

Homework 2
Polymer Physics 2023
Due Tuesday January 23 at noon
(Please submit one pdf file per group on Canopy)

van Westerveld L, Pelras T, Hofman AH, Loos K, Kamperman M, Es Sayed J *Effect of Polyelectrolyte Charge Density on the Linear Viscoelastic Behavior and Processing of Complex Coacervate Adhesives* Macromolecules in Press (2024)

<https://pubs.acs.org/action/showCitFormats?doi=10.1021/acs.macromol.3c02352&ref=pdf>

discuss coacervates that can be used as salt concentration/charge density tunable pressure sensitive adhesives. They introduce “time–salt” and “time–salt–charge density” superpositions in analogy to time/temperature superposition (that is fast dynamic properties (e.g. flow) can be scaled to low temperature properties) to describe the dynamic viscoelastic properties. This supports the concept that the same mechanism can describe viscoelastic behavior as salt content and charge density are varied for these coacervates.

Van Westerveld investigates the introduction of hydrophilic groups on the polyelectrolyte chains to control charge and enhance chain interactions to improve injectability and wet adhesion at the same time where these properties are usually at odds with chain structure modification using hydrophobic groups (when you improve injectability, wet adhesion is diminished). Unfortunately, he was not successful in this endeavor.

a) What is a coacervate and how can they be used for pressure sensitive adhesives in medicine? How is Debye charge screening involved in this biomedical application of coacervates?

<https://en.wikipedia.org/wiki/Coacervate>

https://en.wikipedia.org/wiki/Primordial_soup

https://en.wikipedia.org/wiki/Pressure-sensitive_adhesive

https://en.wikipedia.org/wiki/Debye_length

https://en.wikipedia.org/wiki/Bjerrum_length

b) In class it was mentioned that Pluronic's (<https://en.wikipedia.org/wiki/Pluronic>), composed of PEO/PPO block copolymers are common non-ionic surfactants, and the hydrophilic PEO or PEG group is common to many non-ionic surfactants such as Triton X100

(https://en.wikipedia.org/wiki/Triton_X-100). Explain how the PEO group is used in this study to modify the acrylic polyanion. Postulate, i.e. use cartoons, to explain how this modification (Scheme 1) might impact the injectability and wet adhesion of these coacervates. That is, why did Van Westerveld propose this project, what is the concept behind where this could work?

c) Explain what RAFT polymerization is and why it is used in this study.

https://en.wikipedia.org/wiki/Reversible_addition%E2%88%92fragmentation_chain-transfer_polymerization#:~:text=Reversible%2Daddition%2Dfragmentation%20chain%2D,%2Dstep%20addition%2Dfragmentation%20mechanism.

d) What is time-temperature superposition (TSS) and how is it related to the Arrhenius equation? What is a Vogel temperature? What is the WLF equation? Show how the WLF equation can be obtained from the Arrhenius equation using the Vogel temperature and $\Delta G = \Delta H - T\Delta S$.

e) What is the “linear viscoelastic regime”? How can it be determined? Figure 4 c, f, i, l show TSS curves with three power-laws. Explain to what these power-laws correspond. (Refer to the Winter Chambon Criterion

<https://www.eng.uc.edu/~beaucag/Courses/Properties/Books/WinterandChambonGelpoint1.549853.pdf>)