080416 Quiz 2 Introduction to Polymer Science

1) Low molecular weight materials display a single value for the molar mass but synthetic polymers display a spectrum of molar mass.

a) Why do you think a single molecular weight isn't seen for polymers (we didn't go through this in class so just guess from what you know and thinking of the mechanisms of initiation of growth, growth and termination of growth for a polymer chain). You may want to describe the conditions that could lead to a monodisperse polymer (PDI = 1) in answering this question.

b) Describe the difference between a unimodal molecular weight distribution and a bimodal or multimodal distribution. Why might a bimodal distribution be seen in polyethylene?

c) Other than GPC name two methods that could be used to measure the molecular weight of a polymer and what moments of the molecular weight distribution they measure.

2) a) Briefly explain what a GPC is and how it measures molecular weight.

b) How is retention time or retention volume converted to a molecular weight scale? Include what must be measured and how you would go about using these measurements to convert retention time to molecular weight.

c) Describe a detector used in a GPC.

3) a) Explain how the third moment of a distribution $P(M)$ is obtained.

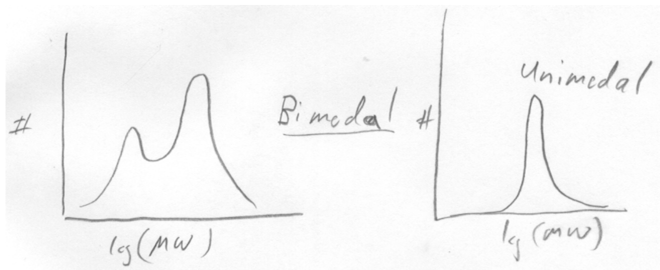
b) What is the weight average molecular weight?

c) How is the polydispersity index, *PDI*, related to the standard deviation, σ, of a distribution?

ANSWERS: ***080416 Quiz 2 Introduction to Polymer Science***

1) a) If polymers initiate simultaneously, grow by chain-growth polymerization with no termination during growth and if termination happens at the same time in a controlled manner then a monodisperse polymer results with almost no polydispersity, i. e. $PDI = 1$, $\sigma = 0$. If polymerization begins sporatically rather than spontaneously, if termination occurs throughout growth and branching occurs during growth and if the termination event is not a coordinated event, i.e. if it does not occur at the same time for all chains, then a polydisperse polymer results.

b) A unimodal population has one peak in the distribution. A bimodal has two peaks and a multimodal has many peaks. A bimodal population in polyethylene could arise due to branching of chains by macromolecular addition where the branched chains form a high molecular weight fraction when long chain radicals attach the polyethylene chain and add to the chain making a three arm star polymer structure.



c) Titration of end groups is a colligative method (counting method) and leads to the number average.
Light Scattering yields the weight average molecular weight.
Membrane osmometry measures number average molecular weight.
Viscosity from dilute solution leads to a viscosity average (high moment).
Melt viscosity (melt index) gives an index that decreases with molecular weight.

2) a) A GPC is composed of a chamber with a dilute ($c < c^*$) solution that is pumped through a high pressure pump through columns filled with a gel (like jello) that might be composed of polystyrene swollen in the solvent used to make the solution, typically tetrahydrofuran (THF) or toluene. After elution from the gel a detector (such as an IR detector or an index of refraction detector) quantifies the amount of polymer in the fluid as a function of retention time or retention volume.

