

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.

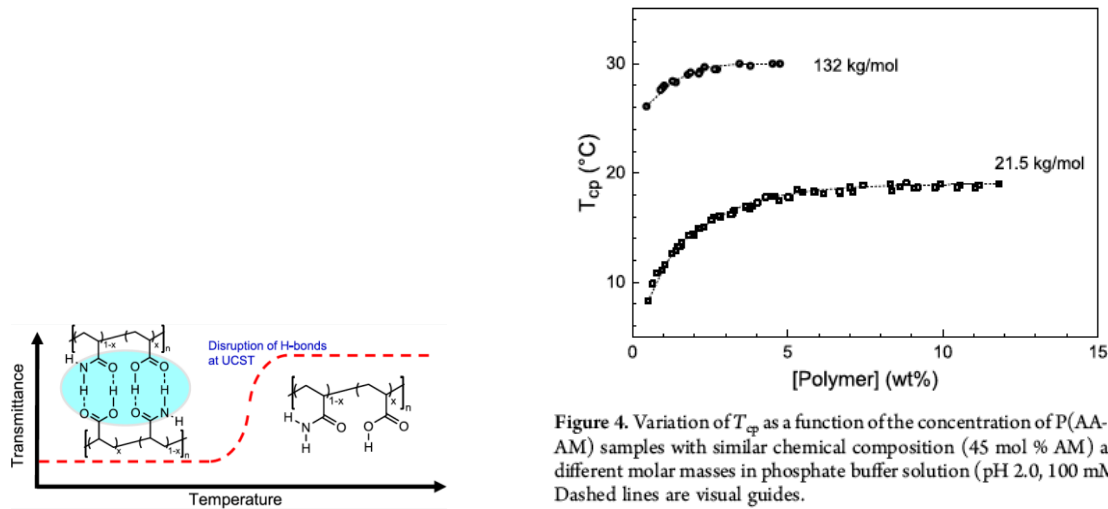


Figure 4. Variation of T_{cp} as a function of the concentration of P(AA-co-AM) samples with similar chemical composition (45 mol % AM) and different molar masses in phosphate buffer solution (pH 2.0, 100 mM). Dashed lines are visual guides.

- 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 LCST and UCST behavior can be created using these parameters. Define non-combinatorial entropy.
- 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?
- Figure 4 doesn't show the spinodal curve. What is the spinodal curve and how would you obtain the spinodal curve?
- 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^* ?
- For a chain below c^* how does the coil size depend on the interaction parameter and the temperature?

1 a. $\Delta G_m = kT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi_{12})$

χ_{12} : parameter of Flory interaction.

$\chi_{12} = Z\Delta W/kT$ The interaction energy / solvent molecule and divided by kT .

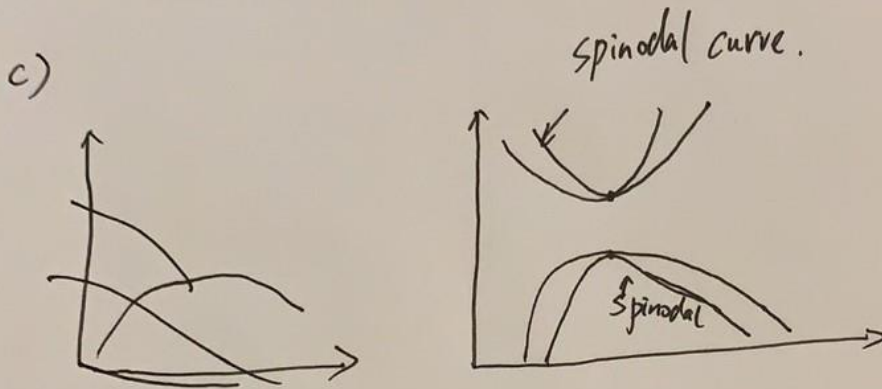
~~is~~ UCST behavior created by increasing T , when

$\left(\frac{\partial^3 \Delta G_m}{\partial \phi_2^3} \right)_{P,T} = 0$ the miscible happen when T higher than this point.

