = 1.987 cal·mol⁻¹·K⁻¹. Estimate the modulus of the sample at low extensions.

Problem 4.17 (Not on 2nd edition)

The stress relaxation behavior of a particular grade of polymer under constant strain is given by the following expression:

$$\tau(t) = G\gamma_0 e^{-t/\lambda} + \tau_0$$

where G is a constant, γ_0 is the initial strain imposed on the polymer, τ_0 is the residue stress that is related to γ_0 in the form of $\tau_0 = \gamma_0^2$, and λ is the relaxation time.

- (a) What is the relaxation modulus of the polymer?
- (b) What are the initial and final stresses?
- (c) Given that $G = 0.8$ MPa and $\gamma_0 = 0.15$, calculate the percentage of the original stress that has decayed when $t = \lambda$.
- (d) It has been found that the above model is a better model than the Maxwell model to describe the stress of the polymer, especially at long times. Why?

Problem 4.18 (Not on 2nd edition)

The complex shear strain γ^* and complex shear stress τ^* are given by the following expressions:

$$\gamma^* = \gamma_0 e^{i\omega t} \quad ; \quad \tau^* = \tau_0 e^{i(\omega t + \delta)}$$

Based upon the above expressions, show that the real and imaginary parts of the complex shear compliance J^* are given by the following equations:

$$J' = \frac{\gamma_0}{\tau_0} \cos(\delta) \quad ; \quad J'' = \frac{\gamma_0}{\tau_0} \sin(\delta)$$

Also show that $J''/J' = \tan(\delta)$. If the magnitudes of γ^* and τ^* are 10% and 10^5 Pa and the phase angle of the material is 45°, calculate the amount of energy that is dissipated per full cycle of deformation (J/m³).

Problem 4.19 (Not on 2nd edition)

Consider a sinusoidal shear strain with angular frequency ω and strain amplitude γ_0 (i.e., $\gamma(t) = \gamma_0 \sin(\omega t)$).

- (a) What is the corresponding time dependent shear stress for a perfectly elastic material that has a shear modulus of G and is subjected to the above sinusoidal shear strain?
- (b) Show that the shear stress of a Newtonian liquid with a viscosity of η still oscillates with the same angular frequency but is out-of-phase with the sinusoidal shear strain by $\pi/2$.
- (c) What is the time-dependent shear stress of a viscoelastic material with a stress amplitude σ_0 and in which stress leads the strain by a phase angle δ ?
- (d) What is the corresponding expression of the above described sinusoidal shear strain written in the complex number form?
- (e) If a sinusoidal shear strain is in the form of $\gamma(t) = \gamma_0 e^{i\omega t}$, determine the magnitudes of the shear strains and the corresponding shear stresses for a viscoelastic material when $\omega t = 0, \pi/2, \pi, 3\pi/2, \text{ and } 2\pi$. Note that the time-dependent shear stress has a stress amplitude σ_0 and that its stress leads the strain by a phase angle δ .
- (f) The following expression shows the complex compliance of a viscoelastic material which is subjected to a sinusoidal shear strain in the form of $\gamma(t) = \gamma_0 e^{i\omega t}$. Comment on the viscoelastic behavior of the material as a function of angular frequency.

$$J^* = J' - iJ'' = \frac{G}{G^2 + \eta^2 \omega^2} - i \frac{\eta \omega}{G^2 + \eta^2 \omega^2}$$

■ Chapter 5 – Polymer Mixtures

Problem 5.1 (2nd edition: 12.1)

Toluene (molecular weight = 92, density = 0.87 g/cm³) boils at 110.6°C at 1 atm pressure. Calculate its solubility parameter at 25°C. [The enthalpy of vaporization can be approximated from the normal boiling point T_b (K) of a solvent from $\Delta H_{(25^\circ\text{C})} = 23.7T_b + 0.020T_b^2 - 2950$ cal/mol].

Problem 5.2 (2nd edition: 12.2)

Calculate the solubility parameter for a methyl methacrylate-butadiene copolymer containing 25 mol% methyl methacrylate.

Problem 5.3 (2nd edition: 12.3)

Calculate the solubility parameter for poly(vinyl butyl ether). Take the polymer density as 1.0 g/cm³.

Problem 5.5 (2nd edition: 12.5)

Calculate the composition by volume of a blend of *n*-hexane, *t*-butanol, and dioctyl phthalate that would have the same solvent properties as tetrahydrofuran. (Use Table 5.4 and match δ_p and δ_H values.)

Problem 5.8 (Not on 2nd edition)

Consider a hypothetical binary blend composed of linear polymers A and B with $DP_A = 1000$ and $DP_B = 500$. The Hildebrand solubility parameters of the polymers are $\delta_A = -0.001T + 10.0$ and $\delta_B = -0.0008T + 10.2$, respectively, where δ is in (cal/cm³)^{1/2} and T is in K. The reference volume for the blend has a functional form of $V_0 = 20 + 0.015T$; here, V_0 is in cm³/mol while T is in K. Note that the universal gas constant $R = 1.987$ cal·mol⁻¹·K⁻¹.

- Determine the critical Flory-Huggins interaction parameter χ_{critical} for the blend.
- Calculate χ_{AB} at 200 K and 600 K based upon their Hildebrand solubility parameters.
- Based upon the results in part (b), what conclusion can you make on the phase behavior of the blend? Why?

Problem 5.9 (Not on 2nd edition)

Consider the following empirical expression for the Flory-Huggins interaction parameter χ ,

$$\chi = \frac{3.70 \times 10^{-2}}{T} + 7.64 \times 10^{-10} T^2$$

- What are the units of the constants in the above expression?
- What type of phase behavior should one expect from the above expression? Why?
- If a binary polymer blend containing polymers A ($M_n = 275,000$ g·mol⁻¹; $\rho = 1.06$ g/cm³; molar volume of repeating unit (v_A) = 25 cm³/mol) and B ($M_n = 650,000$ g/mol; $\rho = 1.20$ g/cm³; $v_B = 53$ cm³/mol), calculate χ_{critical} based upon the geometric mean of the molar volumes of the repeating units of polymers A and B.
- Plot χ against T over the temperature range of 100 to 500 K and determine the UCST and LCST of the blend.

Problem 5.10 (Not on 2nd edition)

The weight fraction activity coefficient at infinite dilution (i.e., the concentration of the solvent in the polymer is very low), Ω_1^∞ , can be measured by a technique called inverse gas chromatography. In a particular experiment, Ω_1^∞ and the ratio of the specific volume of the solvent to that of the polymer, v_1/v_2 , at 150°C are measured to be 4.49 and 1.1, respectively. Also, the relationship between Ω_1^∞ and the Flory-Huggins interaction parameter, χ , is given by the following equation:

$$\ln(\Omega_1^\infty) = \ln\left(\frac{v_1}{v_2}\right) + 1 + \chi$$

Note that the activity of the solvent in the polymer, a_1 , is given by the following equation:

$$a_1 = \Omega_1^\infty w_1 = \gamma_1 x_1$$

where w_1 and x_1 are the weight and mole fractions of the solvent and γ_1 is the activity coefficient of the solvent in the polymer.

(a) Are the solvent and polymer miscible under the above described conditions?

(b) What is the volume fraction of the solvent in the polymer if $w_1 = 0.002$?

Problem 5.11 (Not on 2nd edition)

It is generally observed that the Flory-Huggins interaction parameter depends not only on the temperature but also on the composition of a binary polymer solution. For solutions of polystyrene in cyclohexane, the Flory-Huggins interaction parameter is determined to have the following relation:

$$\chi = 0.2035 + \frac{90.65}{T} + 0.3092\phi + 0.1554\phi^2$$

where T is the temperature in K and ϕ is the polymer volume fraction.

(a) Assuming that volume change of mixing is negligible, what is the Gibbs free energy change when we mix 1 g of polystyrene with a number-average molecular weight of 10^5 g/mol and 1 mol of cyclohexane (J/mol) at 400 K? The molar volumes of polystyrene and cyclohexane are 9.5×10^4 and $108 \text{ cm}^3/\text{mol}$, respectively. Note that $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

(b) What is the critical Flory-Huggins interaction parameter of the polystyrene/cyclohexane system?

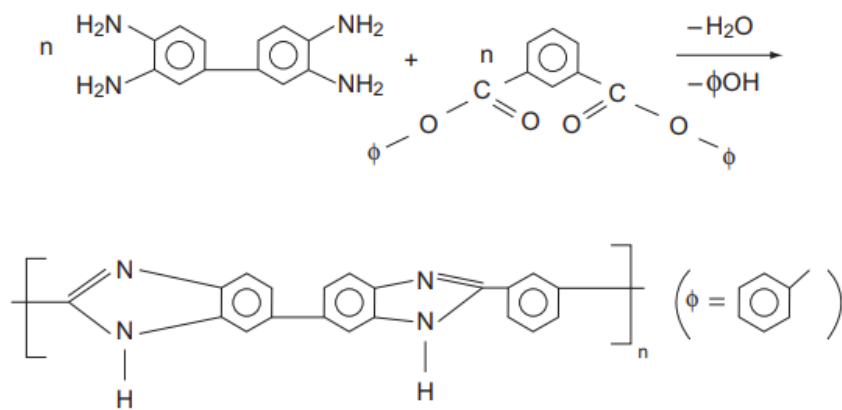
(c) Does the polystyrene/cyclohexane system have a UCST or LCST?

(d) Determine the theta temperature (K) at $\phi = 0.1$.

Chapter 7 – Step-Growth Polymerizations

Problem 7.1 (2nd edition: 5.1)

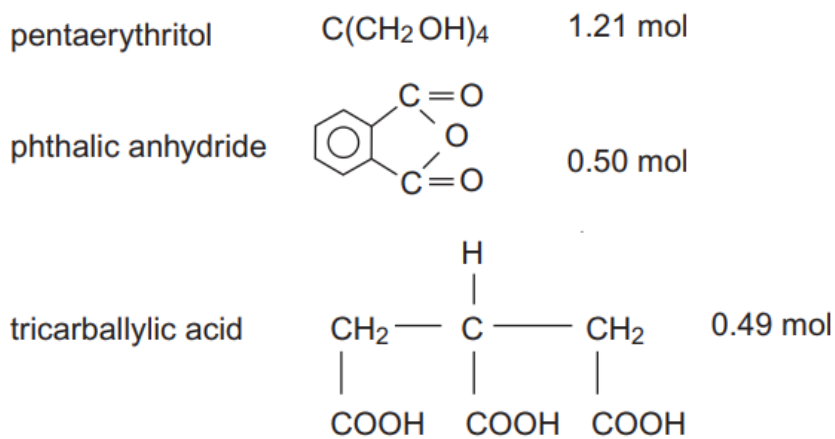
Polybenzimidazoles are made by a two-stage step-growth melt polymerization:



What extent of reaction is needed to produce $n = 200$ in the above formula? Carry four decimal places in your answer.

Problem 7.3 (2nd edition: 5.3)

Can the following alkyd recipe be carried to “complete” conversion without gelling?

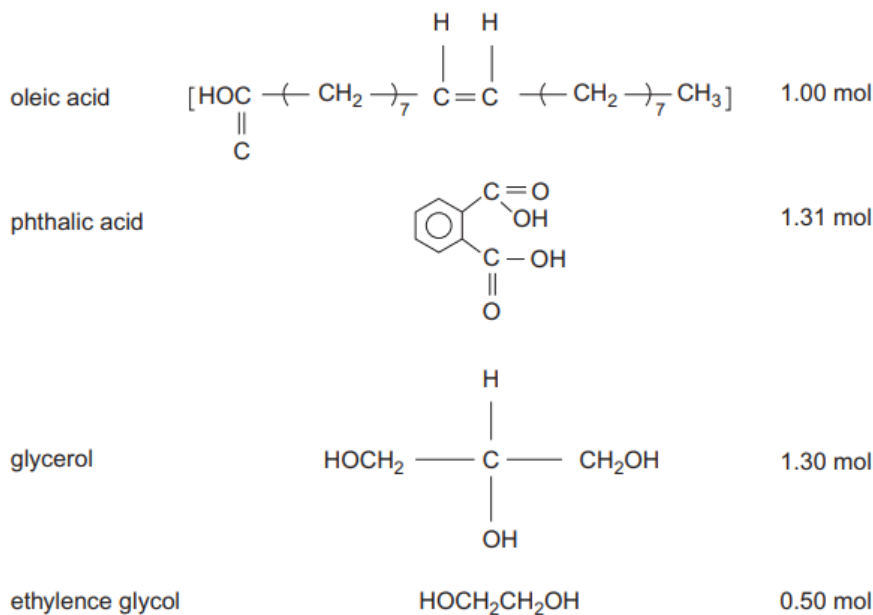


Problem 7.5 (2nd edition: 5.5)

Shown on the next page is a simplified alkyd recipe.

