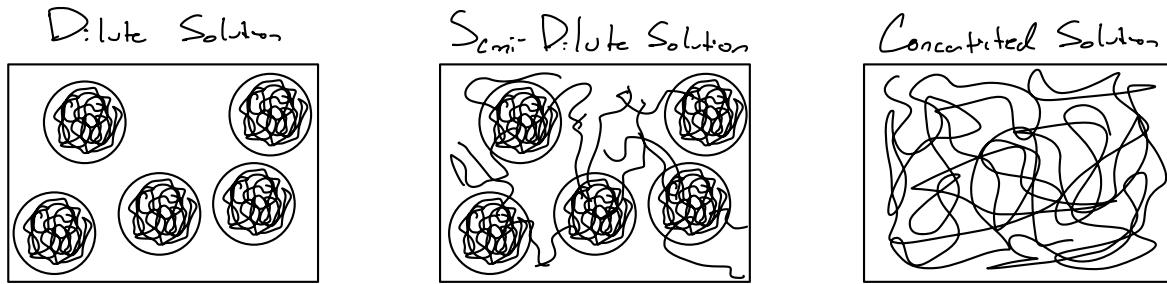


Chapter 3 Homework: Properties of Polymers

Due:

Available Points: 50

- 1. Please draw a polymer ball in a dilute solution, semi-dilute solution, and concentrated solution. (3 points)**



- 2. In general, what is the end-to-end distance in a poor solvent? In a good solvent? (2 points)**

The end-to-end distance, R , is the vector sum of vectors b_i along a polymer chain given by $R = \sum_{i=1}^n b_i$ where ' b ' is the length of the bond between i -th atoms. In a good solvent, polymer chains can move more freely and thus R is larger. For a poor solvent, the chain forms a tight ball and R is generally much smaller.

- 3. Define the following qualitatively: (7 points)**

- Radius of gyration Easier to measure than end-to-end distance as it is measured with a light scattering technique. Average distance from center of gravity to chain segment, denoted S . Varies with branching, and is smaller for polymers in a poor solvent as good solvents swell & separate polymer chains.
- Glass Transition Temperature The temperature at which the amorphous polymer or the amorphous component of a semi-crystalline polymer undergoes a change from glassy to rubbery state. This occurs in both amorphous & semi-crystalline polymers and results in considerable material softening. Specific volume change past T_g .
- Characteristics of rubber elasticity A unique property of polymers. Crosslinked rubbers can maintain elastic deformation at very large strain. Characterized by a large deformation and extremely low modulus.
- Ideal Elastic A material that completely recovers from deformation
- Stress Relaxation A polymer under constant strain over time results in the stress of the material relaxing. Maxwell model is used for this.
- Creep Characterizes how the strain of a polymer responds over time to a constant applied stress. Voigt is used for this
- Time Temperature Superposition Principle Allows predicting properties at time t without having to perform a long-term experiment. At a higher temperature T , there is a shorter time to achieve the same structural change.

4. Define the following quantitatively (7 points)

- Value for fraction of free volume at T_g Measured to be about $f_g = 0.025$ from exp. results
- Equations for T_g of symmetric molecules vs T_g of asymmetric molecules

Symmetric	
$T_g \approx \frac{1}{2} T_m$	

Asymmetric	
$T_g \approx \frac{2}{3} T_m$	
- Value for Poisson's ratio of an ideal rubber $\sqrt{\nu} = 0.5$ for ideal rubbers
- Equation for Dynamic Storage Modulus $G' = \left| \frac{\tau'}{\gamma} \right|$ for τ' being stress in phase with strain γ
- Equation for Dynamic Loss Modulus $G'' = \left| \frac{\tau''}{\gamma} \right|$ for τ'' being stress out of phase with strain γ
- Equation for Loss Tangent Given as $\tan \delta = \frac{G''}{G'}$
- Equation for Hildebrand Solubility Parameter $\delta = \frac{\sum F^*}{\sum V^*}$ F^* ← molar attraction contribution
 V^* ← molar volume contribution

