1 331 Problems

Basic chemistry review

Some basic problems having to do with the chemical structures of polymers.

1) Calculate the repeat unit molecular weights for each of the 22 polymers shown in the 'common polymers' section of the text.

2) Draw Lewis diagrams illustrating the valence shell configurations for polystyrene, poly(methyl methacrylate) and poly(dimethylsiloxane).

3) Draw Lewis diagrams illustrating the valence shell configurations for amide, ester and urethane linkages.

Polymerization Reactions

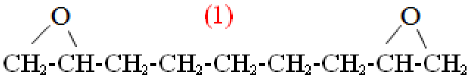
4) Suppose a polyester is formed by combining 1.00 mol of a diacid (2 acid groups per molecule) with 1.01 mol of a dialcohol in a homogeneous solution. The molecular weight of the diacid is 160g/mol and the molecular weight of the dialcohol is 180 g/mol.

(a) What is the highest value of M_n that can be expected from this combination?

(b) How many grams of water will be produced during the polymerization reaction?

5) Consider the following 5 monomers:

(1)



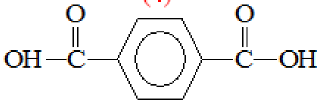
(2)

$O=C=NR_1N=C=0$

(3)

$H_2NCH_2CH_2NH_2$

(4)



(5)

HOCH2CH2OH

(a) Draw the repeat units for three linear polymers that can be produced by reactions between the monomers in this list. Identify these polymers according to their type (polyamides, polyesters, etc.), and indicate whether each polymerization reaction is condensation reaction or not.

(b) What combination of monomers from this list would you choose in order to produce a three-dimensional network?

(c) Draw the repeat unit structure of a linear polyamide formed by a condensation polymerization involving a combination of the molecules from this list, and identify the condensation product.

6) Suppose a diamine (primary amines at each of the molecule) is reacted with a di-epoxide (epoxide groups at each end of the molecule).

(a) What ratio of diamine molecules to di-epoxide molecules would you use in order to optimize the ability of the system to gel (i.e., form a network)?

(b) Estimate the fraction of amine groups will need to react in order for a gel to form? Identify any assumptions that you have made in arriving at this number.

7) Why is tacticity relevant for polystyrene or polypropylene, but not polyethylene?

8) Describe methods that could be used to make the following two block copolymers:

(a) A polystyrene/polyisoprene diblock polymer

(b) A mutiblock copolymer consisting of alternating Nylon 6-6 and Nylon 6-10 blocks.

(c) Comment on the polydispersity of block lengths, and of the number of blocks within a molecule, which can obtained by the methods described in parts a and b.

9) A step-growth reactions takes place between 1.2 moles of dicarboxylic acid, 0.4 moles of glycerol (a trifunctional alcohol) and 0.6 moles of ethylene glycol (a difunctional alcohol). Calculate the critical extent of reaction for gelation using the Carothers theory. Describe why you would expect gelation to occur for values of p that are different from this predicted value. (Hint: you will need to generalize the expression for the average functionality,f_{av}, to include the possibility of more than two different monomers.)

10) In 1963 Karl Ziegler and Giulio Natta received the Nobel prize in chemistry for the development of processes which could be used to produce (among other things) linear, unbranched isotactic polypropylene. Why was this an important development? What useful properties does isotactic polypropylene have when compared to atactic polypropylene? Describe some applications where isotactic polypropylene could be used, but where it would be impractical to use atactic polypropylene. (Note: the glass transition temperature of both forms of polypropylene is well below room temperature.)

11) "Living" polymerizations are chain growth polymerizations that proceed without termination or chain transfer reactions.

(a) Discuss the conditions that must be met in order for polymers with a low polydispersity to be formed by a living polymerization.

(b) What type of reactions must be avoided in order to produce block copolymers by radical chain growth polymerization.

(c) Proteins are perfectly disperse copolymers, with a polydispersity index of exactly 1. While relatively monodisperse polymers ($M_w/M_n < 1.05$) can be made by living polymerization methods like anionic polymerization, it is not possible to make perfectly monodisperse polymer by these methods, even when termination and chain transfer events are completely eliminated. Why is that?

12) Suppose 100 moles of styrene monomer are polymerized by anionic polymerization, using 0.1 mole of initiator.

(a) Draw the repeat unit structure of the polymer which is formed in this reaction.

(b) Below what temperature will this polymer behave as a rigid material?

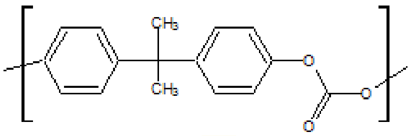
(c) Suppose that there are no chain transfer or termination events during the resulting polymerization. Calculate the number average molecular weight (M_n) of the polymer that is produced.

13) Suppose nylon is formed in two separate batches by reacting the same sets of monomers with one another. In the first reaction, an extent of reaction of 0.999 is obtained. In the second reaction, an extent of reaction of 0.9999 is obtained. Assume that an ideal distribution of molecular weights is obtained for each reaction.