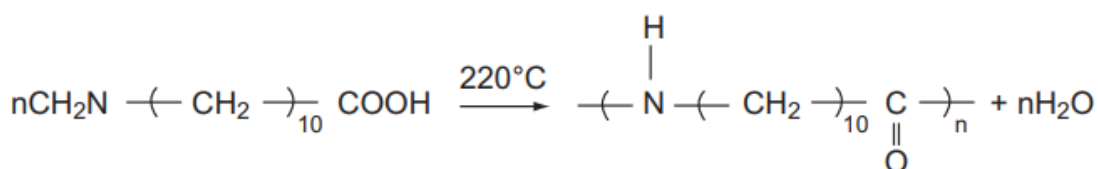
(a) Calculate the number average degree of polymerization when the esterification reaction is complete ($p = 1$).

(b) An operator makes up this mixture and forgets to add the ethylene glycol. He tries to run the reaction to completion. At what extent of conversion will he notice the results of this omission?



Problem 7.6 (2nd edition: 5.6)

Nylon-11 is poly(11-aminoundecanoic acid). This polymer has a crystal melting point around 190°C and has lower water absorption than nylon-6,6 or nylon-6. It can be used to make mechanical parts, packaging films, bristles, monofilaments, and sprayed and fluidized coatings.



In the step-growth polymerization of this monomer,

(a) How much monomer (in terms of weight fraction of the reaction mixture) is left when 90% of the functional groups have reacted?

(b) Calculate \bar{M}_n , \bar{M}_w , and \bar{M}_z of the reaction mixture at this stage.

Problem 7.11 (Not on 2nd edition)

Consider the following alkyd recipe:

Pentaerythritol	1.21 moles
Phthalic anhydride	0.54 moles
Tricarballic acid	0.49 moles

Can the above reaction be carried out to complete conversion without gelling?

Explain why equations such as $x_i = (1 - p)p^{i-1}$ and $w_i = i(1 - p)^2 p^{i-1}$ cannot be used to calculate the fractions of the monomers in the above reaction mixture.

Problem 7.12 (Not on 2nd edition)

Consider a step-growth polymerization using a bi-functional monomer which contains two co-reactive sites, the so-called AB-type monomer.

(a) What is the average functionality of the monomer?

(b) Would the reaction mixture gel?

(c) At a given extent of reaction p , what are the respective probabilities of finding the co-reactive sites reacted and un-reacted?

(d) What are the mole and weight fractions of the molecules containing 10 monomers in the reaction mixture when $p = 0.99$?

(e) What are the most probable sizes of the molecules in the reaction mixture in terms of mole and weight fractions when $p = 0.99$ and what are the corresponding mole and weight fractions?

(f) Given that GPC analysis shows that M_n of the reaction mixture described in part (d) is 12,000 g/mol, what are the polydispersity index and standard deviation of the number weight molecular distribution of the reaction mixture?

Problem 7.13 (Not on 2nd edition)

Given that the variance of the number distribution of the molecular weight of a step-growth polymerization reaction mixture is given by the following equation:

$$\sigma_n^2 = M_w M_n - M_n^2$$

(a) Show that the corresponding standard deviation is given by the following equation:

$$\sigma_n = \sqrt{p} M_n$$

Consider the following step-growth polymerization in which A can react with both B and C but B and C do not react with each other.

Monomer	Molecular weight	Mass (g)
A	350	875
AA		
BB	1000	2000
CC	150	15
C	225	225

- (b) What are the functionalities of the above monomers?
- (c) What are the functionalities of the above monomers?
- (d) Calculate f_{avg} of the formulation.
- (e) At what level of the extent of reaction does gelation occur?
- (f) What is the polydispersity index of the final product?
- (g) GPC analysis shows that M_w of the final product is 12,000. What is the standard deviation of the number distribution of the molecular weight of the polymer made?

■ Chapter 8 – Free-Radical Polymerization

Problem 8.1 (2nd edition: 6.1)

Rate constants for termination k_t may be of the order of 10^8 liter/mol·sec in free-radical polymerizations. Consider the polymerization of styrene initiated by di-*t*-butyl peroxide at 60°C. For a solution of 0.01 M peroxide and 1.0 M styrene in benzene, the initial rate of polymerization is 1.5×10^{-7} mol/liter·sec and \bar{M}_n of the polymer produced is 138,000.

- (a) From the above information, estimate k_p for styrene at 60°C.
- (b) What is the average lifetime of a macroradical during initial stages of polymerization in this system?

Problem 8.2 (2nd edition: 6.2)

For a particular application, the molecular weight of the polymer made in Problem 8-1 is too high. What concentration of *t*-butyl mercaptan should be used to lower the number molecular weight of the polymer to 85,000? For this, transfer agent constant *C* is 3.7 in the polymerization of styrene.

Problem 8.3 (2nd edition: 6.3)

When bulk styrene is heated to 120°C, polymerization occurs because of thermal initiation in the absence of an added initiator. It is observed that polystyrene with $\bar{M}_n = 200,000$ is produced under these conditions at a rate of 0.011 g polymer/liter/min. Using this information, calculate the total initial rate of polymerization expected if an initiator with concentration 0.1 M, initiation rate constant $k_d = 10^{-4} \text{ sec}^{-1}$ and efficiency $f = 0.8$ is added to this system at 120°C. (Molar mass of styrene = 104, $k_t = k_{tc}$; $k_{td} = 0$.)

Problem 8.5 (2nd edition: 6.5)

For acrylamide, $k_p^2/k_t = 22$ liter/mol·sec at 25°C and termination is by coupling alone. At this temperature the half-life of isobutyryl peroxide is 9.0 h and its efficiency in methanol can be taken to be equal to 0.3. A solution of 100 g/liter acrylamide in methanol is polymerized with 10^{-1} M isobutyryl peroxide.

- (a) What is the initial steady-state rate of polymerization?
- (b) How much polymer has been made in the first 10 min of reaction in 1 liter of solution?

Problem 8.6 (2nd edition: 6.6)

One hundred liters of methyl methacrylate is reacted with 10.2 mol of an initiator at 60°C.

- (a) What is the kinetic chain length in this polymerization?
- (b) How much polymer has been made in the first 5 h of reaction?

$$k_p = 5.5 \text{ liter/mol·sec}$$

$$k_t = 25.5 \times 10^6 \text{ liter/mol·sec}$$

$$\text{Density of monomer} = 0.94 \text{ g/cm}^3$$

$$t_{1/2} \text{ for this initiator} = 50 \text{ h}$$

$$\text{Efficiency } f = 0.3$$

Problem 8.10 (2nd edition: 6.10)

Vinyl acetate was polymerized in a free-radical reaction. The initial monomer concentration was 1 mol/liter and its concentration after 1 h was 0.85 mol/liter. Chloroform was present as a chain transfer agent, with concentrations of 0.01 mol/liter at time zero and 0.007 mol/liter after 1 h. What is the chain transfer constant C in this case?

Chapter 9 – Copolymerization**Problem 9.1 (2nd edition: 7.1)**

(a) Calculate the copolymer composition (in mole percent) formed at an early stage of the reaction of methyl methacrylate (monomer 1) at 5 mol/liter and 5-ethyl-2-vinyl pyridine at 1 mol/liter concentration. Reactivity ratios are $r_1 = 0.40$ and $r_2 = 0.69$.

(b) What molar ratio of monomers in the feed produces a copolymer composition which is the same as the feed composition?

Problem 9.2 (2nd edition: 7.2)

Calculate the composition (mole fractions) of the initial terpolymer which would be formed from the radical polymerization of a feed containing 0.414 mol fraction methacrylonitrile (MAN), 0.424 mol fraction styrene (S), and 0.162 mol fraction α -methylstyrene (AMS). Reactivity ratios are:

$$\text{MAN}(M_1)/\text{S}: r_1 = 0.44, r_2 = 0.37$$

$$\text{MAN}(M_1)/\text{AMS}: r_1 = 0.38, r_2 = 0.53$$

$$\text{S}(M_1)/\text{AMS}: r_1 = 1.124, r_2 = 0.627$$

Problem 9.3 (2nd edition: 7.3)

When 0.3 mol fraction methacrylonitrile is copolymerized with styrene in a radical reaction, what is the average length of sequences of each monomer in the copolymer?

Problem 9.5 (2nd edition: 7.5)

(a) Acrylonitrile (monomer 1, $r_1 = 0.9$) is copolymerized with 0.25 mol fraction vinylidene chloride (monomer 2, $r_2 = 0.4$). What fraction of the acetonitrile sequences contain 3 or more acrylonitrile units? (Polyacrylonitrile is used to make “acrylic” fibers. Copolymerization with vinylidene chloride reduces the flammability of such products. Such copolymers form the basis of “mod-acrylic” fibers.)

(b) What is the feed composition for copolymerization of vinylidene chloride and acrylonitrile such that the copolymer composition does not vary with the conversion of monomers to polymer?

Problem 9.9 (2nd edition: 7.9)

The copolymerization of ethylene and propylene is found to be essentially random ($r_1 r_2 \approx 1$) with $(\text{C}_2\text{H}_5)_2\text{AlCl}/\text{VO}(\text{OC}_2\text{H}_5)_3$ catalyst in chlorobenzene at 30°C. (Such polymerizations are discussed in Chapter 11.) The control of such systems is frequently on monomer concentration in the gas phase over the reaction mixture. This is because gas phase concentrations vary less with temperature, pressure, and solvent. What monomer composition in the gas phase is needed to produce a copolymer containing 30 mol% propylene? The reactivity ratio of ethylene (r_1) has been found to be 5, based on gas phase concentrations.

Problem 9.10 (2nd edition: 7.10)

In the copolymerization of vinyl chloride and vinyl acetate, what monomer feed composition is needed to produce a copolymer containing 5 mol% vinyl acetate? (The reactivity ratios are listed in Table 9.1.)

SOLUTIONS**P2.1**

Since equal masses of A and B are mixed, we have $w_A = w_B = 0.5$. The number-average molecular weight then becomes

$$\bar{M}_n = \frac{1}{\sum \frac{w_i}{(M_n)_i}} = \left(\frac{0.5}{35,000} + \frac{0.5}{150,000} \right)^{-1} = \boxed{56,800}$$

In turn, the weight-average molecular weight is

$$\bar{M}_w = \sum w_i (\bar{M}_w)_i = 0.5 \times 90,000 + 0.5 \times 300,000 = \boxed{195,000}$$

■ P2.2

The molar mass of calcium stearate is $607 \text{ g}\cdot\text{mol}^{-1}$. Letting \bar{M}_n^* denote the number-average MW of the balance of the PVC compound, we may write

$$\begin{aligned}\bar{M}_n &= 25,000 = \left(\frac{0.02}{607} + \frac{0.98}{\bar{M}_n^*} \right)^{-1} \\ \therefore \frac{1}{25,000} &= \frac{0.02}{607} + \frac{0.98}{\bar{M}_n^*} \\ \therefore \frac{0.98}{\bar{M}_n^*} &= \frac{1}{25,000} - \frac{0.02}{607} \\ \therefore \frac{\bar{M}_n^*}{0.98} &= \left(\frac{1}{25,000} - \frac{0.02}{607} \right)^{-1} \\ \therefore \bar{M}_n^* &= 0.98 \times \left(\frac{1}{25,000} - \frac{0.02}{607} \right)^{-1} = \boxed{139,000}\end{aligned}$$

■ P2.3

Taking the appropriate formula from Table 2.2, we may write

$$\bar{M}_z = \frac{\sum w_i M_i^2}{\sum w_i M_i} = \frac{0.5 \times 5000^2 + 0.5 \times 50,000^2}{0.5 \times 5000 + 0.5 \times 50,000} = \boxed{45,900}$$

■ P2.4

The weight-average degree of polymerization is

$$\begin{aligned}\overline{DP}_w &= \sum w_i (\overline{DP})_i = \left[\begin{array}{l} 0.3 \times 20 + 0.2 \times 25 + 0.15 \times 30 + 0.11 \times 35 + 0.08 \times 40 \\ + 0.06 \times 45 + 0.04 \times 50 + 0.03 \times 60 + 0.03 \times 80 \end{array} \right] \\ \therefore \overline{DP}_w &= 31.45\end{aligned}$$

The repeating unit in polystyrene polymer has molar mass equal to 104, hence \bar{M}_w is

$$\bar{M}_w = 104 \times \overline{DP}_w = 104 \times 31.45 = \boxed{3270}$$

The number-average degree of polymerization is

$$\overline{DP}_n = \frac{1}{\sum \frac{w_i}{(DP)_i}}$$

where

$$\sum \frac{w_i}{(DP)_i} = \left[\begin{array}{l} \frac{0.3}{20} + \frac{0.2}{25} + \frac{0.15}{30} + \frac{0.11}{35} + \frac{0.08}{40} \\ + \frac{0.06}{45} + \frac{0.04}{50} + \frac{0.03}{60} + \frac{0.03}{80} \end{array} \right] = 0.0362$$

so that

$$\overline{DP}_n = \frac{1}{0.0362} = 27.6$$

and

$$\bar{M}_n = 104 \times \overline{DP}_n = 104 \times 27.6 = \boxed{2870}$$

Lastly, the variance of the number distribution is

$$s_n^2 = \bar{M}_w \bar{M}_n - \bar{M}_n^2 = 3270 \times 2870 - 2870^2 = \boxed{1.15 \times 10^6}$$

This corresponds to a standard deviation of approximately 1070.