On the other hand., LCST can not be created by using this parameters.

b) Yes. it is following the functionality. -5

UCST decrease when the Mw is decreasing



because of $\left(\frac{\partial^2 \Delta G_m}{\partial \phi^2}\right)_{P,T} = 0$ Therefore, there is no spinodal curve.

(d) -5
 $C^* \sim N/R^3$. C^* is point. which the concentration higher than a point then the conformation of individual chain ~~s~~ begin to overlap each other. and ~~most~~ molecules start to perform entanglement. When Lower than C^* UCST happen on another, decrease Mw lead increase C^* When phase separation below C^* , the H bond formed between molecules.

e. -15

When blow c^* , the coil size will be decrease with χ_{12} increase. because ~~under~~ c^* blow c^* the molecule is difficult to ~~interact~~ interact with each other.

* Since $c^* \sim (Mw/Mn) R_g^3$
 R_g related to the size.

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, $\dot{\epsilon} = 1/\gamma^*$. The Wissenberg number, Wi , is defined as $\tau/\dot{\epsilon}^*$. 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 $1/2$ power law, and explain why this elongation is reached with $Wi > 1$. How would the material behave at a slower extension rate with $Wi < 1$?

-15

a) Rouse relaxation time is used ~~to~~ for Rouse model

The origine of $\frac{1}{2}$ power law is determine the $\lambda = N_{ee}^{1/2}$.
which equal end to end distance.

When $Wi > 1$ it will reach ^{at} the max length of N_{ee} for
~~the~~ larger elongation.

- 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?

-15

b). Yes, it is ^{good for entangled} ~~because~~. Although it is stiff but the length
is short and size is small. and less than the
characteristic tube size.

However is not good for melt

- 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.

C. -8

The origin of the 2 and 1 power law regimes.

is @ the melts polymer flow behavior at low frequency.

G'' peak is T_m Temperature of melt.

At High frequency, it will become glass property.

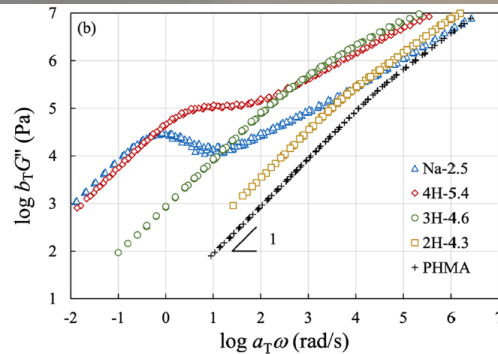
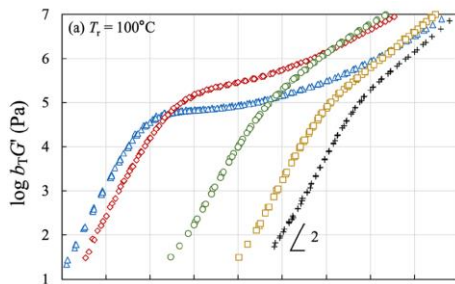


Figure 2. Comparison of the (pseudo-) master curves of the storage and loss moduli, G' and G'' , obtained for pure PHMA, 2H-4.3, 3H-4.6, 4H-5.4, and Na-2.5 samples. All (pseudo-) master curves are reduced at $T_r = 100^\circ\text{C}$.

- 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?

d) When PHMA doesn't show ~~stickers~~ stickers, the rouse relation will behave mainly. therefore, the result shows start ~~at~~ at high frequency. Then rouse relation time is shorter.

More hydrogen will offer a stronger bond ~~force~~ force.

~~Therefore~~ Therefore, the relation time will be shorter.

and when 3H, it will have ^{the} highest modulus at G' and G''

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

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

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

$$WLF = \log a_T = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)} \quad \therefore \begin{aligned} C_1 &= -7.64 \\ C_2 &= 187. \end{aligned}$$

-2

$$\text{Arrhenius equation} \quad \eta = \eta_r \exp \left[\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_r} \right) \right]$$

$$G^*(\omega) = G'(\omega) \sin \omega t + i G''(\omega) \cos \omega t$$

At $T_r = 100^\circ\text{C}$ can get G' and G''

the get shift factor by using $\log a_{iso} = -7.64(T - T_{iso}) / (187 + T - T_{iso})$