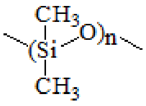
(a) What is the ratio of M_w for the second reaction to M_w for the first reaction?

(b) Suppose equal weights of the polymers formed by these two reactions are mixed with one another. What is the polydispersity index of the resultant mixture?

14) Draw the chemical structures of the monomers from which the following polymers are formed.



a



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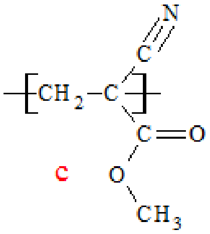
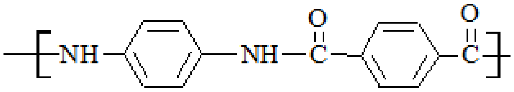


c



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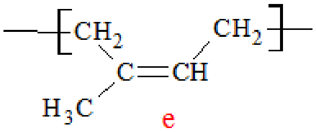

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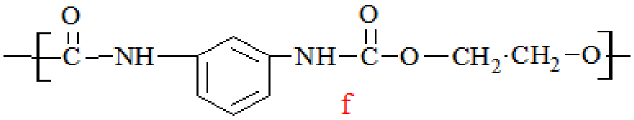


f

15) Suppose you want to sell a set of cheap plastic mugs which are suitable for drinking coffee. Briefly discuss the potential applicability of the following materials for this purpose:

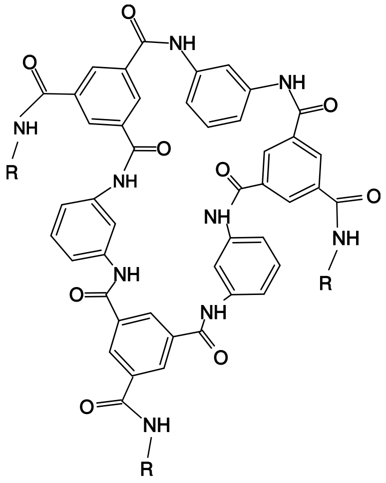
(a) atactic polystyrene

(b) atactic poly(vinyl chloride)

(c) high density polyethylene

16) Consider the the piece of the highly crosslinked chemical structure shown below.

(a) Draw the chemical structures of the two different monomers that were used to form this material. (Note that the R groups just represent connections to the rest of the material, they are not part of the structures you need to draw).



(b) What type of polymer is this (polyester, polyamide, polyurethane, epoxy, etc.)

(c) Next to each structure that you have drawn in part a, indicate its chemical functionality.

(d) What is the relative amount of each of the two monomers from part a (in moles) that you should be added to one another to optimize the polymerization?

(e) Assuming that the two monomers are added together in optimum proportions you mentioned in part d, what fraction of reactive groups need to react to form an insoluble gel.

The Glass Transition

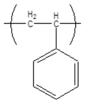
17) An amorphous polymer has$T_\infty = 50^\circ C$. The thermal expansion coefficient in the glassy state is$3 \times 10^{-4}/^\circ C$, and the thermal expansion coefficient in the liquid state is$4.5 \times 10^{-4}/^\circ C$.

(a) Calculate the glass transition temperature if the fractional free volume at the glass transition is 0.025.

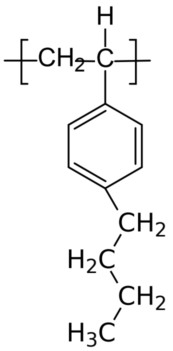
(b) The glass transition temperature measured at a different cooling rate is found to correspond to a fractional free volume of 0.021. Is this cooling rate higher of lower than the cooling rate from part a?

(c) Rank these three polymers in the order of highT_g to lowT_g, and provide an explanation for your prediction:

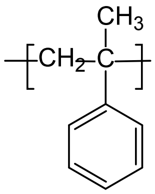
Polystyrene



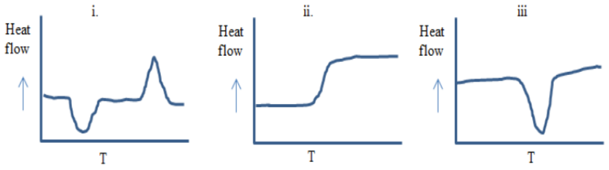
Poly(para butylstyrene)



Poly(α-methylstyrene)



18) The DSC curves below correspond to the 3 polymers listed below. Identify which is which, and identify on the curves any crystallization (T$_c$), glass transition (T$_g$) or melting (T$_m$) temperatures, and give your reasoning in each case.



(a) Atactic polystyrene being heated from room temperature to 200^{o}C.

(b) High density polyethylene being cooled from 200^{o}C to room temperature.

(c) Poly(ethylene terephthalate) that had originally been cooled rapidly from 300^{o}C to room temperature, and is now being slowly heated from room temperature back up to 300^{o}C.