■ P2.6

For all the homopolymers formed, the number-average molecular weight \bar{M}_n is given by

$$\bar{M}_n = \frac{1}{\sum (w_i/M_i)}$$

$$\therefore \bar{M}_n = \left(\frac{0.05}{10,000} + \frac{0.25}{50,000} + \frac{0.20}{80,000} + \frac{0.20}{100,000} + \frac{0.15}{150,000} + \frac{0.10}{200,000} + \frac{0.05}{500,000} \right)^{-1} = \boxed{62,100}$$

Then, the degree of polymerization for each polymer is obtained by dividing the number-average molecular weight by the molar mass of the corresponding monomer; mathematically,

$$DP = \frac{\bar{M}_n}{(\text{Molar mass of monomer})}$$

For example, structure (a) is polypropylene, whose monomer has a molar mass of 42 g·mol⁻¹, and the DP is

$$DP = \frac{62,100}{42} = \underline{1479}$$

DP values for all five polymers are listed below.

Monomer	Molar mass of monomer	DP
(a)	42	1479
(b)	62.5	994
(c)	100	621
(d)	44	1411
(e)	28	2218

■ P2.7

Firstly, the number-average molecular weight is

$$\bar{M}_n = \frac{1}{\sum \frac{w_i}{(M_n)_i}} = \left(\frac{200}{1100 \times 45,000} + \frac{300}{1100 \times 100,000} + \frac{500}{1100 \times 80,000} + \frac{100}{1100 \times 300,000} \right)^{-1} = \boxed{78,420}$$

In turn, the weight-average molecular weight is

$$\bar{M}_w = \sum w_i (M_w)_i = \left(\frac{200 \times 65,000}{1100} + \frac{300 \times 200,000}{1100} + \frac{500 \times 85,000}{1100} + \frac{100 \times 900,000}{1100} \right) = \boxed{186,800}$$

The polydispersity index follows as

$$PDI = \frac{\bar{M}_w}{\bar{M}_n} = \frac{186,800}{78,420} = \boxed{2.38}$$

Assuming that the number distribution of the molecular weight can be described by a normal distribution, the standard deviation σ_n is computed as

$$\sigma_n = \sqrt{\bar{M}_w \bar{M}_n - \bar{M}_n^2} = \sqrt{186,800 \times 78,420 - 78,420^2} = \boxed{92,200}$$

■ P2.11

Part (a): We must first determine constant K . To do so, we note that the sum of weight fractions w_i , $i \in [1; 10]$ must add up to one:

$$\sum_{i=1}^{10} w_i = K \sum_{i=1}^{10} (i^3 - i^2 + 1) = 1$$

The summation in the middle can be evaluated in Mathematica:

```
In[551]:= Sum[i3 - i2 + 1, {i, 1, 10}]
```

```
Out[551]= 2650
```

so that

$$K \underbrace{\sum_{i=1}^{10} (i^3 - i^2 + 1)}_{=2650} = 1$$

$$\therefore K = \frac{1}{2650} = 3.77 \times 10^{-4}$$

To compute the number-average degree of polymerization, we write

$$\bar{i}_n = \frac{1}{\sum_{i=1}^{10} \frac{w_i}{i}}$$

Resorting to Mathematica a second time,

```
In[558]:=
      1
-----
3.77 * 10^-4 * Sum[ $\frac{i^3 - i^2 + 1}{i}$ , {i, 1, 10}]
Out[558]=
7.96722
```

As shown,

$$\boxed{\bar{i}_n = 7.97}$$

Part (b): The standard deviation of the weight distribution is given by

$$s_w = \sqrt{\bar{i}_z \bar{i}_w - \bar{i}_w^2} \quad (\text{I})$$

where \bar{i}_w and \bar{i}_z are the weight-average and z-average degrees of polymerization, respectively. The weight-average DoP can be evaluated as

$$\bar{i}_w = \sum_{i=1}^{10} w_i i = K \sum_{i=1}^{10} (i^3 - i^2 + 1) i$$

```
In[559]:=
3.77 * 10^-4 * Sum[(i^3 - i^2 + 1) * i, {i, 1, 10}]
Out[559]=
8.43085
\therefore \bar{i}_w = 8.43
```

In turn, the z-average DoP is

$$\bar{i}_z = \frac{\sum_{i=1}^{10} w_i i^2}{\sum_{i=1}^{10} w_i i}$$

```
In[560]:=
3.77 * 10^-4 * Sum[(i^3 - i^2 + 1) * i^2, {i, 1, 10}]
-----
3.77 * 10^-4 * Sum[(i^3 - i^2 + 1) * i, {i, 1, 10}]
Out[560]=
8.75898
\therefore \bar{i}_z = 8.76
```

Substituting in (I),

$$s_w = \sqrt{8.76 \times 8.43 - 8.43^2} = \boxed{1.67}$$

Part (c): The z-average DoP was determined in part (b) and equals $\bar{i}_z = 8.76$.

Part (d): The z-average molecular weight of the polymer specified is

$$\bar{M}_z = 100 \times \bar{i}_z = 100 \times 8.76 = \boxed{876}$$

■ P3.1

We first compute the viscosity-average molecular weight,

$$\bar{M}_V = \left[\sum (w_i M_i^a) \right]^{\frac{1}{a}}$$

$$\therefore \bar{M}_V = \left(0.5 \times 39,000^{0.74} + 0.5 \times 292,000^{0.74} \right)^{\frac{1}{0.74}} = 150,600$$

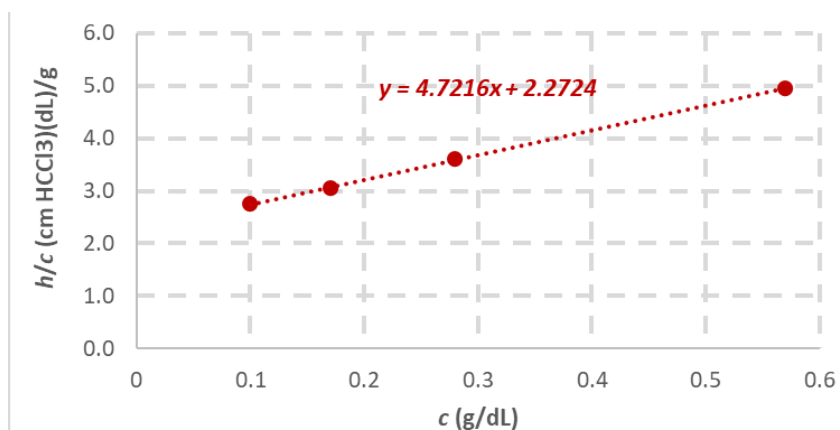
Substituting in the MHS equation, we get

$$\bar{M}_V = K\bar{M}_V^a = \left(9.18 \times 10^{-5} \right) \times 150,600^{0.74} = \boxed{0.623}$$

■ P3.2

The first step is to plot (h/c) against c , as shown next.

c (g/dL)	h (cm HCl ₃)	h/c (cm HCl ₃)(dL)/g
0.57	2.829	4.963
0.28	1.008	3.600
0.17	0.521	3.065
0.1	0.275	2.750



As shown in the linear fit equation, the intercept at $c = 0$ is 2.272 (cm HCl₃)(100 cm³)/g. The pressure associated with a 2.272-cm long HCl₃ column is

$$p = \rho gh = 1.48 \times 981 \times 2.272 = 3300 \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-2}$$

The osmotic pressure π has units of $\text{M} \cdot \text{L}^{-1} \cdot \text{T}^{-2}$ and the concentration c has units of $\text{M} \cdot \text{L}^{-3}$, hence (π/c) has units of $\text{L}^2 \cdot \text{T}^{-2}$. Noting that 1 dL = 100 cm³, we may write

$$\left(\frac{\pi}{c} \right)_0 = 3300 \frac{\text{g}}{\text{cm} \times \text{s}^2} \times \frac{100 \text{ cm}^3}{\text{g}} = 330,000 \frac{\text{cm}^2}{\text{s}^2}$$

Finally, we can estimate \bar{M}_n using van't Hoff's law of osmotic pressures; importantly, since π/c is given in cm²/s², R should be in ergs/(mol·K) to yield a molar mass \bar{M}_n in g/mol.

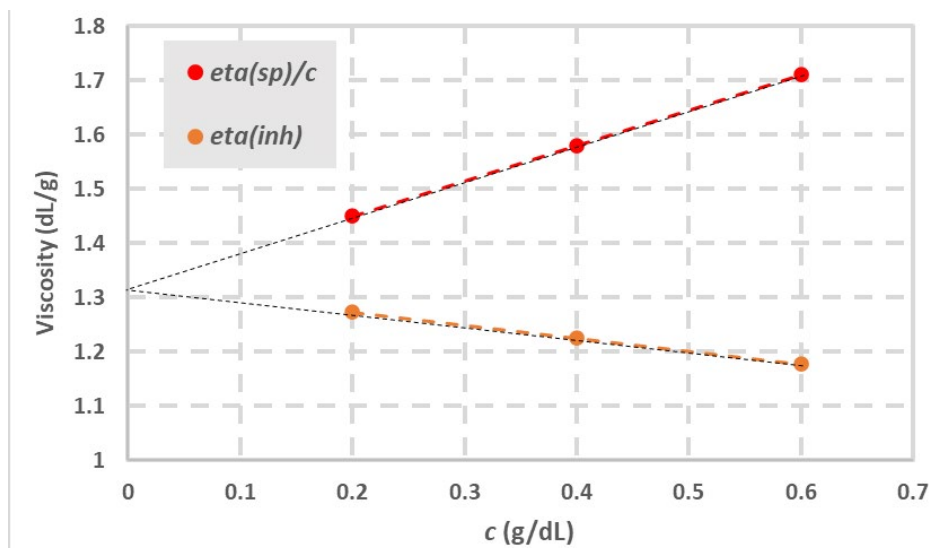
$$\left(\frac{\pi}{c} \right)_0 = \frac{RT}{\bar{M}_n} \rightarrow \bar{M}_n = \frac{RT}{(\pi/c)_0}$$

$$\therefore \bar{M}_n = \frac{(8.314 \times 10^7) \times 293}{330,000} = \boxed{73,800 \text{ g/mol}}$$

■ P3.5

Part (a): The pertaining data are processed and plotted below.

Concentration (g/dL)	t/t_0	η_r	η_{sp}/c	η_{inh}
0.2	1.29	1.29	1.45	1.273
0.4	1.632	1.632	1.58	1.225
0.6	2.026	2.026	1.71	1.177



As shown, the two lines intersect the vertical axis at viscosity $[\eta] \approx 1.31$ dL/g.

Part (b): Substituting $[\eta] = 1.31$ dL/g into the given MHS equation and solving for \bar{M}_v , we obtain

$$\begin{aligned}
 [\eta] &= 3.4 \times 10^{-5} \bar{M}_v^{0.80} \rightarrow 1.31 = 3.4 \times 10^{-5} \bar{M}_v^{0.80} \\
 \therefore \bar{M}_v^{0.80} &= \frac{1.31}{3.4 \times 10^{-5}} \\
 \therefore \bar{M}_v &= \left(\frac{1.31}{3.4 \times 10^{-5}} \right)^{\frac{1}{0.8}} = \boxed{540,000}
 \end{aligned}$$

■ P3.7

The weight-average molecular weight of the contaminated polymer is

$$\bar{M}_w = \sum w_i M_i = 0.97 \times 10^6 + 0.03 \times 30,000 = 971,000$$

which is only 2.9% lower than the \bar{M}_w of the pure polymer. Similarly, the number-average molecular weight of the contaminated polymer is

$$\bar{M}_n = \frac{1}{\sum \left(\frac{w_i}{M_i} \right)} = \left(\frac{0.97}{430,000} + \frac{0.03}{30,000} \right)^{-1} = 307,000$$

which is 28.6% lower than the \bar{M}_n of the pure polymer. Since light scattering measures \bar{M}_w , the results will not be appreciably affected within experimental uncertainty. In turn, membrane osmometry measures \bar{M}_n , so results will be significantly affected for this particular procedure.

■ P3.8

Membrane osmometry is optimal to measure the \bar{M}_n of polymers with molecular weight ranging from 30,000 to 10^6 . Hence, this technique is suitable for polyisobutene B. Vapor phase osmometry is used to measure the \bar{M}_n of polymers with molecular weight less than 3000 or so. Therefore, this technique is suitable for polyisobutene A. Light scattering can be used to estimate the weight-average molecular weight \bar{M}_w of both polyisobutene samples. Finally, it is worth noting that, with the proper calibration, gel permeation/size exclusion chromatography could be used to estimate \bar{M}_n and \bar{M}_w of both polyisobutene samples.

■ P3.10

Part (a): As mentioned in the solution to Problem 3.8, vapor phase osmometry is used to measure the \bar{M}_n of polymers with molecular weight less than 3000 or so.

