

090116 Quiz 2 Introduction to Polymers

- 1) Synthetic polymers generally do not display a single molecular weight. Consider the polymerization process that includes chemical steps for initiation, propagation and termination.
 - a) Explain how the nature of initiation (sporadic versus spontaneous) can affect polydispersity.
 - b) Explain how the nature of propagation (linear, branched, uniformity of rate of propagation etc.) might affect polydispersity.
 - c) Explain how the nature of termination (combination of two propagating species versus combination with a low molecular weight species etc.) could affect polydispersity.
 - d) How could a bimodal distribution result in a polyethylene sample? (Explain a possible synthetic scheme that could lead to a bimodal distribution of molecular weight.)
 - e) Describe a synthetic scheme that could lead to a monodisperse polymer including a description of initiation, propagation and termination.
- 2) Proteins are bio-polyamides that have a single value for molecular weight. Nylon is a synthetic polyamide that generally has a polydispersity index of about 2.5.
 - a) What is the polydispersity index for a protein?
 - b) What are the units of the polydispersity index?
 - c) Polydisperse polymers generally have better properties compared to monodisperse polymers. The modulus of a polymer chain is inversely proportional to the molecular weight and the extensibility increases with molecular weight. Explain why polydispersity might help mechanical properties. Is high or low molecular weight better for mechanical properties?
 - d) Viscosity depends on the molecular weight to the 3.4 power. Explain why a polydisperse polymer might be better for processing (flow) properties for a polymer. (The formation of fibers and films in processing requires high “melt-strength” meaning that the melt displays elastic properties.) Is high or low molecular weight better for processing?
 - e) Do you think a protein would have very good engineering properties compared to nylon?
- 3)
 - a) Explain how a membrane osmometer measures the molecular weight of a polymer.
 - b) How does a GPC measure molecular weight.
 - c) How would you calculate the molecular weight measured in the membrane osmometer if you had the GPC curve for a polymer.
 - d) How is the standard deviation related to the polydispersity index.
 - e) GPC's are sometimes equipped with a viscometer and index detector. What is the advantage of using these two detectors on the GPC rather than just an index of refraction detector. (The index of refraction is proportional to the concentration.)

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- 1) a) If initiation starts sporadically, that is at random points during time, and if growth occurs for the same length of time, then the chains will have differing lengths.
b) If there is variability in the rate of propagation or if chains branch by formation of multiple growth sites on the same chain structure a polydisperse molecular weight distribution can result.
c) Termination can occur by destruction of the active site, by combination with a low-molecular weight material or by combination of two chains of different or the same molecular weights. Variability in the conditions of termination can lead to polydispersity.
d) One mechanism for a bimodal distribution is formation of some chains with branches by combination at the termination step. Chains that do not combine to make a branched polymer will have about 1/3 the molecular weight of chains with one branch for instance.
e) Initiation would need to be spontaneous (occurring at one time), propagation would need to be of a fixed rate with no branching, termination would need to occur spontaneously and by the same mechanism for all growing chains.
- 2) a) $PDI = 1$
b) PDI is unitless
c) Contributions from high and low modulus chains can lead to a tough material that has high modulus and some extensibility due to contributions of different chain lengths. Low molecular weight is good for high modulus and high molecular weight is good for high extensibility.
d) High molecular weight gives “melt strength” for fiber formation and for coherency of the melt, low molecular weight eases flow with low viscosity. A blend of the two is needed for processing since you want melt strength as well as lower viscosity.
e) A protein would have poor engineering properties from a synthetic polymer perspective because it would be basically a brittle highly viscous material with low melt strength.
- 3) a) Two baths are separated by a semi-permeable membrane that allows solvent to pass but not polymer. One side has a dilute polymer solution and the other has only solvent. Solvent will flow from the low to high concentrated sides in an attempt to dilute the polymer solution leading to an increase in the pressure. This increase is called the osmotic pressure, π . We can think of the osmotic pressure, in the first order approximation, as being caused by the suspended particles acting as a gas. Then the osmotic pressure is given by the ideal gas law, $\pi = cRT$ where c is the number of polymer molecules in the volume of the polymer bath. If we know the mass that was added and the volume of the bath then we can calculate the mass per polymer by dividing the added mass/vol by the measured number/vol. This results in a number average molecular weight.
b) A GPC measures molecular weight by a size exclusion principle. A high pressure pump pumps a dilute solution of a polymer through a swollen gel such as a polystyrene gel. Large molecules can only probe large pores which make up a small volume of the gel so large molecules pass through the gel quickly. Small molecules probe into the gel structure at a smaller scale and can visit a much larger volume of the gel so the residence time of small molecules is much higher. The GPC/SEC/HPLC separate molecules based on their “hydrodynamic” size, meaning the size they present during flow.
c) If the GPC curve is $P(M)$ versus M , the number average, measured in membrane osmometry, is calculated by,

$$M_1 = \frac{\int_0^{\infty} MP(M)dM}{\int_0^{\infty} P(M)dM}$$

d) The standard deviation is given by,

$$\begin{aligned}\sigma &= \frac{\int_0^{\infty} (M - M_1)^2 P(M)dM}{\int_0^{\infty} P(M)dM} = \frac{\int_0^{\infty} M^2 P(M)dM - 2 \int_0^{\infty} MM_1 P(M)dM + M_1^2 \int_0^{\infty} P(M)dM}{\int_0^{\infty} P(M)dM} \\ &= M_2 - M_1^2 = M_1^2 \left(\frac{M_2}{M_1^2} - 1 \right) = M_1^2 (PDI - 1) \\ &= M_2 \left(1 - \frac{M_1^2}{M_2} \right) = M_2 \left(1 - \frac{1}{PDI} \right)\end{aligned}$$

e) The viscometer yields the viscosity average molecular weight in an absolute measurement. For a narrow fraction in the GPC all of the molecular weight moments are equal so that the viscosity average is an absolute measure of the molecular weight for a narrow fraction and can be used to internally calibrate the GPC curve without the use of secondary standards. The viscometer measures the intrinsic viscosity, $[\eta]$ which is proportional to kM^a , where the values of k and a can be obtained in the Polymer Handbook. k and a are known as the Mark-Houwink constants. a varies from 0.5 to 2 with 0.8 being the expected value for a dilute solution.