19) Short, bulky side groups (like methyl of phenyl groups) increase the fractional free volume required for the motion of polymer chain segments, whereas long, thin groups (like the n-butyl group - $CH_2CH_2CH_2CH_3$) increase the available free volume.

(a) Describe how each of these two types of groups is expected to affect the glass transition temperature.

(b) Polymers with very little flexibility along the backbone of the polymer chain have very high glass transition temperatures. Give a brief explanation for this in terms of free volume theory.

Chain Dimensions

20) The value ofR_0, the rms (root mean squared) end-to-end distance for a polystyrene molecule in the bulk material (no solvent) is 200Å. The molecular weight, M, of this molecule is 100, 000 g/mol.

(a) What is the rms end-to-end distance for a polystyrene molecule with M=250,000 g/mol?

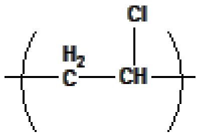
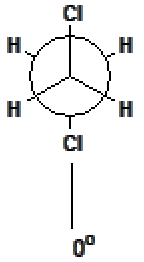
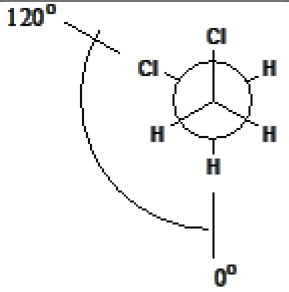
(b) What is the characteristic ratio (C_∞) for polystyrene?

(c) What is the statistical segment length (equivalent length of a repeat unit in a random walk model of chain dimensions) for polystyrene?

(d) The volume pervaded by a single molecule is given approximately byR_0^3. For a polystyrene molecule with M=250, 000 g/mol, compare this volume to the volume actually occupied by the polystyrene molecule. How many different molecules overlap with one another in polystyrene with this molecular weight?

(e) Consider a simple model of polystyrene for which all of the bonds are in either gauche or trans configurations. What fraction of bonds are in the trans configuration?

21) Consider a simple model for the chain dimensions of amorphous poly(vinyl chloride) where only trans and gauche bonds are possible.

Poly(vinyl chloride)	Trans Configuration	Gauche Configuration
		

(a) What fraction of the backbone bonds are in the gauche configuration if C_∞ for the polymer is 8?

(b) Calculate the statistical segment length of a repeat unit, assuming the value ofC_∞ from part a.

22) What fraction of molecules in an equilibrated amorphous polymer melt have end-to-end vectors with magnitudes larger than the root-mean-square end-to-end distance? (note – this will require a numerical or graphical solution.)

Mechanical Properties

23) A thermoset is cooled to a very low temperature. As the temperature is increased, the elastic modulus remains roughly constant until T_g, at which point the elastic modulus rapidly decreases. Above the glass transition temperature the elastic modulus slowly increases. Describe in qualitative terms what is going on at the glass transition, and why the modulus actually increases slightly aboveT_g.

24) Values of Young's moduli (E) for elastomers are typically near 10^6 Pa (1 MPa).

(a) What is the average molecular weight between crosslinks for a polymer with this value of E? Assume the polymer has a specific gravity of 1. What fraction of cis 1-4 polyisoprene repeat units contain crosslinks if the modulus is 10^6 Pa?

(b) Plot the predicted tensile stress/strain curve for this material for engineering strains from -0.5 to 2 (extension ratios from 0.5 to 3).

25) The yield point of a material is often defined as the onset of nonlinear behavior in the stress-strain curve. Can this definition be used for an elastomeric material that is deformed in tension? Why or why not?

26) Suppose a sample of Sylgard 184 is cured, and the degree of polymerization of the prepolymer is 60. Estimate the value for both the shear modulus and Young's modulus of this polymer. Describe any assumptions that you've made.

27) Consider the deformation behavior of a uniaxially stretched rubber.

(a) Plot the free energy of a uniaxially stretched rubber as a function of the extension ratio from λ = 0.1 (compressive strain to λ =4 (tensile strain). (The extension ratio of interest here corresponds to the direction in which the rubber is stretched.)

(b) At what value of the strain is the free energy minimized?

(c) For what compressive value of the extension ratio is the free energy of the rubber equal to the free energy it has for an extension ratio equal to 4?

28) Calculate the force required to fix the ends of a 1,4 polyisoprene molecule with M = 100,000 g/mol at the separation of 1000Å. Assume C_∞ = 8, and that the double and single bonds have equal lengths of 1.54 Å.

29) Consider a material which is defined between two circular plates that are parallel to one another. Each plate has a diameter of 2.5 cm, and the plates are separated by 1mm.

(a) Calculate the maximum shear strain at the outer periphery of the disks, if the top disk is rotated by 1°with respect to the bottom disk.

(b) Calculate the torque required to rotate the top plate by1°, in terms of the magnitude of the complex shear modulus,$G*$. (You will need to integrate contributions from all portions of the disk, keeping in mind that the local stress is equal to the shear modulus multiplied by the local strain.)