Part (b): Light scattering is the way to go when measuring weight-average molecular weights, although gel permeation/size exclusion chromatography with proper calibration could be used as well.

Part (c): Membrane osmometry is the best choice for measuring the number-average molecular weight of moderately heavy copolymers.

■ P3.11

Part (a): No. Osmometry measures the number-average molecular weight, whereas light scattering is used to measure the weight-average molecular weight.

Part (b): No. Osmometry is modeled by a linearization of equation (3-24),

$$\frac{\pi}{c} = RT \left(\frac{1}{M_n} + A_2 c \right)$$

whereas light-scattering analysis is modeled by equation (3-53),

$$\frac{Hc}{\tau} = \frac{1}{M} + 2A_2 c$$

As highlighted in red, the slope of the light-scattering zero concentration line will ideally be twice that of the osmometry plot.

■ **P3.13**

Solving equation (3-51) for reduced scattering intensity R_θ , we have

$$\tau = \frac{16}{3} \pi R_\theta \rightarrow R_\theta = \frac{3\tau}{16\pi}$$

But R_θ can also be expressed by equation (3-45),

$$R_\theta = \frac{I'_\theta r^2}{I_0 (1 + \cos^2 \theta)}$$

Equating the two foregoing results and noting that R_θ is defined per unit volume,

$$\begin{aligned} \frac{I'_\theta r^2}{I_0 (1 + \cos^2 \theta)} &= \frac{3\tau}{16\pi} \times \text{Volume} \\ \therefore \frac{I'_\theta}{I_0} &= \frac{3\tau}{16\pi} \frac{(1 + \cos^2 \theta)}{r^2} \times \text{Volume} \\ \therefore \frac{I'_\theta}{I_0} &= \frac{3 \times 0.01}{16\pi} \times \frac{(1 + \cos^2 90^\circ)}{20^2} \times 2.0 = \boxed{2.98 \times 10^{-6}} \end{aligned}$$

■ **P3.14**

The plot in question is based on the linear relationship

$$\frac{1}{c} \left(\frac{\eta - \eta_0}{\eta_0} \right) = [\eta] + k_H [\eta]^2 c$$

Clearly, the intercept with the vertical axis gives the viscosity $[\eta]$,

$$[\eta] = 1.50 \text{ cm}^3 \cdot \text{g}^{-1}$$

In turn, the slope gives Huggins's constant k_H ,

$$\begin{aligned} k_H [\eta]^2 &= 0.9 \rightarrow k_H = \frac{0.9}{[\eta]^2} \\ \therefore k_H &= \frac{0.9}{1.5^2} = \boxed{0.40} \end{aligned}$$

Of note, Huggins's constant is dimensionless.

■ **P4.3**

Part (a): Converting the specific volumes to densities, we have $\rho_c = 1/(0.989 \times 10^{-3}) = 1011 \text{ kg/m}^3$ for crystalline PE and $\rho_a = 1/(1.160 \times 10^{-3}) = 862 \text{ kg/m}^3$ for amorphous PE. Now, the volume fraction ϕ_c of polymer in the crystalline state is given by equation (4-3). With $\rho = 926 \text{ kg/m}^3$,

$$\phi_c = \frac{\rho - \rho_a}{\rho_c - \rho_a} = \frac{926 - 862}{1011 - 862} = \boxed{0.430}$$

With $\rho = 940 \text{ kg/m}^3$,

$$\phi_c = \frac{\rho - \rho_a}{\rho_c - \rho_a} = \frac{940 - 862}{1011 - 862} = \boxed{0.523}$$

With $\rho = 955 \text{ kg/m}^3$,

$$\phi_c = \frac{\rho - \rho_a}{\rho_c - \rho_a} = \frac{955 - 862}{1011 - 862} = \boxed{0.624}$$

Part (b): The main assumption is that the mass and volume of the crystalline and amorphous parts are additive.

■ **P4.5**

Separating variables in the C-C equation and integrating,

$$\begin{aligned} \frac{dP}{dT} &= \frac{\Delta H}{T\Delta V} \rightarrow dP = \frac{\Delta H}{\Delta V} \frac{1}{T} dT \\ \therefore \int_{P_1}^{P_2} dP &= \frac{\Delta H}{\Delta V} \int_{T_1}^{T_2} \frac{1}{T} dT \\ \therefore P_2 - P_1 &= \frac{\Delta H}{\Delta V} \ln\left(\frac{T_2}{T_1}\right) \quad (I) \end{aligned}$$

The volume change associated with melting is

$$\Delta V = V_\ell - V_s = M \left(\frac{1}{\rho_\ell} - \frac{1}{\rho_s} \right)$$

The densities of PE before and after melting may be taken as $\rho_s = 955 \text{ kg/m}^3$ and $\rho_\ell = 855 \text{ kg/m}^3$, respectively. Also, the molar mass of a PE monomer is $M = 28 \text{ kg/kmol}$, so that

$$\Delta V = 28 \times \left(\frac{1}{855} - \frac{1}{955} \right) = 0.00343 \text{ m}^3/\text{kmol} = 3.43 \times 10^{-6} \text{ m}^3/\text{mol}$$

Further, we have $P_2 = 80 \text{ MPa} = 80 \times 10^6 \text{ Pa}$, $P_1 = 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$, $T_1 = 143.5^\circ\text{C} = 416.5 \text{ K}$, and $\Delta H = 7790 \text{ J/mol}$. Substituting all pertaining variables in (I) and solving for temperature T_2 , we get

$$\begin{aligned} 80 \times 10^6 - 1.013 \times 10^5 &= \frac{7790}{3.43 \times 10^{-6}} \times \ln\left(\frac{T_2}{416.5}\right) \\ \therefore 7.99 \times 10^7 &= (2.27 \times 10^9) \times \ln\left(\frac{T_2}{416.5}\right) \\ \therefore 0.0352 &= \ln\left(\frac{T_2}{416.5}\right) \\ \therefore \exp(0.0352) &= \frac{T_2}{416.5} \end{aligned}$$

$$\therefore T_2 = 416.5 \times \exp(0.0352) = 431.42 \text{ K} = \boxed{158.4^\circ\text{C}}$$

■ **P4.6**

Polymer (b) should have a greater melting point T_m because its monomer has a greater molar mass ($192 \text{ g}\cdot\text{mol}^{-1}$ versus $172 \text{ g}\cdot\text{mol}^{-1}$). Further, polymer (b) should have a greater glass transition temperature T_g because the phenyl group in (b) stiffens the macromolecular chain.

■ **P4.10**

The shear modulus G and the Poisson ratio ν can be used to compute Young's modulus E for the rubber material,

$$E = 2G(1 + \nu) = 2 \times 10^7 \times (1 + 0.49) = 2.98 \times 10^7 \text{ dyn/cm}^2$$

The cross-section being loaded has area $A = 0.5 \times 0.25 = 0.125 \text{ cm}^2$. The force being applied to the rubber is $F = 5000 \text{ g} \times 981 \text{ cm/s}^2 = 4.91 \times 10^6 \text{ dyn}$. The corresponding stress σ is

$$\sigma = \frac{F}{A} = \frac{4.91 \times 10^6}{0.125} = 3.93 \times 10^7 \text{ dyn/cm}^2$$

Using Hooke's law, the strain ε becomes

$$\sigma = E\varepsilon \rightarrow \varepsilon = \frac{\sigma}{E}$$

$$\therefore \varepsilon = \frac{3.93 \times 10^7}{2.98 \times 10^7} = 1.32$$

The original length of the specimen is 10 cm. Therefore, the specimen will elongate to $1.32 \times 10 = 13.2$ cm.

■ **P4.12**

Since the rubber band is stretched from 6.0 to 15.0 cm, we have an extension $\Lambda = 15/6 = 2.50$, and

$$\Lambda - \frac{1}{\Lambda^2} = 2.5 - \frac{1}{2.5^2} = 2.34$$

Writing equation (4-29) for stresses at 27°C and 32°C, we have respectively

$$\sigma_{27} = \frac{\rho_{27} R \times 300}{M_c} \left(\Lambda - \frac{1}{\Lambda^2} \right) = \frac{\rho_{27} \times 8.314 \times 300}{M_c} \times 2.34$$

and

$$\sigma_{32} = \frac{\rho_{32} R \times 305}{M_c} \left(\Lambda - \frac{1}{\Lambda^2} \right) = \frac{\rho_{32} \times 8.314 \times 305}{M_c} \times 2.34$$

But, per the problem statement, $\sigma_{32} - \sigma_{27} = 1.5 \times 10^5$ Pa, so that

$$\frac{\rho_{32} \times 8.314 \times 305}{M_c} \times 2.34 - \frac{\rho_{27} \times 8.314 \times 300}{M_c} \times 2.34 = 150,000$$

For an ideal rubber band, the volume remains constant for a certain deformation and, as a consequence, so does the density ρ . Substituting $\rho_{32} = \rho_{27} = \rho$ above and solving for ratio ρ/M_c , we obtain

$$\frac{\rho \times 8.314 \times 305}{M_c} \times 2.34 - \frac{\rho \times 8.314 \times 300}{M_c} \times 2.34 = 150,000$$

$$\therefore \frac{\rho}{M_c} \times (8.314 \times 305 - 8.314 \times 300) \times 2.34 = 150,000$$

$$\therefore \frac{\rho}{M_c} \times 97.27 = 150,000$$

$$\therefore \frac{\rho}{M_c} = 1540$$

We can use this ratio to determine the stress for 1% elongation at 27°C,

$$\sigma_{27} = \frac{\rho_{27} R \times 300}{M_c} \left(\Lambda - \frac{1}{\Lambda^2} \right) = 1540 \times 8.314 \times 300 \times \left(1.01 - \frac{1}{1.01^2} \right)$$

$$\therefore \sigma_{27} = 114,000 \text{ Pa}$$

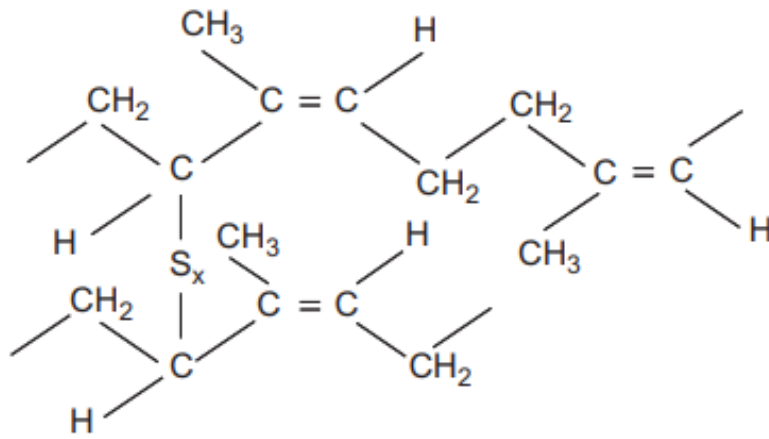
The corresponding elastic modulus is

$$\sigma = E\varepsilon \rightarrow E = \frac{\sigma}{\varepsilon}$$

$$\therefore E = \frac{114,000}{0.01} = 1.14 \times 10^7 \text{ Pa} = \boxed{11.4 \text{ MPa}}$$

■ **P4.13**

There are 150 C atoms between cross-links on the average. This corresponds to $150/4 = 37$ monomer units between cross-links (see structure 1-19, which is reproduced on the next page).



1-19

The molecular weight of an isoprene monomer is 68 g/mol. Accordingly, the molecular weight between cross-links may be determined as

$$M_c = 68 \times 37 = 2516$$

We can estimate Young's modulus using equation (4.31),

$$E = \frac{3\rho RT}{M_c} = \frac{3 \times 0.98 \times (8.3 \times 10^7) \times 298}{2516} = 2.89 \times 10^7 \text{ dyn/cm}^2$$

$$\therefore E = 2.89 \times 10^7 \frac{\text{dyn}}{\text{cm}^2} \times \frac{1}{10^7} \frac{\text{MPa}}{\text{dyn/cm}^2} = \boxed{2.89 \text{ MPa}}$$

■ P4.17

Part (a): The relaxation modulus is

$$G(t) = \frac{\tau(t)}{\gamma_0} = \frac{G\gamma_0 e^{-t/\lambda} + \tau_0}{\gamma_0}$$

$$\therefore G(t) = Ge^{-t/\lambda} + \frac{\tau_0}{\gamma_0}$$

But $\tau_0 = \gamma_0^2$, therefore

$$G(t) = Ge^{-t/\lambda} + \frac{\gamma_0^2}{\gamma_0} = \boxed{Ge^{-t/\lambda} + \gamma_0}$$

Part (b): Substituting $t = 0$ in $\tau(t)$ gives the initial stress,

$$\tau(t = 0) = G\gamma_0 \underbrace{e^{-0/\lambda}}_{=1} + \tau_0 = \boxed{G\gamma_0 + \gamma_0^2}$$

Substituting $t \rightarrow \infty$ in $\tau(t)$ gives the final stress,

$$\tau(t \rightarrow \infty) = \lim_{t \rightarrow \infty} (G\gamma_0 e^{-t/\lambda} + \tau_0) = 0 + \tau_0 = \boxed{\tau_0}$$

Part (c): When $t = \lambda$, the stress is

$$\tau(t = \lambda) = G\gamma_0 e^{-\lambda/\lambda} + \tau_0 = G\gamma_0 e^{-1} + \tau_0$$

$$\therefore \tau(t = \lambda) = G\gamma_0 e^{-1} + \gamma_0^2$$

This is to be compared with initial stress $\tau(0)$, which is given by the expression determined in part (b). Accordingly,

$$\frac{\tau(t = \lambda)}{\tau(t = 0)} = \frac{G\gamma_0 e^{-1} + \gamma_0^2}{G\gamma_0 + \gamma_0^2} = \frac{0.8 \times 0.15 \times e^{-1} + 0.15^2}{0.8 \times 0.15 + 0.15^2} = 0.468$$

$$\therefore \boxed{\frac{\tau(t = \lambda)}{\tau(t = 0)} = 46.8\%}$$

Part (d): It is because the Maxwell model would yield zero stress when $t \rightarrow \infty$, whereas the model at hand includes a finite residual stress.

