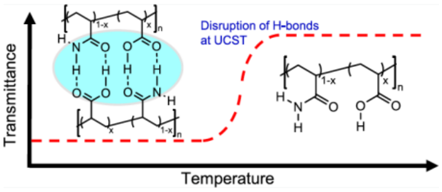
Polymer Physics Question 1

Polymers are unlikely to mix since the entropy of mixing is generally low. The entropy of mixing is also low for polymer solutions. Generally, a negative enthalpy of mixing is required to ensure miscibility. If this is associated with specific interactions between polymers or between a polymer and a solvent, these interactions are often overcome at high temperature leading to LCST behavior. On the other hand, if polymers have self-interactions such as hydrogen bonding in proteins these interactions can lead to phase separation on cooling if other, stronger interactions exist with a solvent. This can lead to UCST behavior. Beaudoin G, Lasri A, Zhao C, Liberelle B, De Crescenzo G, Zhu X-X, *Making Hydrophilic Polymers Thermoresponsive: The Upper Critical Solution Temperature of Copolymers of Acrylamide and Acrylic Acid* Macromolecules **54** 7963-7969 (2021) synthesized copolymers of polyacrylamide and polyacrylic acid which, similar to proteins, can hydrogen bond between polymers. Under certain pH the polymers can display a UCST in water.



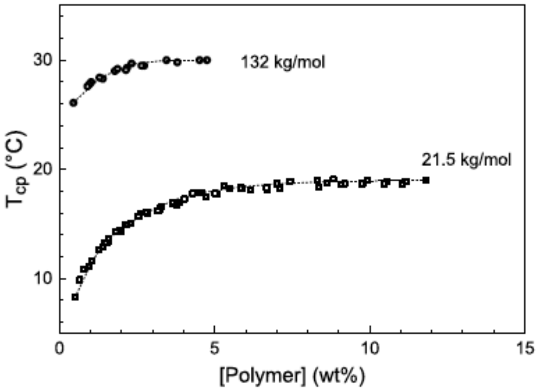


Figure 4. Variation of T_{cp} as a function of the concentration of P(AA-*co*-AM) samples with similar chemical composition (45 mol % AM) and different molar masses in phosphate buffer solution (pH 2.0, 100 mM). Dashed lines are visual guides.

a) Give the Flory-Huggins equation for a polymer solution and a definition of the Flory-Huggins interaction parameter that allows for specific interactions. Explain how LSCT and UCST behavior can be created using these parameters. Define non-combinatorial entropy.

b) Figure 4 shows the binodal curve as measured by the cloud point for two copolymers of different molecular weight. What functionality do you expect for the critical point with molecular weight? Do these curves follow that functionality?

c) Figure 4 doesn't show the spinodal curve. What is the spinodal curve and how would you obtain the spinodal curve?

d) What is the overlap concentration c^*? Define c^* in terms of the chain molecular weight. How would c^* impact Figure 4? How should the cloud point behave below c^*? What happens to a chain if it phase separated below c^*?

e) For a chain below c^* how does the coil size depend on the interaction parameter and the temperature?

Question 1.

a) Flory-Huggins equation of polymer solution:

$$\Delta G_m = kT(n_1 \ln\phi_1 + n_2 \ln\phi_2 + \chi_{12} n_1 \phi_2)$$ -5

χ_{12} is the Flory interaction parameter, means interaction energy per solvent molecule divided by kT.

$$\boxed{\chi_{12} = \frac{z r_1 \Delta w_{12}}{kT}}$$

where, z is lattice coordination number,
r_1 is number of "segments" in a solvent molecule
Δw_{12} is change in internal energy for formation of unlike molecular pair.
k is boltzman constant.

Polymer-solvent phase status is determined by ΔG_m.
totally immiscible at $\Delta G_m > 0$,

totally miscibile when $\Delta G_m < 0$ and $\left(\frac{\partial^2 \Delta G_m}{\partial \phi_2^2}\right)_{P,T} > 0$.

Beside these cases, the miscibility (phase status) is determined by volume fraction (composition) and temperature.

~~At all compositions~~ As temperature increases, compositions of phases become more alike, identical ~~above~~ at UCST. where $\left(\frac{\partial^2 \Delta G_m}{\partial \phi_2^2}\right)_{P,T} = \left(\frac{\partial^3 \Delta G_m}{\partial \phi_2^3}\right)_{P,T} = 0$. All compositions are miscible above this critical temperature.