(c) Suppose the material between the two plates is a purely viscous fluid ($G' = 0$ at the appropriate frequency), and that the viscosity of the fluid is 1000 Pa-sec. Calculate the magnitude of the torque which must be applied to give a sinusoidal rotation with a magnitude of1°. Assume that the angular frequency of the applied torque is 100 radians/second.

30) Consider a polymer with a density of 1g/cm^3 that has the following relaxation modulus at room temperature (the molecular weight is much higher than the average molecular weight between entanglements).

$$G(t) = G_1 \exp\left(\frac{-t}{\tau_1}\right) + G_2 \exp\left(\frac{-t}{\tau_2}\right)$$

Suppose$G_1 = 10^9$ Pa, G_2 =$3x10^5$ Pa, τ_1 =10^{-6} s and τ_2 = 1 s.

(a) Calculate the zero shear viscosity for this polymer.

(b) Is this polymer crosslinked? How do you know?

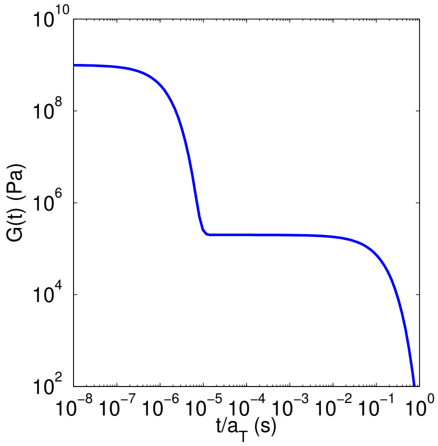
(c) Calculate the average molecular weight between entanglements.

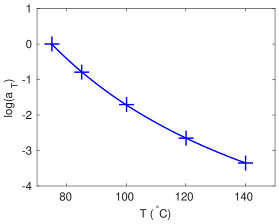
(d) Describe what happens toτ_1 andτ_2 when the temperature is increased (do they remain constant, increase or decrease)?

(e) What vibrational frequencies do you expect to be most efficiently damped by this polymer?

(f) Describe what happens toτ_1 andτ_2 when the molecular weight of the polymer is increased (do they remain constant, increase or decrease)?

31) Consider a polymer with the behavior of the relaxation modulus ($G(t)$) and temperature shift factor(a_T) plotted below. Assume the polymer has a density of 1 g/cm^3.





(a) Describe in qualitative terms what is going on at each of the two characteristic values oft/a_T where$G(t)$ decreases substantially.

(b) Is this polymer crosslinked? Briefly explain your answer.

(c) Estimate the entanglement molecular weight for this polymer.

(d) Estimate the viscosity of this polymer that is obtained at very low shear rates, at a temperature of 40°C.

(e) What is the ratio of viscosity of the polymer at -40°C to the viscosity at 40°C?

(f) Suppose that $G'(\omega)$ is measured at a very high frequency of$10^9\ \mathrm{s}^{-1}$. What value of G' do you expect to obtain from this experiment?

32) Use the PtBA data in the appendix to address the following:

(a) Determine the shift factors as a function of temperature for poly(t-butyl acrylate) (PtBA), using 75°C as the reference temperature. Plot these shift factors as a function of temperature, and determine a value for T_∞ by fitting to the Vogel equation. Compare this value of T_∞ to T_g for PtBA. Values of G' and G'' at different temperatures are included in the data tables at the end of the text.

(b) Determine the zero shear viscosity of PtBA with M=350,000 g/mol at$75°C$.

(c) Determine the entanglement molecular weight,M_e, for PTBA. Assume a density of 1 g/cm^{3}for PtBA.

33) Using the appendix data for poly(2-vinylpyridine), repeat the previous 3 sub-problems for poly(2-vinylpyridine) with a molecular weight of 82,000 g/mol, using 160°C as the reference temperature (where $a_T = 1$), and 130° C for the viscosity calculation.

34) An elastomer is made from a poly(n-butyl acrylate) precursor molecule with double bonds at either end that are able to react with a tetrafunctional crosslinker. The chemical structure is shown at the left below, and a schematic representation of the crosslinked structure is shown at the right.