■ P4.18

Noting that $\gamma^* = \gamma_0 e^{i\omega t}$ and $\tau^* = \tau_0 e^{i(\omega t + \delta)}$, the complex shear compliance becomes

$$J^* = \frac{\gamma^*}{\tau^*} = \frac{\gamma_0 e^{i\omega t}}{\tau_0 e^{i(\omega t + \delta)}} = \frac{\cancel{\gamma_0 e^{i\omega t}}}{\tau_0 \cancel{e^{i\omega t}} e^{i\delta}} = \frac{\gamma_0}{\tau_0} e^{-i\delta}$$

Replacing $e^{i\delta}$ with the Euler formula,

$$J^* = \frac{\gamma_0}{\tau_0} e^{-i\delta} = \frac{\gamma_0}{\tau_0} (\cos \delta - i \sin \delta) = \frac{\gamma_0}{\tau_0} \cos \delta - i \frac{\gamma_0}{\tau_0} \sin \delta$$

Defining $J' = (\gamma_0/\tau_0)\cos(\delta)$ and $J'' = (\gamma_0/\tau_0)\sin(\delta)$, we have

$$J^* = \frac{\gamma_0}{\tau_0} \cos \delta - i \frac{\gamma_0}{\tau_0} \sin \delta = J' - iJ''$$

Dividing J'' by J' ,

$$\frac{J''}{J'} = \frac{(\gamma_0/\tau_0)\sin \delta}{(\gamma_0/\tau_0)\cos \delta} = \tan \delta$$

Now, the loss modulus is given by

$$G'' = \frac{\tau_0}{\gamma_0} \sin(\delta)$$

so the energy W dissipated in a cycle of deformation becomes

$$W = \pi \gamma_0^2 G'' = \pi \times 0.1^2 \times \frac{10^5}{0.1} \times \sin(45^\circ) = \boxed{22,200 \text{ J/m}^3}$$

■ P4.19

Part (a): The shear stress and strain are related by Hooke's law for shear:

$$\tau(t) = G\gamma(t) = G\gamma_0 \sin(\omega t)$$

Part (b): The shear stress in a Newtonian liquid is given by the product of viscosity η and strain rate $d\gamma/dt$,

$$\tau(t) = \eta \frac{d\gamma(t)}{dt} = \eta \frac{d}{dt} [\gamma_0 \sin(\omega t)]$$

$$\therefore \tau(t) = \eta \gamma_0 \frac{d}{dt} [\sin(\omega t)]$$

$$\therefore \tau(t) = \eta \gamma_0 \omega \cos(\omega t)$$

$$\therefore \tau(t) = \eta \gamma_0 \omega \sin\left(\omega t + \frac{\pi}{2}\right)$$

This latter result indicates that the shear stress is out of phase with the sinusoidal shear strain by 90° or $\pi/2$ rad.

Part (c): The stress function in question is

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta)$$

Part (d): We can state the shear strain in complex number form as

$$\gamma(t) = \gamma_0 e^{i\left(\omega t + \frac{\pi}{2}\right)}$$

Part (e): The strains and stresses obtained for each of the proposed values of ωt are listed below.

ωt	γ	σ
0	γ_0	$\sigma_0 \cos(\delta)$
$\pi/2$	0	$\sigma_0 \cos\left(\frac{\pi}{2} + \delta\right)$
π	$-\gamma_0$	$\sigma_0 \cos(\delta)$
$3\pi/2$	0	$\sigma_0 \cos\left(\frac{3\pi}{2} - \delta\right)$
2π	γ_0	$\sigma_0 \cos(\delta)$

Part (f): At low frequencies, the material has sufficient time to relax, and $J' > J''$ (i.e., storage compliance > loss compliance). At high ω the opposite is true, that is, $J'' > J'$.

■ **P5.1**

The solubility parameter can be estimated with equation (5-12),

$$\delta^2 = \frac{(\Delta H_v - RT)\rho}{M} \quad (I)$$

The boiling point of toluene at 1 atm was given as 110.6°C or 383.6 K, and the enthalpy of vaporization can be estimated with the formula provided in the problem statement,

$$\Delta H_v = 23.7T_b + 0.02T_b^2 - 2950$$

$$\therefore \Delta H_v = 23.7 \times 383.6 + 0.02 \times 383.6^2 - 2950 = 9080 \text{ cal/mol}$$

Also, noting that the gas constant $R = 1.987 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$,

$$RT = 1.987 \times (273 + 25) = 592 \text{ cal/mol}$$

Substituting in (I) brings to

$$\delta = \sqrt{\frac{(9080 - 592) \times 0.87}{92}} = \boxed{8.96 \text{ (cal/cm}^3)^{1/2}}$$

■ **P5.2**

The solubility parameter of a statistical copolymer can be estimated with the weighted sum $\delta = \sum w_i \delta_i$, where δ_i is the solubility parameter of monomer i and w_i is the weight fraction of monomer i in the copolymer. The molar masses of butadiene and methyl methacrylate monomers are 54 and 100, respectively. Since the copolymer is 25 mol% methyl methacrylate, we surmise that for every mol of methyl methacrylate the copolymer contains 3 mol of butadiene. The weight fraction of methyl methacrylate is then

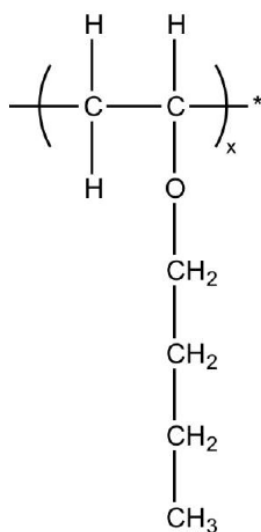
$$\chi = \frac{1 \times 100}{1 \times 100 + 3 \times 54} = 0.382$$

With reference to Table 5.3, we glean solubility parameters $\delta = 17.2 \text{ (MPa)}^{1/2} = 8.43 \text{ (cal/cm}^3)^{1/2}$ for polybutadiene and $\delta = 19.0 \text{ (MPa)}^{1/2} = 9.31 \text{ (cal/cm}^3)^{1/2}$ for poly(methyl methacrylate). Appealing to equation (5-14), the solubility parameter is then

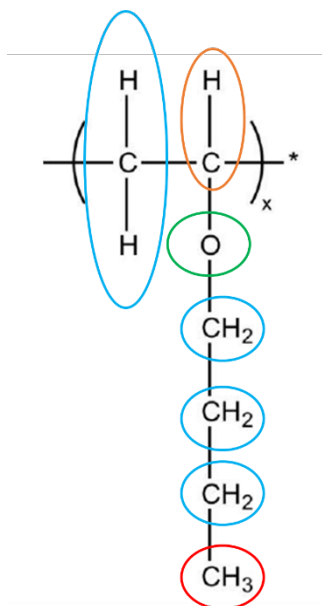
$$\delta = 0.382 \times 9.31 + (1 - 0.382) \times 8.43 = \boxed{8.77 \text{ (cal/cm}^3)^{1/2}}$$

■ **P5.3**

The polymer in question has the structure illustrated below.



Since this polymer is not listed in typical solubility parameter tables, use of molar attraction constants becomes the best way to proceed. The pertaining calculations are summarized below.



Group	F_i	No. Groups	ΣF_i
-CH ₂	131.5	4	526
-CH ₃	85.99	1	85.99
-O-	114.98	1	114.98
>CH-	148.3	1	148.3
		Total:	875.3

The molar mass of the vinyl butyl ether monomer is $108 \text{ g}\cdot\text{mol}^{-1}$. The solubility parameter can be estimated with equation (5-13):

$$\delta = \rho \sum \frac{F_i}{M_0} = 1.0 \times \frac{875.3}{108} = \boxed{8.10 \text{ (cal/cm}^3)^{1/2}}$$

■ P5.5

The ordinary solubility parameters can be read from Table 5.3; the three-dimensional solubility parameters can be gleaned from Table 5.4. Bear in mind that solubility parameters can be converted from $(\text{MPa})^{1/2}$ to $(\text{cal/cm}^3)^{1/2}$ by multiplying by a factor of 0.49.

Solvent	δ (Table 5.3)	H-bonding	Three-dim. sol. parameters (Table 5.4)		
			δ_d	δ_p	δ_H
Tetrahydrofuran	9.1	Moderate	8.3	2.8	4.0
<i>n</i> -Hexane	7.3	Poor	7.3	0	0
1-Butanol	11.4	Strong	7.9	2.8	7.8
Diethyl phthalate	7.9	Moderate	8.2	3.4	1.5

The δ_d values for the different solvents are quite close, so we need only match the δ_p and δ_H values of the solvent mixture and tetrahydrofuran. Let φ_1 , φ_2 , and φ_3 denote the volume fractions of *n*-hexane, 1-butanol, and diethyl phthalate in the mixture, respectively. Since the volume fractions must add up to 1, we may write $\varphi_3 = 1 - \varphi_1 - \varphi_2$, so that

$$\delta_p [\text{Hydrofuran}] = 2.8 = \varphi_1 \times 0 + \varphi_2 \times 2.8 + (1 - \varphi_1 - \varphi_2) \times 3.4$$

$$\therefore 2.8 = 2.8\varphi_2 + 3.4(1 - \varphi_1 - \varphi_2)$$

$$\therefore 2.8 = 2.8\varphi_2 + 3.4 - 3.4\varphi_1 - 3.4\varphi_2$$

$$\therefore -0.6 = -0.6\varphi_2 - 3.4\varphi_1$$

$$\therefore 3.4\varphi_1 + 0.6\varphi_2 = 0.6 \quad (\text{I})$$

$$\delta_H [\text{Hydrofuran}] = 4.0 = \varphi_1 \times 0 + \varphi_2 \times 7.8 + (1 - \varphi_1 - \varphi_2) \times 1.5$$

$$\therefore 4.0 = 7.8\varphi_2 + 1.5(1 - \varphi_1 - \varphi_2)$$

$$\therefore 4.0 = 7.8\varphi_2 + 1.5 - 1.5\varphi_1 - 1.5\varphi_2$$

$$\therefore 2.5 = 7.8\varphi_2 - 1.5\varphi_1 - 1.5\varphi_2$$

$$\therefore 2.5 = -1.5\varphi_1 + 6.3\varphi_2 \quad (\text{II})$$

Clearly, (I) and (II) constitute a system of linear equations with φ_1 and φ_2 as the unknowns. We can speed things up by solving this system with Mathematica's `Solve` command:

```
In[641]:= Solve[{3.4 * phi1 + 0.6 * phi2 == 0.6,
               -1.5 * phi1 + 6.3 * phi2 == 2.5}, {phi1, phi2}]
Out[641]= {{phi1 -> 0.102151, phi2 -> 0.421147}}
```

As shown, $\varphi_1 = 0.102$ and $\varphi_2 = 0.421$. The volume fraction of dioctyl phthalate easily follows,

$$\varphi_3 = 1 - \varphi_1 - \varphi_2 = 1 - 0.102 - 0.421 = 0.477$$

Thus, the desired mixture should consist of 10.2 vol% *n*-hexane, 42.1 vol% 1-butanol, and 47.7 vol% dioctyl phthalate. We can check whether this mixture indeed has a δ_d that is close to that of tetrahydrofuran:

$$\delta_d[\text{mixture}] = 0.102 \times 7.3 + 0.421 \times 7.9 + 0.477 \times 8.2 \approx 8.0$$

This is fairly close to the δ_d of THF, which is 8.3.