LCST behavior cannot be predicted by Flory-Huggins equati
Equation of State (EOS), which includes both internal and external degree of freedom contribution. (non-combinational and combinatory).

b) UCST moves downward in temperature with decreasing molecular weight. The curves in figure 4 followed this functionality. -5

c) Spinodal curve is boundary between unstable and metastable region, coincide with binodal curve at critical point.

All points in spinodal curve satisfies $\left(\frac{\partial^2 \Delta G_m}{\partial \phi_2^2}\right)_{P,T} = 0$.

d) Overlap concentration, C^*, is the critical concentration of monomer unit, where the entanglement began so that individual chain cannot be resolved. C^* is the number of segments per unit volume.
(molecular weight) (chain)

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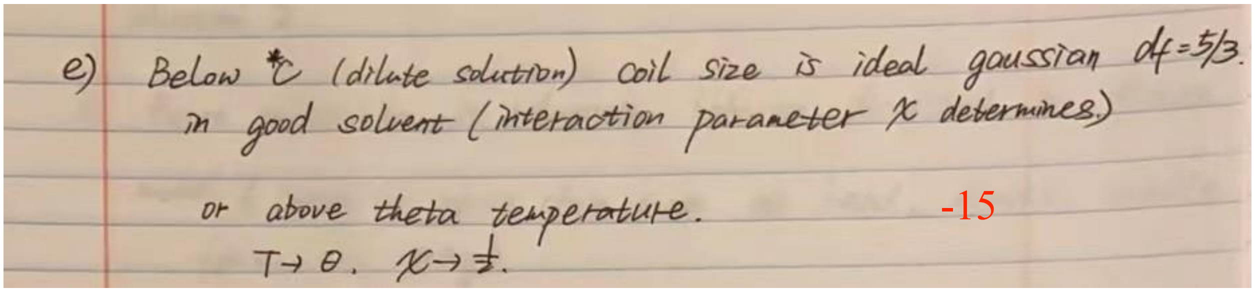
The cloud point behave as UCST below C^*. Increasing Tcp with increasing concentration at same composition (molar mass).

Figure 4 shows, higher molecular weight causes lower C^* (reach plateau at lower wt% of polymer), but higher Tcp. ~~Chain seperat~~ Phase seperation below C^* means interaction between polymer molecules occured, such as hydrogen bonding.



e) Below c^* (dilute solution) coil size is ideal gaussian $d_f = 5/3$. in good solvent (interaction parameter χ determines)

or above theta temperature.

$T \to \theta$. $\chi \to \frac{1}{2}$.

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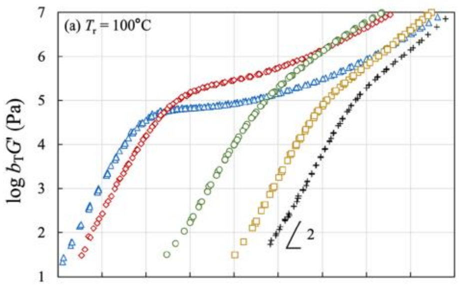
Polymer Physics Question 2

Polymers are viscoelastic materials with a native relaxation time, τ. In a mechanical measurement a strain is applied at a rate, $t^* = 1/\dot{\gamma}$. The Wissenberg number, *Wi*, is defined as τ/t^*. Yang H, Wu S, Chen Q, How to *Choose a Secondary Interaction to Improve Stretchability of Associative Polymers?* Macromolecules **54** 8112-8121 (2021) Consider the brittle to ductile transition for polymers through introduction of multiple relaxation times. One relaxation time, the Rouse time, relates to the chains, and secondary relaxation times associated with ionic interactions (strong) and hydrogen bonding (weak). The number and type of these relaxation time has a dramatic impact on the mechanical properties.

a) For a material displaying only Rouse relaxation and with $Wi > 1$, the elongation, $\lambda = N_{bb}^{1/2}$, where N_{bb} is an average number of Kuhn segments per network strand. Define Rouse relaxation, explain the origin of the ½ power law, and explain why this elongation is reached with $Wi > 1$. How would the material behave at a slower extension rate with $Wi < 1$?

b) Is the Rouse time appropriate for entangled polymer chains such as in a melt? The chains in this study are rather stiff and have molecular weights of about 10 kg/mol. Is the Rouse time appropriate for these chains in the melt? Why?

c) Figure 2 shows the linear visco-elastic spectra for several of the samples prepared by Yang. Explain the origin of the 2 and 1 power-law regimes. What does the plateau regime in *G*' indicate? What does the peak in *G*" indicate? Explain the high frequency behavior.