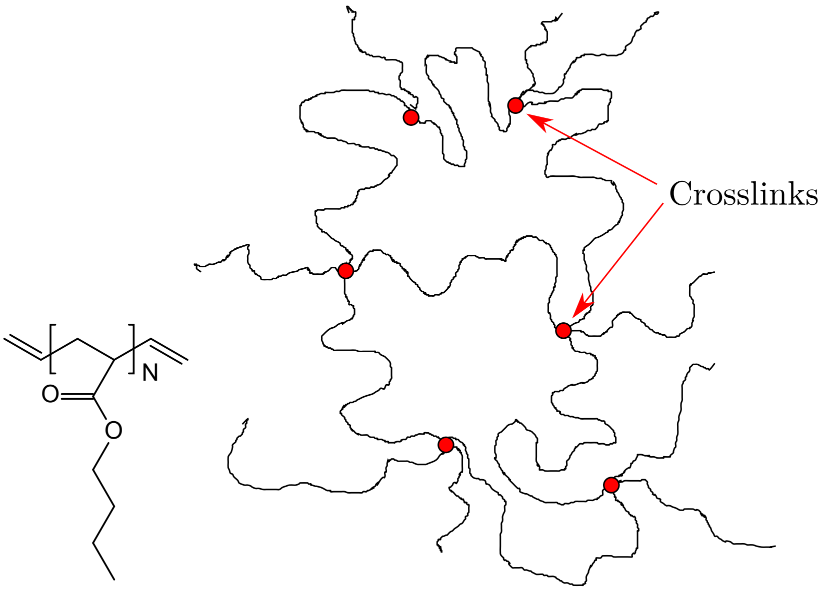
N=100

M_0=128 g/mole

density = 1.0 g/cm^3

a=0.7 nm

T_g=-45 C



(a) Calculate the shear modulus, G, for this material at room temperature.

(b) Give Young's modulus (E) and the Poisson's ratio (ν) for this material.

(c) What is the root mean square end-to-end distance $\langle R^2 \rangle^{1/2}$ for crosslink points at either end of the one of the precursor chains when the material is in its undeformed state?

(d) What is the value of C_∞ for poly(n-butyl acrylate)?

(e) Express the deformation free energies of the elastomer, divided by the shear modulus, G, for the following strain states:

  i Simple shear at a shear strain,γ, of 1.

  ii Uniaxial extension to an engineering strain of 100 % ($\lambda = 2$).

  iii Uniaxial compression to a engineering strain of -50% ($\lambda = 0.5$).

35) For each if the following pairs of quantities, circle the **largest** one. If you expect them to have the same value, write 'same'.

quantity 1	quantity 2
The thermal expansion coefficient of poly(n-butyl acrylate) at temperatures **above** -45 C.	The thermal expansion coefficient of poly(n-butyl acrylate) at temperatures **below** -45 C.
the free volume for a poly(n-butyl acrylate) sample **above** -45 C.	the free volume for a poly(n-butyl acrylate) sample **below** -45 C.
The **free energy** of an undeformed poly(n-butyl acrylate) sample.	The **free energy** of poly(n-butyl acrylate) sample at a shear strain of 0.3
The **entropy** of an undeformed poly(n-butyl acrylate) sample.	The **entropy** of poly(n-butyl acrylate) sample at a shear strain of 0.3
T_g for poly(n-butyl acrylate)	T_g for poly(methyl acrylate) (where the 4-carbon butyl group in poly(n-butyl acrylate) is replaced by a methyl group.

Crystallinity

36) Consider a polyethylene molecule with a molecular weight of 150,000 g/mol.

(a) Estimate the number of times the molecule folds back on itself within a lamellar crystallite with a thickness of 100 Å. Assume for the purposes of this calculation that the molecule remains in the crystallite, and does not move into the amorphous regions of the polymer.

(b) From your answer to part a, what can you say about the ability to stretch a polymer molecule in a semicrystalline polymer without breaking any bonds?

37) Describe how axis of the unit cell in polyethylene is oriented with respect to a spherulite, with respect to an individual lamellar crystallite, and with respect to the molecular chain axis.

38) Consider a polymer that crystallizes with an orthorhombic unit cell (all angle= 90°). The polymer has a carbon backbone, and crystallizes with a 4*1/1 helical structure. The unit cell dimension are a=10.4Å, b=5.3Å with 1.27Å per backbone carbon along the c axis. The molecular weight of a polymeric repeat unit is 125 g/mol, and there are two of these units per unit cell.

(a) What is the theoretical density of a completely crystalline version of this polymer (100% crystalline)?

(b) The percent crystallinity of a sample with a density of 1.35 g/cc is 60%. What is the density of the amorphous regions of this polymer?

39) Poly(ethylene terephthalate) has a relatively high equilibrium melting point (265 °C), but the polymer at room temperature is almost completely amorphous. Based on this result, do you expect thatT_g for PET is above room temperature or below room temperature? Explain your reasoning.

40) Consider two perfect single crystals of polyethylene and polypropylene. Polypropylene forms a 3/1 helix, and polyethylene forms a 2/1 helix. Which of these single crystals would you expect to have a higher modulus along the C axis? Include in your discussion the relative importance of bond bending and bond rotation during elastic deformation of the two materials. Also mention the importance of the lateral packing (i.e., the number of helices per unit area in the AB plane).

41) High density polyethylene has an equilibrium melting temperature of 138 °C. Two identical batches of this polymer are crystallized at different temperatures: one at 100 °C and one at 125 °C. Describe one important difference in the resulting structures of these two semicrystalline polymers, and explain the origin of the difference.

42) A linear homopolymer was crystallized from the melt at crystallization temperatures (T_c) within the range 270K to 330K. Following complete crystallization the following melting temperatures (T_m) were measured by differential scanning calorimetry (DSC).

Given:

T_c(K)	T_m(K)
270	300
280	306.5
290	312.5
300	319.0
310	325.0
320	331.0
330	337.5

Graphically determine the equilibrium melting temperature, T_m^0.