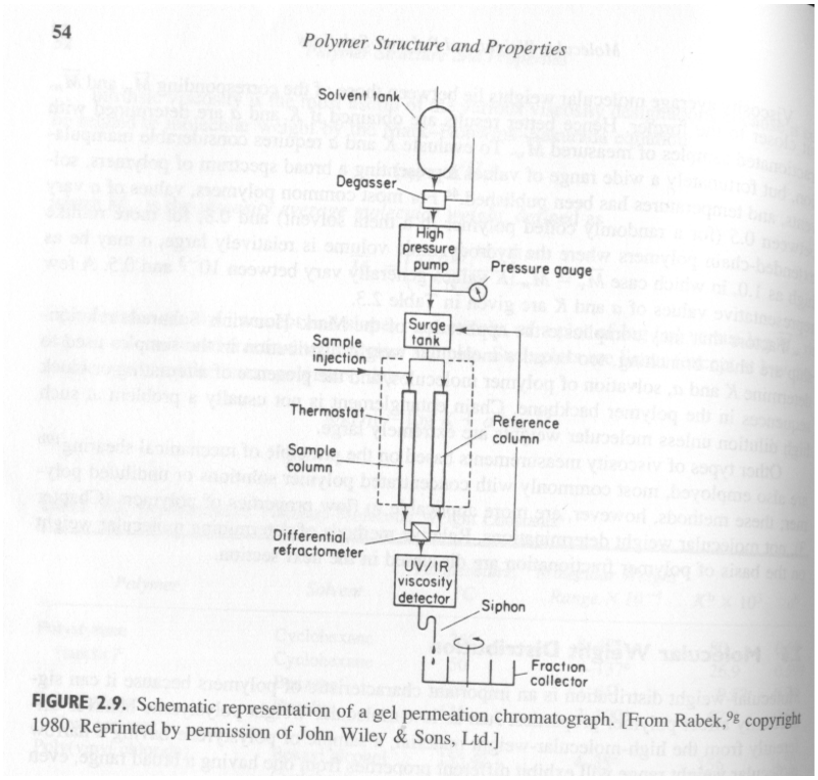
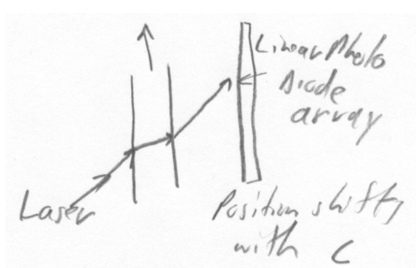


FIGURE 2.9. Schematic representation of a gel permeation chromatograph. [From Rabek,[9g] copyright 1980. Reprinted by permission of John Wiley & Sons, Ltd.]

From our textbook, Stevens Polymer Chemistry

b) The GPC requires the use of standards since it is a secondary technique. Primary techniques that do not use standards include light scattering, viscosity and membrane osmometry, but these do not yield the entire polydispersity curve. Monodisperse polymers are injected in the same solvent as the polymer to be measured. If monodisperse samples do not exist the column is often calibrated using monodisperse polystyrene and the molecular weight is termed the polystyrene equivalent molecular weight. There is basically an exponential relationship between elution time and molecular weight of the form, $M = K_1 \exp(-K_2 t)$, so a minimum of two standards are needed to calculate the conversion function. Generally 4 to 5 standards of variable molecular weight are mixed in the same standard solution since the peaks are discernable from each other for narrow enough molecular weight standards. Then the exponential equation is fit to the data to yield K_1 and K_2. This equation can then be used to convert retention time to molecular weight.

c) Index of refraction detector measures the refraction of laser light which increases with concentration.



3)

a) $M_3 = \dfrac{\int_0^\infty P(m)\, m^3\, dm}{\int_0^\infty P(m)\, dm}$

b) $M_w = \dfrac{M_2}{M_1} = \dfrac{\int P(m)\, m^2\, dm}{\int P(m)\, m\, dm}$

c) $PDI = \dfrac{M_w}{M_n} = \dfrac{M_2}{(M_1)^2}$

$$\sigma = \frac{\int P(m)\,(m - M_1)^2\, dm}{\int P(m)\, dm} = \frac{\int P(m)\, m^2\, dm}{\int P(m)\, dm} - 2 M_1 \frac{\int P(m)\, m\, dm}{\int P(m)\, dm} + M_1^2 \frac{\int P(m)\, dm}{\int P(m)\, dm}$$

$$\sigma = M_2 - 2 M_1^2 + M_1^2$$

$$\boxed{\frac{\sigma}{M_2} = 1 - \frac{1}{(PDI)}}$$