■ P5.8

Part (a): The critical χ can be estimated with equation (5.30),

$$\chi_{\text{critical}} = \frac{1}{2} \left(\frac{1}{\sqrt{DP_A}} + \frac{1}{\sqrt{DP_B}} \right)^2 = \frac{1}{2} \left(\frac{1}{\sqrt{1000}} + \frac{1}{\sqrt{500}} \right)^2 = \boxed{0.00291}$$

Part (b): Firstly, the reference volume at 200 K is found from the expression given in the problem statement:

$$V_0 = 20 + 0.015 \times 200 = 23.0 \text{ cm}^3/\text{mol}$$

Similarly, we use the expressions given for solubility parameters δ_A and δ_B to obtain

$$\delta_A = -0.001 \times 200 + 10 = 9.8 \text{ (cal/cm}^3)^{1/2}$$

and

$$\delta_B = -0.0008 \times 200 + 10.2 = 10.04 \text{ (cal/cm}^3)^{1/2}$$

Lastly, we insert these results into equation (5-23),

$$\chi_{AB} = \frac{V_0}{RT} (\delta_A - \delta_B)^2 = \frac{23.0}{1.987 \times 200} \times (9.8 - 10.04)^2 = \boxed{0.00333}$$

Similar calculations apply for a temperature of 600 K:

$$V_0 = 20 + 0.015 \times 600 = 29.0 \text{ cm}^3/\text{mol}$$

$$\delta_A = -0.001 \times 600 + 10 = 9.4 \text{ (cal/cm}^3)^{1/2}$$

$$\delta_B = -0.0008 \times 600 + 10.2 = 9.72 \text{ (cal/cm}^3)^{1/2}$$

$$\chi_{AB} = \frac{V_0}{RT} (\delta_A - \delta_B)^2 = \frac{29.0}{1.987 \times 600} \times (9.4 - 9.72)^2 = \boxed{0.00249}$$

Part (c): Note that, at 200 K, the interaction parameter χ_{AB} is greater than χ_{critical} , whereas at 600 K we see that χ_{AB} is less than χ_{critical} . This is indicative of an upper critical solution temperature (UCST) behavior, as illustrated in Figure 5.3.

■ P5.9

Part (a): Since 3.70×10^{-2} multiplies T^{-1} , this constant will only yield a dimensionless quantity if it has units of K (that is, kelvin to the first power). Similarly, 7.64×10^{-10} multiplies T^2 and will only yield a dimensionless quantity if it has units of K^{-2} (i.e., kelvin to the negative second power).

Part (b): Since the first term of the empirical equation implies $\chi \propto 1/T$ and the second term implies $\chi \propto T^2$, both lower critical solution temperature (LCST) and upper critical solution temperature (UCST) behaviors are expected.

Part (c): We were told to use the geometric mean of the molar volumes of A and B,

$$v = \sqrt{v_A v_B} = \sqrt{25 \times 53} = 36.4 \text{ cm}^3/\text{mol}$$

The volume associated with polymer A is $275,000/1.06 = 259,430 \text{ cm}^3/\text{mol}$.
Dividing this by the geometric-mean molar volume gives

$$\chi_A = \frac{259,430}{36.4} = 7127$$

In turn, the volume associated with polymer B is $650,000/1.20 = 541,670 \text{ cm}^3/\text{mol}$.
Dividing this by the geometric-mean molar volume yields

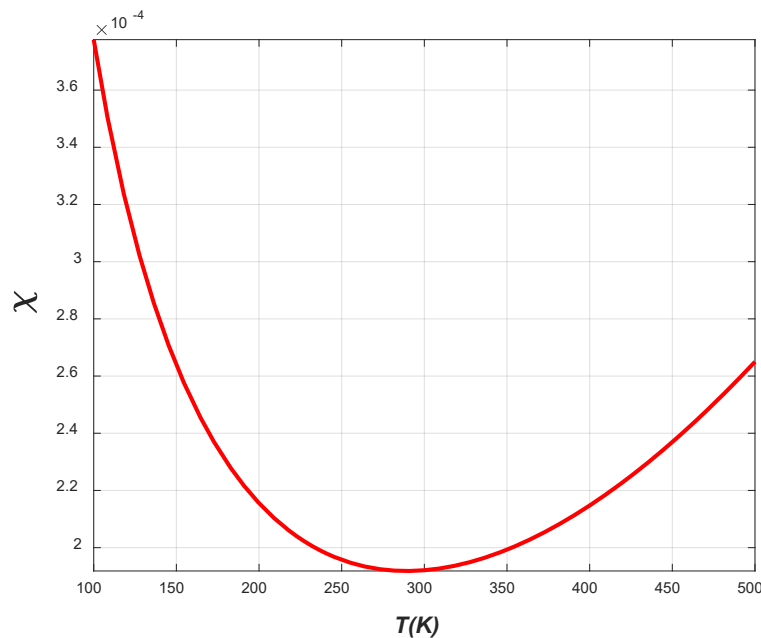
$$\chi_B = \frac{541,670}{36.4} = 14,880$$

Then, we can calculate χ_{critical} using (5.30),

$$\chi_{\text{critical}} = \frac{1}{2} \left(\frac{1}{\sqrt{\chi_A}} + \frac{1}{\sqrt{\chi_B}} \right)^2 = \frac{1}{2} \left(\frac{1}{\sqrt{7127}} + \frac{1}{\sqrt{14,880}} \right)^2 = \boxed{2.01 \times 10^{-4}}$$

Part (d): The function can be plotted with the following MATLAB code.

```
>> flory = @(T) 3.7E-2/T + 7.64E-10*T^2;
fplot(flory, [100, 500], 'LineWidth', 2, 'Color', 'red')
grid on
```



Inspecting the graph above, we see that $\chi \approx 2.01 \times 10^{-4}$ when $T \approx 230 \text{ K}$ and $T \approx 350 \text{ K}$; these are our estimates of the LCST and UCST, respectively.

■ P5.10

Part (a): Substituting $\Omega_1^\infty = 4.49$ and $v_1/v_2 = 1.1$ into the relationship in the problem statement and solving for χ , we have

$$\begin{aligned} \ln(\Omega_1^\infty) &= \ln\left(\frac{v_1}{v_2}\right) + 1 + \chi \rightarrow \ln(4.49) = \ln(1.1) + 1 + \chi \\ \therefore 1.50 &= 0.0953 + 1 + \chi \\ \therefore \chi &= 0.405 \end{aligned}$$

Since $\chi < 0.5$, the solvent and polymer are miscible under the given conditions.

Part (b): We can solve the equation derived in part (a) of Example 5-2 for volume fraction ϕ_1 , giving

$$\begin{aligned} \chi &= \ln(\gamma_1) - \left[1 + \ln\left(\frac{\phi_1}{x_1}\right) \right] \\ \therefore \chi &= \ln(\gamma_1) - 1 - \ln\left(\frac{\phi_1}{x_1}\right) \\ \therefore \chi &= \ln(\gamma_1) - 1 - \ln(\phi_1) + \ln(x_1) \end{aligned}$$

$$\therefore \chi + \ln(\phi_1) = -1 + \ln(x_1\gamma_1)$$

$$\therefore \ln(\phi_1) = \ln(x_1\gamma_1) - 1 - \chi$$

$$\therefore \phi_1 = \exp[\ln(x_1\gamma_1) - 1 - \chi]$$

$$\therefore \phi_1 = \exp[\ln(a_1) - 1 - \chi]$$

Here, we have activity coefficient

$$a_1 = \Omega_1^\infty w_1 = \gamma_1^\infty x_1 = 4.49 \times 0.002 = 0.00898$$

so that

$$\phi_1 = \exp[\ln(0.00898) - 1 - 0.405] = \boxed{0.00220}$$

The volume fraction of the solvent in the polymer is close to 0.22%.

■ P5.11

Part (a): As stated, the molar volume of the specified polystyrene polymer is 95,000 cm³/mol, whereas that of cyclohexane is 108 cm³/mol. Using the molar volume of cyclohexane as the reference volume, the chain length of PS is 95,000/108 ≈ 880. The volume of 1 g of polystyrene polymer with $M_n = 10^5$ g/mol is 95,000/10⁵ = 0.95 cm³, so the total volume of the solution becomes 0.95 + 108 = 108.95 cm³. The volume fractions are $\phi_{PS} = 0.01$ and $\phi_{cyclohexane} = 0.99$. We can determine the interaction parameter from the equation given, namely

$$\chi = 0.2035 + \frac{90.65}{T} + 0.3092\phi + 0.1554\phi^2$$

$$\therefore \chi = 0.2035 + \frac{90.65}{400} + 0.3092 \times 0.01 + 0.1554 \times 0.01^2 = 0.433$$

The change in Gibbs free energy is given by equation (5.24),

$$\Delta G_m = 8.314 \times 400 \times \left[0.433 \times 0.99 \times 0.01 + \frac{0.01}{880} \times \ln(0.01) + \frac{0.99}{1} \times \ln(0.99) \right]$$

$$\therefore \boxed{\Delta G_m = -19.0 \text{ J/mol}}$$

Part (b): The critical interaction parameter follows from equation (5.30),

$$\chi_{\text{critical}} = \frac{1}{2} \left(\frac{1}{\sqrt{880}} + \frac{1}{\sqrt{1}} \right)^2 = \boxed{0.534}$$

Part (c): The PS/CH system has a UCST.

Part (d): Equating the expression in the problem statement to $\chi = 0.5$ and solving for temperature, we have

$$\chi = 0.2035 + \frac{90.65}{T_\theta} + 0.3092\phi + 0.1554\phi^2 = 0.5$$

$$\therefore 0.5 = 0.2035 + \frac{90.65}{T_\theta} + 0.3092 \times 0.1 + 0.1554 \times 0.1^2$$

$$\therefore 0.5 = 0.2035 + \frac{90.65}{T_\theta} + 0.0309 + 0.00156$$

$$\therefore 0.5 = 0.236 + \frac{90.65}{T_\theta}$$

$$\therefore T_\theta = \frac{90.65}{0.5 - 0.236} = \boxed{343.4 \text{ K}}$$

■ P7.1

Two NH₂ groups react with one COOφ group and the number of NH₂ groups is twice that of COOφ, so the average functionality is $f_{av} = 2$. The number-average degree of polymerization is then $\bar{X}_n = 2 \times 200 = 400$. Solving (7-19) for p , we get

$$\bar{X}_n = \frac{2}{2 - pf_{av}} \rightarrow 400 = \frac{2}{2 - 2p}$$

$$\therefore 400 = \frac{1}{1 - p}$$

$$\therefore 1 - p = \frac{1}{400}$$

$$\therefore 1 - p = 0.0025$$

$$\therefore p = 1 - 0.0025 = \boxed{0.9975}$$

An extent of reaction of 99.75% is required.

■ **P7.3**

The functionalities and equivalents are tabulated below.

	Moles	f	Equivalents
Pentarerythritol	1.21	4	$4 \times 1.21 = 4.84$
Phthalic anhydride	0.50	2	$2 \times 0.50 = 1.00$
Tricarballic acid	0.49	3	$3 \times 0.49 = 1.47$
	Total = 2.20		Total = 7.31

The total OH equivalents amount to 4.84; the total acid equivalents amount to $1.0 + 1.47 = 2.47$. Since the acid equivalents are in deficient supply, the average functionality is computed on the basis of acid equivalents, that is,

$$f_{av} = \frac{2 \times 2.47}{2.20} = 2.25$$

Now, the mixture gels when the number-average degree of polymerization given by the Carothers equation tends to infinity, that is,

$$\bar{X}_n = \frac{2}{2 - pf_{av}} = \infty$$

This implies that

$$2 - pf_{av} = 0$$

$$\therefore 2 - p \times 2.25 = 0$$

$$\therefore p = \frac{2}{2.25} = 0.889 = 88.9\%$$

Thus, the system will gel before 100% extent of reaction is achieved.

■ **P7.5**

Part (a): Since acid equivalents are in deficient supply, the average functionality is computed on the basis of COOH,

$$f_{av} = \frac{2 \times 3.62}{4.11} = 1.76$$

The number-average degree of polymerization then becomes

$$\bar{X}_n = \frac{2}{2 - pf_{av}} = \frac{2}{2 - 1.76} = \boxed{8.33}$$

Part (b): The equivalents (without ethylene glycol) are tabulated below.

	Moles	f	Equivalents
Oleic acid	1	1	1.0
Phthalic acid	1.31	2	2.62
Glycerol	1.30	3	3.90

The total acid equivalents are $1.0 + 2.62 = 3.62$; the total OH equivalents are 3.90. The average functionality then becomes

$$f_{av} = \frac{2 \times 3.62}{3.61} = 2.00554$$

The operator will notice his mistake when the mixture gels, that is, when

$$\begin{aligned}\bar{X}_n = \infty &= \frac{2}{2 - p \times 2.00554} \\ \therefore 2 - p \times 2.00554 &= 0 \\ \therefore p &= \frac{2}{2.00554} = 0.9972\end{aligned}$$

The mixture will gel at 99.72% conversion.

■ **P7.6**

Part (a): Using the Flory-Schulz distribution with $i = 1$ and $p = 0.9$, we obtain

$$w_i = i(1-p)^2 p^{i-1} = 1 \times (1-0.9)^2 \times 0.9^{1-1} = 0.01$$

1% by weight of monomer will remain after 90% of functional groups have reacted.