43) Small angle x-ray scattering experiments using x-rays with a wavelength of 1.54 Å were used to measure the distance between crystalline regions. Peaks corresponding to the lamellar period were obtained at the following angles:

$T_c(K)$	$\theta(degrees)$
270	0.44
280	0.39
290	0.33
300	0.27
310	0.22
320	0.17
330	0.11

(a) Use the Bragg equation to calculate the values of the lamellar period for each crystallization temperature.

(b) The degree of crystallinity was measured to be 45% for all samples. Calculate the lamellar thickness in each case, and use this information to graphically obtain the fold surface energy,γ_e. Assume the enthalpy of fusion of the polymer is $150 J/cm^3$, and the value of the equilibrium melting temperature from the previous problem.

44) Poly(ethylene oxide) (PEO) is a semicrystalline polymer with melting point of 65°C and a glass transition temperature of -60°C. Suppose a series of crystalline samples is made by performing the crystallization at temperatures of 40°C and 60°C.

(a) Describe any differences you expect rate of crystallization, and the crystal thicknessℓ_c, at these two temperatures. Be as quantitative as possible.

(b) Suppose the two samples are slowly heated. Describe any differences you expert to observe in the melting temperatures for these two samples.

(c) PEO is always crystalline at room temperature, but PET is often amorphous at room temperature, even though PET has a much higher melting temperature than PEO. Why is this?

Liquid Crystals

45) Consider the liquid crystalline texture from the nematic liquid crystal texture page of a nematic liquid crystalline material confined between two crossed polarizers.

(a) Give an example of the type of defect that can lie at the places where 4 dark bands come together. (show how the molecules are oriented in these regions)

(b) Describe why alternating light and dark bands emanate from these defect points.

(c) Is it possible to obtain a completely black image from a sample that has good nematic order? If so, describe a situation where this would be the case.

Thermodynamics of Solutions and Blends

46) Which contribution to the free energy (enthalpy of entropy) dominates at low temperature?

47) What are the signs of $\triangle h_{mix}$ and $\triangle s_{mix}$ for a system which has an LCST phase diagram?

48) For what values of χ will a polymer be able to completely dissolve in a small-molecular solvent?

49) Measured values of χ for a blend of polymer A with polymer B have the following temperature dependence:

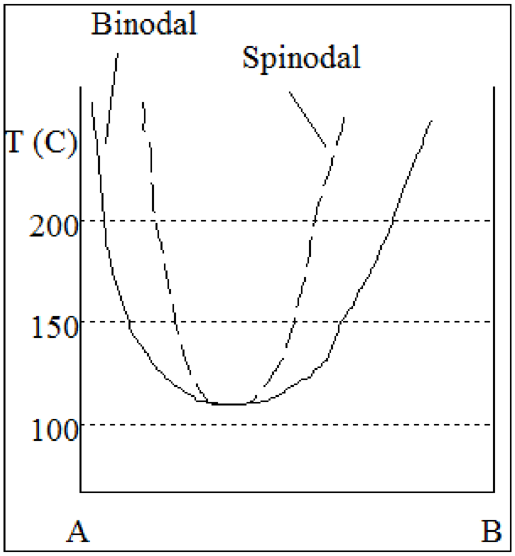
$$\chi = \frac{0.326}{T} - 2.3 \times 10^{-4}$$

where T is the absolute temperature.
Consider a blend with $N_a = 2500$, $N_b = 3500$

(a) What is the predicted critical composition, and the predicted critical temperature for this blend?

(b) Plot free energy curves (free energy as a function of composition) forχ/χ_{crit}= 1.1, 1.2, 1.3, 1.4, and 1.5. Using the common tangent construction from these five curves, construct a phase diagram withχ/χ_{crit} on the vertical axis and the blend composition on the horizontal axis.

50) Consider the following phase diagram:



(a) Is the enthalpy of mixing positive or negative for this system?

(b) Is the entropy of mixing positive or negative for this system?

(c) Draw free energy of mixing vs. composition curves at 100°, 150°, 200° that are consistent with this phase diagram. Show any common tangents points and points of inflection.

51) Consider a polymer/solvent mixture for which the ratio of polymer to solvent volume is 10,000.

(a) Determine the critical value of the chi parameter (χ_{crit})

(b) What is polymer volume fraction at the critical point?

(c) Plot the solvent chemical potential for this system as a function of polymer volume fraction for $\chi/\chi_{crit} = 0.9$, $\chi/\chi_{crit} = 1.0$, $\chi/\chi_{crit} = 1.2$, $\chi/\chi_{crit} = 1.5$.

(d) Suppose that the polymer is dipped into a pure solvent (solvent chemical potential equals zero). Solvent will diffuse into the polymer until the solvent chemical potential in the polymer reaches zero. From the plots made for part c, determine the equilibrium solvent volume fractions for $\chi/\chi_{crit} = 1.2$, and $\chi/\chi_{crit} = 1.5$.