5. What are the 4 assumptions of the Flory-Huggins Theory? What are the shortcoming of these assumptions? (7 points)

Assumptions

- A polymer solution can be regarded as chemical repeat units of the polymer chains occupying each lattice unit.
- The lattice units have equal size, and each lattice unit can be occupied either by a solvent molecule or the chemical repeat unit.
- Number of neighboring chemical repeat units is called the valence number.
- Placement of N_2 polymer chains in N_1 lattice units $\omega(N_1, N_2)$, provides the entropy of mixing denoted ΔS according to the Boltzmann Equation as: $\Delta S = V k \log[\omega(N_1, N_2)]$ and $\Delta S = -R(\phi_1 \log \phi_1 + \frac{\phi_2}{N_2} \log \frac{\phi_2}{N_2})$ ϕ = volume fraction, m = mole of polymer, N = number of lattice sites

Shortcomings

- Assumption of Lattice units being filled in a binary fashion implies volume of mixing $\Delta V = 0$, which is false.
- Fixed lattice size does not allow us to evaluate thermal expansion of the system.
- Effect of different size solant molecule cannot be evaluated.

Advantages

- Derived and used equations are relatively simple.
- m_1 corresponds to small molecular weight compounds and m_2 can thus be used to describe polymer blends.

6. How does the end-to-end distance in the restricted bond angle case compare to the end-to-end distance in the unrestricted bond angle case? (1 point)

For the unrestricted bond angle case, average angle is 0° , so end-to-end distance is $R = b\sqrt{n}$. For the restricted bond angle case, the end-to-end distance is dependent on the angle between molecules i and j given as θ_{ij} . Therefore end-to-end distance is $R = \sqrt{n}b^2 \frac{1-\cos\theta}{4\cos\theta}$.

For a common polymer backbone consisting of C-C bonds $\theta_{ij} \approx 109.28^\circ$ and hence the restricted bond angle is about $\sqrt{2}$ times smaller than the unrestricted bond angle. Hence the unrestricted end-to-end distance is given as $R = \sqrt{2}(b\sqrt{n})$.

7. For a given polymer with end-to-end distance of 24 nm, what is the radius of gyration? (1 points)

Given: $R = 24 \text{ nm}$ $\langle S^2 \rangle = \frac{1}{6} \langle R^2 \rangle$ $\rightarrow S = \sqrt{\frac{1}{6} \langle R^2 \rangle}$ $= \frac{1}{\sqrt{6}} \cdot R $	$S = \frac{1}{\sqrt{6}} \cdot 24 \text{ nm} $ $= 4.7979$ <div style="border: 1px solid black; padding: 5px; display: inline-block;"> $S = 4.798 \text{ nm}$ </div>
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8. You are creating an alternating copolymer between two monomers, monomer A and monomer B, and want to estimate the Tg of this copolymer. Estimate the Tg of the following blends. (3 points)

$$\frac{1}{T_g} = \frac{\omega_1}{T_{g1}} + \frac{\omega_2}{T_{g2}} \Rightarrow T_g = \left(\frac{\omega_1}{T_{g1}} + \frac{\omega_2}{T_{g2}} \right)^{-1}$$

- a. Monomer A has a Tg of 150°C. Monomer B has a Tg of 200°C. Both monomers have the same molecular weight. $\omega_1 + \omega_2 = 1$, $\omega_1 = \omega_2$

$$T_g = \left(\frac{0.5}{150^\circ C} + \frac{0.5}{200^\circ C} \right) \approx 171.42^\circ C$$

- b. Monomer A has a Tg of 150°C. Monomer B has a Tg of 20°C. Both monomers have the same molecular weight. $\omega_1 + \omega_2 = 1$, $\omega_1 = \omega_2$

$$T_g = \left(\frac{0.5}{150^\circ C} + \frac{0.5}{20^\circ C} \right) = 35.2941^\circ C$$

- c. Monomer A has a Tg of 150°C. Monomer B has a Tg of 200°C. The weight fraction of Monomer A is 0.68. $\omega_1 = 0.68$ $\omega_2 = 1 - 0.68 = 0.32$

$$T_g = \left(\frac{0.68}{150^\circ C} + \frac{0.32}{200^\circ C} \right) = 163.043^\circ C$$