Part (b): The number-average degree of polymerization is

$$\bar{X}_n = \frac{1}{1-p} = \frac{1}{1-0.9} = 10$$

and the corresponding molecular weight is

$$\bar{M}_n = \bar{X}_n \times 183 = 10 \times 183 = \boxed{1830}$$

Next, the weight-average degree of polymerization is

$$\bar{X}_w = \frac{1+p}{1-p} = \frac{1+0.9}{1-0.9} = 19$$

and the corresponding molecular weight is

$$\bar{M}_w = \bar{X}_w \times 183 = 19 \times 183 = \boxed{3480}$$

Finally, the z-average degree of polymerization is

$$\bar{X}_z = \frac{1+4p+p^2}{1-p^2} = \frac{1+4 \times 0.9+0.9^2}{1-0.9^2} = 28.5$$

and the corresponding molecular weight is

$$\bar{M}_z = \bar{X}_z \times 183 = 28.5 \times 183 = \boxed{5220}$$

■ **P7.11**

The equivalents are tabulated below.

	Moles	f	Equivalents
Pentaerythritol	1.21	4	4.84
Phthalic anhydride	0.54	2	1.08
Tricarballic acid	0.49	3	1.47
	Total: 2.20		

The total acid equivalents = (1.08 + 1.47) = 2.55; the total OH equivalents = 4.84. Since the acid equivalents are in deficient supply, the average functionality is computed on the basis of acid equivalents,

$$f_{av} = \frac{2 \times 2.55}{2.20} = 2.32$$

Writing the Carothers equation for this mixture,

$$\bar{X}_n = \frac{2}{2 - pf_{av}} = \frac{2}{2 - 2.32p}$$

When the mixture gels, \bar{X}_n is infinite and $2 - 2.32p = 0$, giving

$$2 - 2.32p = 0$$

$$\therefore p = \frac{2}{2.32} = 0.862 = 86.2\%$$

The extent of reaction at gelling is about 86%. The equations mentioned in the problem statement ($x_i = (1 - p)p^{i-1}$ and $w_i = i(1 - p)^2p^{i-1}$) are based on bifunctional monomers and cannot be used for the present case, which involves branching units constituted of multiple functional groups.

■ P7.12

Part (a): Given that N is the number of bifunctional monomers, the average functionality becomes

$$f_{av} = \frac{\cancel{N} \times 2}{\cancel{N}} = 2$$

Part (b): The reaction mixture will not gel because $\bar{X}_n \rightarrow \infty$ when $p = 1$.

Part (c): According to equation (7-22), we may write the step-growth polymerization distribution

$$x_i \equiv (1 - p)p^{i-1}$$

When $i = 1$, co-reactive sites are unreacted. The probability of finding unreactive monomers is

$$x_1 = (1 - p) \times p^{1-1} = (1 - p)$$

Similarly, the probability of finding sensitive monomers is

$$1 - x_1 = 1 - (1 - p) = p$$

Part (d): Substituting $p = 0.99$ and $i = 10$ into (7-22) yields

$$x_{10} = (1 - 0.99) \times 0.99^{10-1} = \boxed{0.00914}$$

Part (e): According to Figure 7.5(a), the monomer is the most prevalent species on a mole basis at $p = 0.99$ and $x_1 = (1 - 0.99) = 0.01$. As discussed in page 327, the value of i for peak probable size is given by

$$i = -\frac{1}{\ln p} = -\frac{1}{\ln(0.99)} = 99.5 \approx 100$$

The corresponding weight fraction is

$$w_{100} = 100 \times (1 - 0.99)^2 \times 0.99^{100-1} = \boxed{0.00370}$$

Part (f): The polydispersity index is given by equation (7.36),

$$PDI = \frac{\bar{X}_w}{\bar{X}_n} = 1 + p = 1 + 0.99 = \boxed{1.99}$$

The standard deviation is given by equation (7.38):

$$s_n = \sqrt{p\bar{M}_n} = \sqrt{0.99} \times 12,000 = \boxed{11,940}$$

■ P7.13

Part (a): We were given the equation

$$\sigma_n^2 = M_w M_n - M_n^2 \quad (I)$$

Solving the polydispersity index equation (7-36) for M_w ,

$$\frac{M_w}{M_n} = 1 + p \rightarrow M_w = (1 + p)M_n$$

Substituting in (I),

$$\sigma_n^2 = M_w M_n - M_n^2 = (1 + p)M_n \times M_n - M_n^2$$

$$\therefore \sigma_n^2 = (1 + p - 1)M_n^2$$

$$\therefore \sigma_n^2 = p \times M_n^2$$

$$\therefore \boxed{\sigma_n = \sqrt{p} \times M_n}$$

as we intended to show.

Part (b): The functionalities are listed in part (c).

Part (c): The equivalents are calculated in the following table.

Monomer	Functionality	Moles	Equivalents
A AA	3	875/350 = 2.5	3 × 2.5 = 7.5
BB	2	2000/1000 = 2.0	2 × 2.0 = 4.0
CC	2	15/150 = 0.1	2 × 0.1 = 0.2
C CC	3	225/225 = 1.0	3 × 1.0 = 3.0

Part (d): The total equivalents of A amount to 7.5; the total amounts of B and C amount to 4.0 + 0.2 + 3.0 = 7.2. Since B and C are in deficient supply, the average functionality is computed on the basis of these components. The value of f_{av} is

$$f_{av} = \frac{2 \times 7.2}{2.5 + 2.0 + 0.1 + 1.0} = \boxed{2.57}$$

Part (e): At gelation, the Carothers equation tends to infinity,

$$\bar{X}_n = \frac{2}{2 - pf_{av}} = \infty$$

so that

$$\begin{aligned} 2 - pf_{av} &= 0 \\ \therefore 2 - p \times 2.57 &= 0 \\ \therefore p &= \frac{2}{2.57} = 0.778 = \boxed{77.8\%} \end{aligned}$$

Gelation occurs at an extent of reaction close to 78%.

Part (f): The polydispersity index is given by equation (7-36), namely

$$PDI = \frac{\bar{M}_w}{\bar{M}_n} = 1 + p = 1 + 0.778 = \boxed{1.78}$$

Part (g): We have $M_w = 12,000$ and the extent of reaction $p = 0.778$, which was determined in part (e); then, the number-average molecular weight follows from equation (7-36),

$$\begin{aligned} \frac{\bar{M}_w}{\bar{M}_n} &= 1 + p \rightarrow \bar{M}_n = \frac{\bar{M}_w}{1 + p} \\ \therefore \bar{M}_n &= \frac{12,000}{1 + 0.778} = 6750 \end{aligned}$$

The standard deviation of the number distribution is given by (7-38),

$$s_n = \sqrt{p\bar{M}_n} = \sqrt{0.778 \times 6750} = \boxed{5950}$$

■ P8.1

Part (a): The number-average degree of polymerization for the polymer in question is $\bar{DP}_n = 138,000/104 = 1330$. Resorting to equation (8.64) with $k_{tc} = k_t$ and $k_{td} = 0$, we may write

$$\bar{DP}_n = 1330 = \frac{k_p^2 [M]^2}{k_t R_p} = \frac{k_p^2 \times 1.0^2}{10^8 \times (1.5 \times 10^{-7})}$$

$$\therefore 1330 = 0.0667 k_p^2$$

$$\therefore k_p = \sqrt{\frac{1330}{0.0667}} = \boxed{141 \text{ L}/(\text{mol} \cdot \text{s})}$$

Part (b): The radical lifetime can be estimated with equation (8-94),

$$\tau = \frac{k_p [M]}{2k_t R_p} = \frac{141 \times 1.0}{2 \times 10^8 \times (1.5 \times 10^{-7})} = \boxed{4.7 \text{ s}}$$

■ P8.2

The equation to use is (8-77b), with the result that

$$\frac{1}{(\overline{DP}_n)} = \frac{1}{(\overline{DP}_n)_0} + C \frac{[\text{Ta}]}{[\text{M}]}$$

$$\therefore \frac{104}{85,000} = \frac{104}{138,000} + 3.7 \times \frac{[\text{Ta}]}{1.0}$$

$$\therefore [\text{Ta}] = \frac{1}{3.7} \times \left(\frac{104}{85,000} - \frac{104}{138,000} \right) = 1.27 \times 10^{-4} \text{ mol/L}$$

$$\therefore \boxed{[\text{Ta}] = 0.127 \text{ mmol/L}}$$

■ P8.3

The degree of polymerization of the polystyrene polymer mentioned in the problem statement is $\overline{DP}_n = 200,000/104 = 1923$. Converting the polymerization rate from (g polymer)/liter/min to (mol polymer)/liter/sec, we have

$$R_p = \frac{0.011}{104 \times 60} = 1.763 \times 10^{-6} \text{ (mol monomer)/L/sec}$$

Appealing to equation (8-64) with $k_{tc} = k_t$ and $k_{td} = 0$, we may write

$$\overline{DP}_n = \frac{k_p^2 [\text{M}]^2}{R_p k_t} \rightarrow \frac{[\text{M}] k_p}{k_t^{1/2}} = \sqrt{\overline{DP}_n \times R_p}$$

$$\therefore \frac{[\text{M}] k_p}{k_t^{1/2}} = \sqrt{1923 \times (1.763 \times 10^{-6})} = 0.0582$$

When an initiator is included in the mixture, we obtain an additional contribution R'_p to the polymerization rate, namely

$$R'_p = \frac{k_p [\text{M}]}{k_t^{1/2}} (fk_d [\text{I}])^{1/2} = 0.0582 \times (0.8 \times 10^{-4} \times 0.1)^{1/2} = 1.646 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$$

The total rate of polymerization is

$$R_p + R'_p = 1.763 \times 10^{-6} + 1.646 \times 10^{-4} = 1.664 \times 10^{-4} \text{ (mol monomer)} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$$

$$\therefore R_p + R'_p = 1.664 \times 10^{-4} \frac{\text{(mol monomer)} \cdot \text{L}^{-1} \cdot \text{s}^{-1} \times 104 \text{ g}}{\text{(mol monomer)}}$$

$$\therefore R_p + R'_p = \boxed{0.0173 \text{ (g polymer)} \cdot \text{L}^{-1} \cdot \text{s}^{-1}}$$

■ P8.5

Part (a): Noting that the molar mass of acrylamide is $71 \text{ g} \cdot \text{mol}^{-1}$, the molar concentration of the acrylamide solution mentioned in the problem statement is $[\text{M}] = 100/71 = 1.41 \text{ mol/L}$. Given the half-life of isobutyryl peroxide $t_{1/2} = 9 \text{ h} = 32,400 \text{ sec}$, we proceed to compute the initiation constant k_d ,

$$k_d = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{32,400} = 2.14 \times 10^{-5} \text{ s}^{-1}$$

so that, referring to equation (8-29), we obtain

$$R_d = \frac{k_p [\text{M}]}{k_t^{1/2}} (fk_d [\text{I}])^{1/2} = \sqrt{22} \times 1.41 \times \left[0.3 \times (2.14 \times 10^{-5}) \times 0.1 \right]^{1/2}$$

$$\therefore R_d = 5.30 \times 10^{-3} \text{ (mol monomer)} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$$

$$\therefore R_d = 5.30 \times 10^{-3} \times 76 = \boxed{0.403 \text{ (g polymer)} \cdot \text{L}^{-1} \cdot \text{s}^{-1}}$$

Part (b): The amount of polymer at time $t = 10 \text{ min} = 600 \text{ sec}$ can be estimated with equation (8-35),

$$-\ln\left(\frac{[M]}{[M]_0}\right) = \frac{2k_p}{k_t^{1/2}} \left(\frac{f[I]_0}{k_d}\right)^{1/2} (1 - e^{-k_d t/2})$$

$$\therefore -\ln\left(\frac{[M]}{[M]_0}\right) = 2 \times \sqrt{22} \times \left(\frac{0.3 \times 0.1}{2 \times 10^{-5}}\right)^{1/2} \times \left\{1 - \exp\left[-\frac{(2.14 \times 10^{-5}) \times 600}{2}\right]\right\}$$

$$\therefore -\ln\left(\frac{[M]}{[M]_0}\right) = 2.33$$

$$\therefore \frac{[M]}{[M]_0} = e^{-2.33}$$

$$\therefore [M] = e^{-2.33} \times [M]_0 = 0.0973[M]_0$$

Accordingly, the amount of polymer made is 10 minutes is

$$[M]_0 - [M] = (1 - 0.0973) \times [M]_0$$

$$\therefore [M]_0 - [M] = (1 - 0.0973) \times 100 = \boxed{90.3 \text{ g/L}}$$

■ P8.6

Part (a): Firstly, the molar concentration of the MMA solution is

$$[M] = 0.94 \frac{\text{g}}{\text{cm}^3} \times 1000 \frac{\text{cm}^3}{\text{L}} \times \frac{1}{100 \text{ g/mol}} = 9.4 \text{ mol/L}$$

Similarly, the concentration of initiator in the solution is $[I] = 10.2 \text{ mol}/100 \text{ L} = 0.102 \text{ M}$. We also need the initiation constant, which can be found from the given half-life of initiator,

$$t_{1/2} = \frac{\ln 2}{k_d} \rightarrow k_d = \frac{\ln 2}{t_{1/2}}$$

$$\therefore k_d = \frac{\ln 2}{50 \times 3600} = 3.85 \times 10^{-6} \text{ s}^{-1}$$

Then, the kinetic chain length is given by equation (8-60),

$$\nu = \frac{k_p [M]}{2(fk_d k_t [I])^{1/2}} = \frac{5.5 \times 9.4}{2 \times [0.3 \times (3.85 \times 10^{-6}) \times (25.5 \times 10^6) \times 0.102]^{1/2}} = \boxed{14.9}$$

Part (b): Using equation (8-35), we find that

$$-\ln\left(\frac{[M]}{[M]_0}\right) = \frac{2k_p}{k_t^{1/2}} \left(\frac{f[I]_0}{k_d}\right)^{1/2} (1 - e^{-k_d t/2})$$

$$\therefore -\ln\left(\frac{[M]}{[M]_0}\right) = \frac{2 \times 5.5}{\sqrt{25.5 \times 10^6}} \times \left(\frac{0.3 \times 0.102}{3.85 \times 10^{-6}}\right)^{1/2} \times \left\{1 - \exp\left[-\frac{(3.85 \times 10^{-6}) \times (5 \times 3600)}{2}\right]\right\}$$

$$\therefore \frac{[M]}{[M]_0} = 0.9934$$

The amount of monomer consumed is

$$[M]_0 - [M] = (9.40 - 0.9934 \times 9.40) \times 100 = 6.20 \text{ mol}$$

and the amount of monomer made is $6.20 \times 100 = 620 \text{ g}$.