52) Describe in your own words why most pairs of different types of polymers do not mix with each other in the liquid state.

53) Most liquids mix better at high temperatures than they do at low temperatures. However, polymeric liquids often mix better at low temperatures than high temperatures. Explain in as much detail as possible why this is the case.

54) Consider the following osmotic pressure data obtained for polyethylene oxide solutions in water (1MPa =10^6 Pa) at 20 °C.

ϕ_P	$\Pi(MPa)$
0.0457	0.0411
0.0917	0.145
0.138	0.346
0.185	0.685
0.232	1.212
0.280	2.010
0.329	3.161
0.377	4.868
0.427	7.323
0.476	10.77
0.516	14.54

(a) Plot the osmotic pressure as a function of the polymer volume fraction, using logarithmic axes for both the pressure and the polymer volume fraction. On the same plot, include the Flory Huggins expression for Π, using the value of χ that gives the best fit to the data.

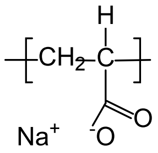
(b) Repeat part a, but now compare the data to the scaling expression forϕ in the semidilute regime (Eq.), where a_o^3/v_s is the adjustable parameter. (Note that v_s is the solvent molecular volume, obtained from the molar volume, V_s, by dividing by N_{av}).

55) Use the PEO solution data from the previous problem to calculate the following:

(a) The concentration of PEO at 20°C that gives an osmotic pressure large enough to support a column of water that is 100 meters tall.

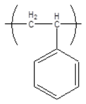
(b) What is the correlation length ξ, for a PEO solution in water with $\phi_P = 0.1$?

56) For charged molecules, the osmotic pressure is often dominated by the counterions. Suppose a solution of sodium polyacrylate at a concentration of 0.05 g/cm^{3}is made in water. Estimate the osmotic pressure, assuming that the counterions can be treated as an ideal gas.

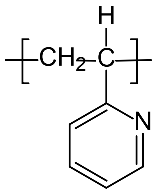


57) The interfacial free energy characterizing the interface high molecular weight versions of polystyrene (PS) and poly(2-vinyl pyridine) (P2VP) is$3x10^{-3}$ J/m^2 at 180 °C. Assume the volume per repeat unit is the same for both polymers (165Å^3, and use this as your reference volume. Also assume that the statistical segment length for both polymers is 6.7 Å.

PS



P2VP



(a) What is χ for the PS/P2VP system at 180 °C?

(b) Suppose PS and P2VP polymers with equal degrees of polymerization are mixed with one another. What range of molecular weights will form mixtures that are completely miscible with one another at all compositions at 180 °C?

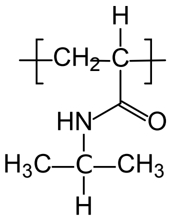
(c) Suppose monodisperse PS and P2VP samples with degrees of polymerization of 1000 are mixed with one another. What is the solubility of the PS in the P2VP at 180 °C? (hint: for a symmetric system like this, where both degrees of polymerization are equal to one another, the common tangent construction is satisfied at the point where the first derivative of the free energy of mixing with respect to volume fraction is equal to zero).

58) Use the data from the PS/P2VP system from the previous problem to answer the following questions:

(a) A diblock copolymer is synthesized that has a PS block with a degree of polymerization of 500 attached to a 2nd block with a degree of polymerization of 500. Calculate the periodicity of the lamellar structure that is formed by this material at equilibrium.

(b) Describe in qualitative terms the equilibrium geometries of the structures formed when the P2VP block length is fixed, but the PS block degree of polymerization is steadily increased.

59) Poly(n-isopropylacrylamide) (chemical structure shown below) exhibits a lower critical solution temperature in water. It is fully soluble in water at temperatures below 32°C, but the phase diagram with water has a two phase region for temperatures above 32°C.



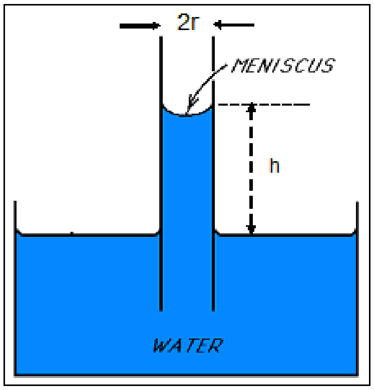
(a) The temperature dependence of χ for the Poly(n-isopropylacrylamide)/water system can be written in the following form: $\chi = A + BT$, where A and$B$ are constants and T is the temperature in°C. What is the sign (positive or negative) of B in this equation?

(b) Is the entropy of mixing for this system positive or negative? Briefly explain your answer.

(c) Calculate the osmotic pressure of an aqueous solution of high molecular weight poly(n-isopropylacrylamide) with a polymer volume fraction of 0.2.

Capillarity

60) A hollow glass tube is immersed in water as shown in the illustration below:



(a) Calculate the internal tube diameter that gives a capillary rise of 10 cm, assuming that water completely wets the glass (contact angle of zero).