E = modulus

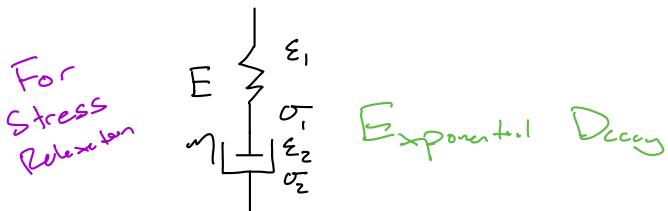
ϵ = strain

σ = stress

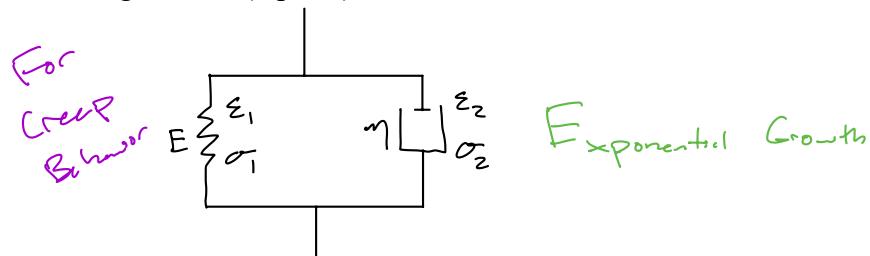
η = viscosity

9. Draw the following (10 points)

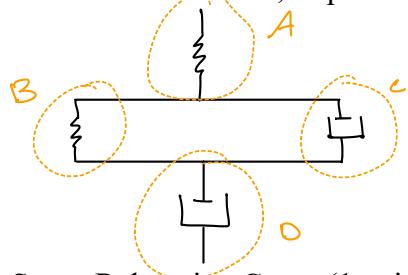
a. Maxwell Model (1 point)



b. Voigt Model (1 point)



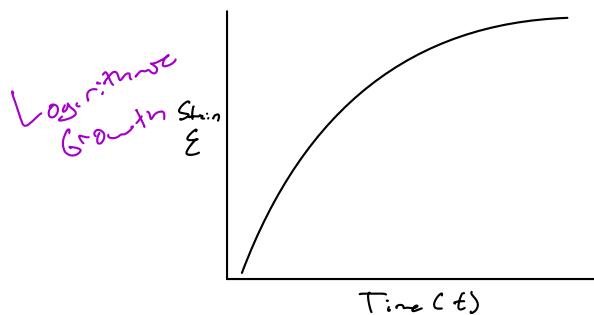
c. Four Element Model, as presented in class (1 point)



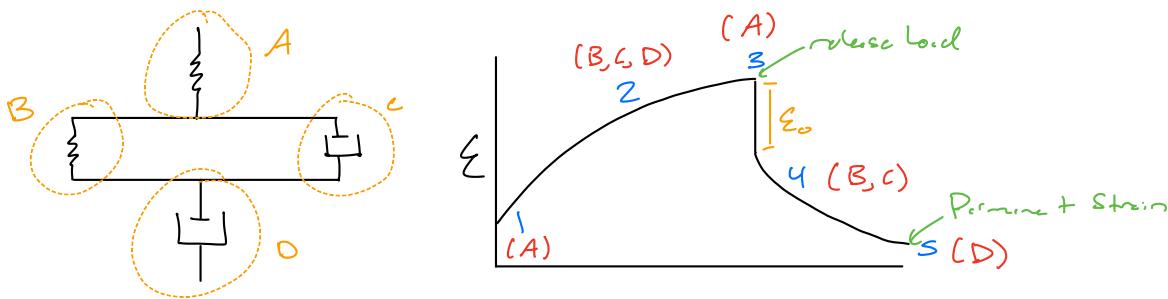
d. Stress Relaxation Curve (1 point)