■ P8.10

We first write kinetic differential equations for the monomer M and the transfer agent TH,

$$-\frac{d}{dt}[\text{TH}] = k_{tr} [\text{M}^*][\text{TH}] \quad (\text{I})$$

$$-\frac{d}{dt}[\text{M}] = k_p [\text{M}][\text{M}^*] \quad (\text{II})$$

Dividing (I) by (II), separating variables and integrating,

$$\begin{aligned} \frac{-d[\text{TH}]/dt}{-d[\text{M}]/dt} &= \frac{k_{tr} \cancel{[\text{M}^*]}[\text{TH}]}{k_p [\text{M}] \cancel{[\text{M}^*]}} \\ \therefore \frac{d[\text{TH}]}{d[\text{M}]} &= \frac{k_{tr} [\text{TH}]}{\underbrace{k_p}_{=C} [\text{M}]} \\ \therefore \frac{d[\text{TH}]}{[\text{TH}]} &= C \frac{d[\text{M}]}{[\text{M}]} \\ \therefore \int_{[\text{TH}]_0}^{[\text{TH}]} \frac{d[\text{TH}]}{[\text{TH}]} &= C \int_{[\text{M}]_0}^{[\text{M}]} \frac{d[\text{M}]}{[\text{M}]} \\ \therefore \ln\left(\frac{[\text{TH}]}{[\text{TH}]_0}\right) &= C \times \ln\left(\frac{[\text{M}]}{[\text{M}]_0}\right) \\ \therefore C &= \frac{\ln([\text{TH}]/[\text{TH}]_0)}{\ln([\text{M}]/[\text{M}]_0)} = \frac{\ln(0.007/0.01)}{\ln(0.85/1.0)} = \boxed{2.19} \end{aligned}$$

■ P9.1

Part (a): The copolymer composition ratio is given by equation (9-13),

$$\frac{d[\text{M}_1]}{d[\text{M}_2]} = \frac{[\text{M}_1](r_1[\text{M}_1] + [\text{M}_2])}{[\text{M}_2](r_2[\text{M}_2] + [\text{M}_1])} = \frac{5.0 \times (0.40 \times 5.0 + 1.0)}{1.0 \times (0.69 \times 1.0 + 5.0)} = 2.64$$

The copolymer shall have 2.64 moles of methyl methacrylate for every mole of 5-ethyl-2-vinyl pyridine.

Part (b): The azeotropic composition ratio is given by equation (9-22),

$$\left(\frac{[\text{M}_1]}{[\text{M}_2]}\right)_{\text{azeotrope}} = \frac{1-r_2}{1-r_1} = \frac{1-0.69}{1-0.40} = \boxed{0.517}$$

■ P9.2

Let subscripts 1, 2 and 3 refer to methacrylonitrile (MAN), styrene (S) and α -methylstyrene (AMS), respectively. We then have $M_1 = 0.414$, $M_2 = 0.424$, $M_3 = 0.162$, $r_{12} = 0.44$, $r_{21} = 0.37$, $r_{13} = 0.38$, $r_{31} = 0.53$, $r_{23} = 1.124$, and $r_{32} = 0.627$. We proceed to compute the composition ratio given by (9-44),

$$\begin{aligned} \frac{dM_1}{dM_3} &= \frac{M_1(M_1 r_{23} r_{32} + M_2 r_{31} r_{23} + M_3 r_{32} r_{21})(M_1 r_{12} r_{13} + M_2 r_{13} + M_3 r_{12})}{M_3(M_1 r_{12} r_{23} + M_2 r_{13} r_{21} + M_3 r_{12} r_{21})(M_3 r_{31} r_{32} + M_1 r_{32} + M_2 r_{31})} \\ \frac{dM_1}{dM_3} &= \frac{\left[\begin{array}{c} 0.414 \times (0.414 \times 1.124 \times 0.627 + 0.424 \times 0.53 \times 1.124 + 0.162 \times 0.627 \times 0.37) \\ \times (0.414 \times 0.44 \times 0.38 + 0.424 \times 0.38 + 0.162 \times 0.44) \end{array} \right]}{\left[\begin{array}{c} 0.162 \times (0.414 \times 0.44 \times 1.124 + 0.424 \times 0.38 \times 0.37 + 0.162 \times 0.44 \times 0.37) \\ \times (0.162 \times 0.53 \times 0.627 + 0.414 \times 0.627 + 0.424 \times 0.53) \end{array} \right]} \\ \therefore \frac{dM_1}{dM_3} &= 2.867 \end{aligned}$$

In turn, using (9-45),

$$\frac{dM_2}{dM_3} = \frac{M_2(M_1 r_{32} r_{13} + M_2 r_{13} r_{31} + M_3 r_{12} r_{31})(M_2 r_{21} r_{23} + M_1 r_{23} + M_3 r_{21})}{M_3(M_1 r_{12} r_{23} + M_2 r_{13} r_{21} + M_3 r_{12} r_{21})(M_3 r_{31} r_{32} + M_1 r_{32} + M_2 r_{31})}$$

$$\frac{dM_2}{dM_3} = \frac{\left[\begin{array}{l} 0.424 \times (0.414 \times 0.627 \times 0.38 + 0.424 \times 0.38 \times 0.53 + 0.162 \times 0.44 \times 0.53) \\ \times (0.424 \times 0.37 \times 1.124 + 0.414 \times 1.124 + 0.162 \times 0.37) \end{array} \right]}{\left[\begin{array}{l} 0.162 \times (0.414 \times 0.44 \times 1.124 + 0.424 \times 0.38 \times 0.37 + 0.162 \times 0.44 \times 0.37) \\ \times (0.162 \times 0.53 \times 0.627 + 0.414 \times 0.627 + 0.424 \times 0.53) \end{array} \right]}$$

$$\therefore \frac{dM_2}{dM_3} = 2.603$$

If $dM_3 = 1$ for every mole of M_3 in the copolymer, $dM_2 = 2.603$ and $dM_1 = 2.867$. The corresponding mole fractions are calculated below.

$$F_1 = \frac{2.867}{1 + 2.867 + 2.603} = \boxed{0.443}$$

$$F_2 = \frac{2.603}{1 + 2.867 + 2.603} = \boxed{0.402}$$

$$F_3 = 1 - F_1 - F_2 = 1 - 0.443 - 0.402 = \boxed{0.155}$$

■ P9.3

Denoting methacrylonitrile and styrene with subscripts 1 and 2, respectively, we may write

$$f_1 = \frac{[M_1]}{[M_1] + [M_2]} = 0.3$$

$$f_2 = \frac{[M_2]}{[M_1] + [M_2]} = 0.7$$

so that

$$\frac{\frac{[M_1]}{\cancel{[M_1] + [M_2]}}}{\frac{[M_2]}{\cancel{[M_1] + [M_2]}}} = \frac{[M_1]}{[M_2]} = \frac{0.3}{0.7} = 0.429$$

Now, the number average length \bar{N}_1 is given by (9-57),

$$\bar{N}_1 = \frac{1}{P_{12}}$$

where P_{12} can be taken from (9-50), giving

$$\bar{N}_1 = \frac{1}{\left(\frac{1}{r_1 ([M_1]/[M_2]) + 1} \right)} = r_1 ([M_1]/[M_2]) + 1$$

We already have $[M_1]/[M_2] = 0.429$. In turn, reactivity ratio $r_1 = 0.44$ for MAN/S copolymer can be taken from the statement of Problem 9.2, so that

$$\bar{N}_1 = 0.44 \times 0.429 + 1 = \boxed{1.19}$$

Similarly, for the sequence of styrene units, we combine (9-58) and (9-52) to obtain

$$\bar{N}_2 = \frac{1}{P_{21}} = \frac{1}{\left(\frac{[M_1]/[M_2]}{[M_1]/[M_2] + r_2} \right)} = \frac{[M_1]/[M_2] + r_2}{[M_1]/[M_2]}$$

$$\therefore \bar{N}_2 = \frac{0.429 + 0.37}{0.429} = \boxed{1.86}$$

Note that $r_2 = 0.37$ was taken from Problem 9.2.

■ P9.5

Part (a): We first use equation (9-49) to compute probability P_{11} ,

$$P_{11} = \frac{r_1 f_1}{r_1 f_1 + f_2} = \frac{0.9 \times 0.75}{0.9 \times 0.75 + 0.25} = 0.730$$

Now, the fraction of acrylonitrile sequences with one acrylonitrile unit is (see equation (9-53))

$$N(M_1, n_i = 1) = P_{11}^{1-1} \times (1 - P_{11}) = 1 \times (1 - 0.730) = 0.270$$

while the fraction with two units is

$$N(M_1, n_i = 2) = P_{11}^{2-1} \times (1 - P_{11}) = 0.730 \times (1 - 0.730) = 0.197$$

Subtracting these results from 1 gives the fraction of sequences with 3 or more acrylonitrile units,

$$N(M_1, n_i \geq 3) = 1 - N(M_1, 1) - N(M_1, 2) = 1 - 0.270 - 0.197 = \boxed{0.533}$$

Part (b): The azeotropic mole fraction of acrylonitrile is given by (9-23),

$$(f_1)_{\text{azeotrope}} = \frac{1 - r_2}{2 - r_1 - r_2} = \frac{1 - 0.4}{2 - 0.9 - 0.4} = \boxed{0.857}$$

■ P9.9

Let subscripts 1 and 2 denote ethylene and polypropylene, respectively. From the problem statement, we have $r_1 = 5$. Since the polymer is to have 70 mol% ethylene (or 30 mol% polypropylene), we have $F_1 = 0.70$. Solving for mole fraction f_1 , we may write

$$F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2} = 0.7$$

$$\therefore \frac{r_1 f_1}{r_1 f_1 + (1 - f_1)} = 0.7$$

$$\therefore \frac{5f_1}{5f_1 + 1 - f_1} = 0.7$$

$$\therefore \frac{5f_1}{4f_1 + 1} = 0.7$$

$$\therefore 5f_1 = 0.7 + 2.8f_1$$

$$\therefore 2.2f_1 = 0.7$$

$$\therefore f_1 = \frac{0.7}{2.2} = 0.318$$

Thus, the gas phase composition desired is 31.8 mol% ethylene and 68.2 mol% propylene.

■ P9.10

Referring to Table 9.1, we read reactivity ratios $r_1 = 1.4$ and $r_2 = 0.65$. Setting $F_1 = 0.95$ in equation (9-14), we have

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} = 0.95$$

$$\therefore \frac{1.4f_1^2 + f_1 f_2}{1.4f_1^2 + 2f_1 f_2 + 0.65f_2^2} = 0.95$$

$$\therefore \frac{1.4f_1^2 + f_1 \times (1 - f_1)}{1.4f_1^2 + 2f_1 \times (1 - f_1) + 0.65 \times (1 - f_1)^2} = 0.95$$

$$\therefore \frac{0.4f_1^2 + f_1}{0.05f_1^2 + 0.7f_1 + 0.65} = 0.95$$

$$\therefore 0.4f_1^2 + f_1 = 0.0475f_1^2 + 0.665f_1 + 0.618$$

$$\therefore -0.353f_1^2 - 0.335f_1 + 0.618 = 0$$

$$\therefore f_1 = \frac{0.335 - \sqrt{(-0.335)^2 - 4 \times (-0.353) \times 0.618}}{2 \times (-0.353)} = 0.931$$

In conclusion, the monomer feed should consist of 93.1 mol% vinyl chloride and 6.9% vinyl acetate.



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