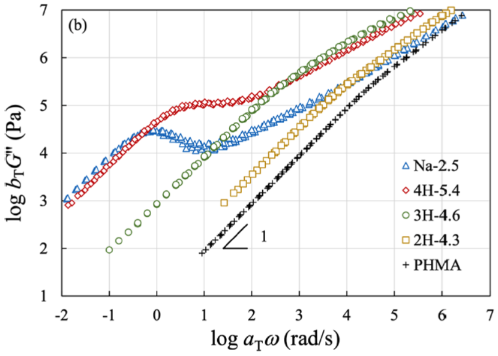


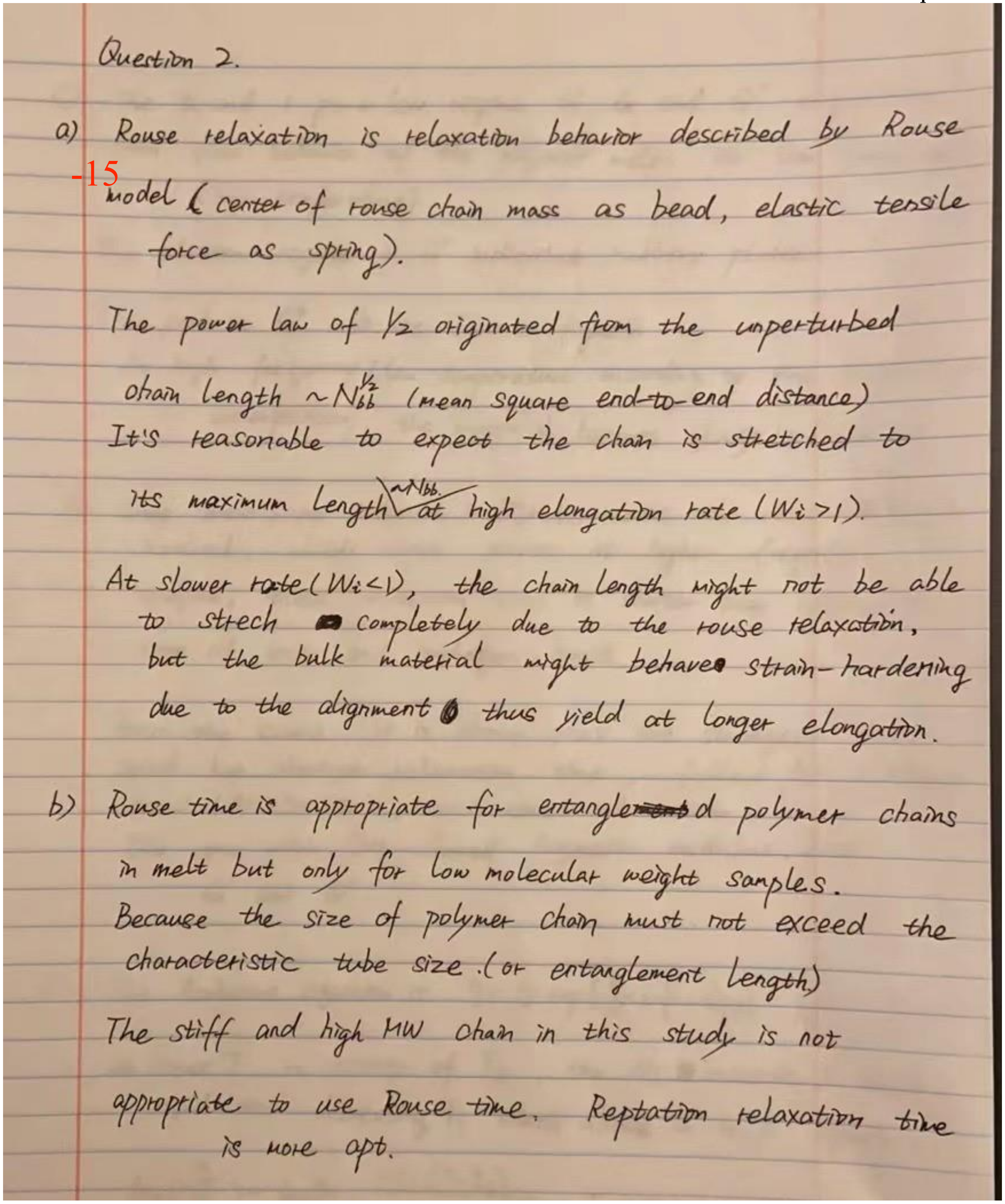
Figure 2. Comparison of the (pseudo-) master curves of the storage and loss moduli, *G*′ and *G*″, obtained for pure PHMA, 2H-4.3, 3H-4.6, 4H-5.4, and Na-2.5 samples. All (pseudo-) master curves are reduced at T_r = 100 °C.