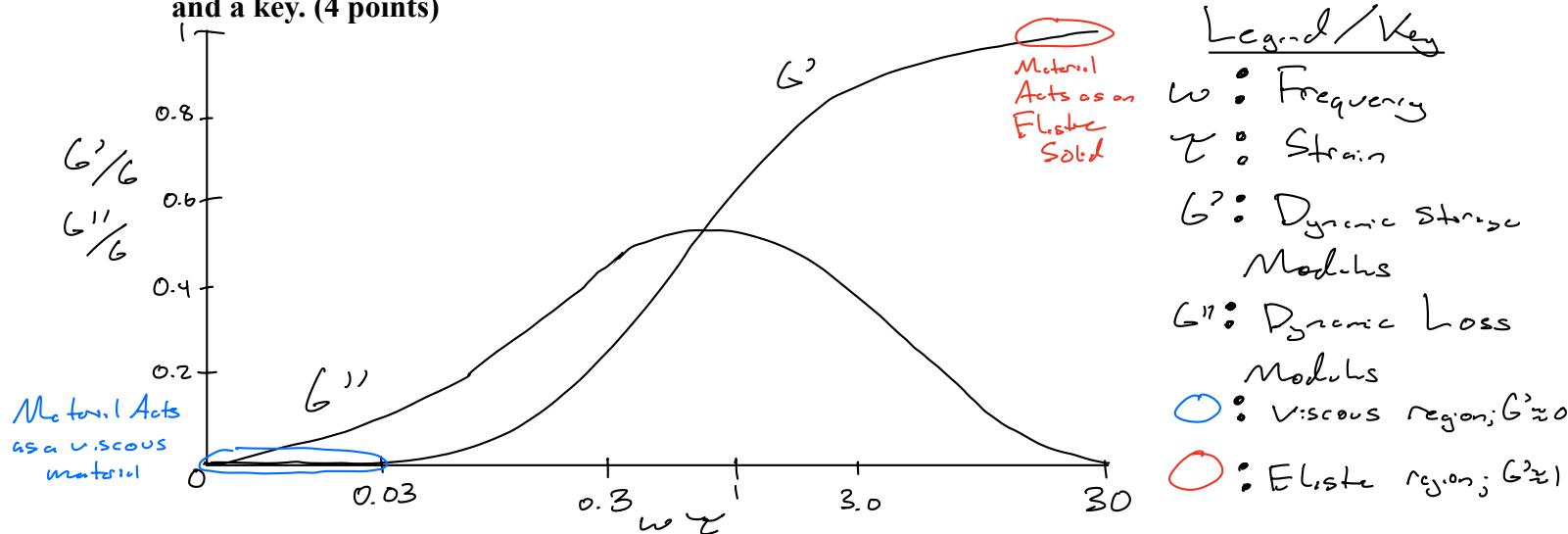
e. Strain Curve (1 point)



- f. Four Element Curve, indicate which aspect of the model is reacting at each transition point on the curve (5 points)



1. (A) spring's elastic component
 2. (B, C, D) B, C for time element, D for driving force
 3. (A)
 4. (B, C) no weight \rightarrow no extant driving force, only internal press (B) \rightarrow C follows Brummt
 5. D Permane + deformation on D as external driving force is removed
10. Plot the dynamic storage and dynamic loss moduli as a function of frequency and strain. Indicate at which areas on the graph the material is viscous and elastic. Include axes labels and a key. (4 points)

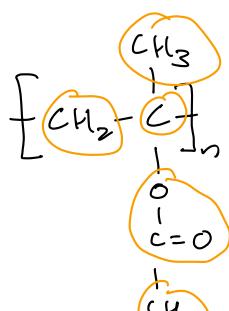


11. The solubility parameter of n-hexane is 7.24 and ethyl acetate is 9.10. Which solvent is a better solvent to dissolve poly(methyl methacrylate)? Show your work. (5 points)

Solubility parameter of polymer near solvent then polymer will dissolve well in it.
n-hexane: 7.24 vs. ethyl acetate: 9.10 for poly(methyl methacrylate): ?

Calculate PMMA S

Group structure	Molar volume contribution, V^* ($\text{cm}^3/\text{mol}^{1/2}$)	Molar attraction contribution, F^* [$(\text{cal} \cdot \text{cm}^3)^{1/2} \text{ mol}^{-1}$]
-CH ₃	31.8	218
-CH ₂ -	16.5	132
>CH-	1.9	23
>C<	-14.8	-97
CsH ₃	41.4	562
CsH ₂	58.5	652
CsH ₁	75.5	735
CH ₂ =	29.7	203
-CH=	13.7	113
>C=	-2.4	18
-OCO-	19.6	298
-CO-	10.7	262
O-	5.1	95
Cl	23.9	264
CN	23.6	426
-NH ₂	18.6	275
>NH	8.5	143
>N-	-5.0	-3



$$S = \frac{\sum F^*}{\sum V^*} = \frac{132 + 2(218) - 97 + 298}{16.5 + 2(31.8) - 14.8 + 19.6} = \frac{769}{84.9} = 9.06 \left(\frac{\text{cal}}{\text{cm}^3} \right)^{1/2}$$

Ethyl acetate is better for PMMA bc it's $S = 9.10$ which is only $0.4 \left(\frac{\text{cal}}{\text{cm}^3} \right)^{1/2}$ off of PMMA's $S = 9.06$. n-hexane is $1.82 \left(\frac{\text{cal}}{\text{cm}^3} \right)^{1/2}$ off from PMMA's, so it isn't as good.