(b) Calculate the capillary rise if the same glass tube from part a is coated with a thin layer of polystyrene, changing the contact angle to 90° .

61) Answer the following:

(a) Calculate the force required to push a cylindrical fiber with a radius of1 μm into water, if the contact angle the fiber makes with the water is130°.

(b) What stress can be supported if you create an array of these fibers on a square lattice, with a spacing between fiber centers of4 μm? (Assume the density of the fibers is equal to the density of water, so you don't need to worry about forces due to buoyancy).

(c) How much weight could be supported by an object like this with a total area of1 cm^2?

331 Computational Exercises

62) In binary blends where the two components have very different molar volumes (often the case with polymers), the following form of the free energy expression is commonly used:

$$\frac{v_0 G_v}{k_B T} = \frac{\phi_b ln \phi_b}{N_b} + \frac{(1-\phi_b)\ln(1-\phi_b)}{N_a} + \chi\phi_b(1-\phi_b)$$

The expressions for the chemical potentials for the A and B molecules are given by the following expression:

$$\frac{\mu_a}{k_B T} = \ln(1-\phi_b) + \phi_b(1 - N_a/N_b) + \chi N_a \phi_b^2$$

$$\frac{\mu_b}{k_B T} = \ln(\phi_b) + (1-\phi_b)(1 - N_b/N_a) + \chi N_b (1-\phi_b)^2$$

Here G_v is the free energy per volume, $\phi_b$is the volume fraction of B in the system, and N_a and $N_b$are proportional to the molecular volumes of the two components. The quantity v_0 is a reference volume, so the molecular volume of the $'A'$ molecule is $v_0 N_a$ and the molecular volume of the $'B'$ molecule is $v_0 N_b$. Adapt the MATLAB script below to do the following:

```
global na nb chi % these values also get used in function definitions
set(0,'defaultaxesfontsize',16)
set(0,'defaultlinelinewidth',2)
phi=linspace(0.001,0.999,1000);
na=150;
nb=100;
chi=0.02;
% fv is the expression for the free energy of mixing
fv=@(phi) phi.*log(phi)/nb+(1-phi).*log(1-phi)./na+chi.*phi.*(1-phi);

%mua and  mub are the chemical potentials of A and B
mua=@(phi) log(1-phi)+phi*(1-na/nb)+chi*na*phi.^2;
mub=@(phi) log(phi)+(1-phi)*(1-nb/na)+chi*nb*(1-phi)^2;

% now write the function that is equal to zero when the A and B chemical
% potentials are equal to one another for phi=phi(1) and phi=phi(2)

ftosolve=@(phi) [mua(phi(1))-mua(phi(2));
    mub(phi(1))-mub(phi(2))];

plot(phi,fv(phi));
xlabel('\phi_{b}')
ylabel('G_{v}V_{0}/RT')

% start with a guess for the equilibrium volume fractions
phiguess = [0.2; 0.8];      % Make a starting guess at the equilibrium compositions
[phicalc,fval] = fsolve(ftosolve,phiguess);  % Call solver

% now we add the tangent line
slope=(fv(phicalc(2))-fv(phicalc(1)))/(phicalc(2)-phicalc(1));
intercept=fv(phicalc(1))-slope*phicalc(1);
tangentline=intercept+slope.*phi;
hold on
plot(phi,tangentline,'r')
hold off
title(['\chi=' num2str(chi) ', N_a=' num2str(na), ', N_b=' num2str(nb)], 'fontsize', 11)

% now save the plot as a jpg file
saveas(gcf,'commontangent.jpg');

% this saves the file a .eps file, used to embed the figure into the
% solution set - students can comment out this next line if they don't wan
% the .svg file
print(gcf,'-dsvg','commontangent.svg')
```

(a) Plot the free energy expression $\chi = 0.02$, $N_a = 200$, and $N_b = 100$, along with its common tangent construction, and report the values of the equilibrium compositions of the two phases. Include the plot with your solution.

(b) Repeat the previous calculation for $\chi = 0.025$ and $\chi = 0.05$ (you may need to adjust the initial guess for the volume fractions).

(c) Decrease χ to the critical value, χ_{crit}, which can be calculated analytically. Include a plot of G_v as a function of ϕ_b for value of χ.

63) Extend work from the previous problem to obtain a MATLAB code that generates the full phase diagram (with χ on the vertical axis and ϕ_b on the horizontal axis) for a system with $N_a = 200$ and $N_b = 100$.

Show both the bimodal and spinodal curves, and turn in a printout of your actual MATLAB code. **Hint:** You'll want to solve the equations for a variety of χ values above the critical value of χ, which you can calculate analytically. You can use a 'for' loop in MATLAB to do this. Calculation of the spinodal curve is pretty easy, because there's an analytic expression for that. When you're developing your initial guesses for the bimodal compositions to pass to the 'fsolve' command, keep in mind that the bimodal compositions must lie outside the spinodal compositions. This can help you develop sensible guesses to use for this quantity.