d) In Figure 2, PHMA has no stickers per chain, the H samples have 5.4, 4.6 and 4.3 weak hydrogen bonding stickers per chain and the Na-2.5 has 2.5 strong ionic stickers per chain. Explain the behavior of the curves with regard to the presence of these network forming bonds. Is the relaxation time for the ionic and hydrogen bonds shorter or longer than the Rouse relaxation time?

e) Equation (4) is the Williams-Landel-Ferry (WLF) equation.

$$\log a_{\mathrm{iso}} = -7.64(T - T_{\mathrm{iso}})/(187 + T - T_{\mathrm{iso}}) \qquad (4)$$

Explain how this equation is used to produce Figure 2. How is this equation related to the Arrhenius equation?



Question 2.

a) Rouse relaxation is relaxation behavior described by Rouse model (center of rouse chain mass as bead, elastic tensile force as spring).

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The power law of ½ originated from the unperturbed chain length $\sim N_{bb}^{1/2}$ (mean square end-to-end distance)
It's reasonable to expect the chain is stretched to its maximum length $\sim N_{bb}$ at high elongation rate ($Wi > 1$).

At slower rate ($Wi < 1$), the chain length might not be able to strech completely due to the rouse relaxation, but the bulk material might behave strain-hardening due to the alignment thus yield at longer elongation.

b) Rouse time is appropriate for entangle~~ment~~d polymer chains in melt but only for low molecular weight samples.
Because the size of polymer chain must not exceed the characteristic tube size .(or entanglement length)
The stiff and high MW chain in this study is not appropriate to use Rouse time. Reptation relaxation time is more apt.

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c) The 2 and 1 power low regime of G' and G'' originated from flow behavior of the polymer melts at low frequency. (high temperature)

The plateau regime in G' indicates rubbery plateau.

The peak in G'' indicate T_m in figure 2.

At high frequency (low temperature according to time-temperature superposition), the material behaves glassy (solid-like).

d) Since there's no stickers in PHMA, means only rouse relaxation involved, which curve starts at higher frequency, therefore, rouse relaxation time is shorter than relaxation time of ionic and hydrogen bonds.

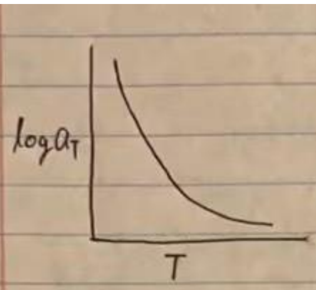
From the curve, it is shown that the strongest ionic bond has shortest relaxation time, folled by hydrogen bond (4H > 3H > 2H), and rouse relaxation.

The one with 3H showed highest modulus. both G' and G''.

e) The Arrhenius equation is $\eta = \eta_r \cdot \exp\left[\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right]$, $T > T_g + 100°C$

at lower T, in vicinity of T_g, the $\Delta\eta$ increase is more rapid with decreasing T, which shows in WLF equation:

$$\log\left(\frac{\eta_T}{\eta_{T_g}}\right) = \log a_T = \frac{-C_1 (T - T_g)}{C_2 + T - T_g}, \quad T_g < T < T_g + 100°C$$



The figure 2 obtained from G' and G'' at $T_r = 100°C$. multiply by $b_T = T_r/T$. , shift along horizontal axis by a_T.

$T_{iso} = T_g + 100°C$, choose this temperature intend to get network-relaxation part modulus over segmental motion part.

Accordingly, $\log a_{iso} = -7.64(T - T_{iso})/(187 + T - T_{iso})$ is been used to get a_{iso} (shift factor) which presents better fit.