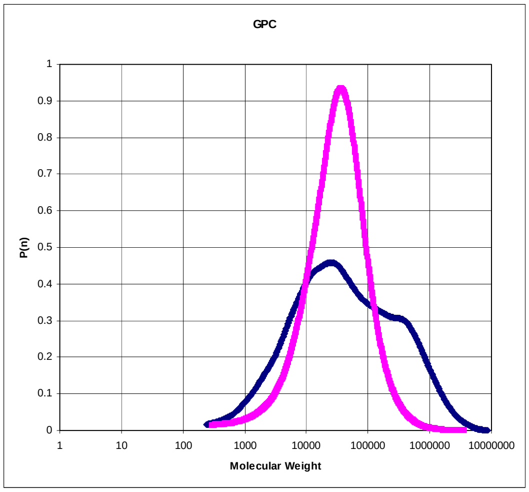
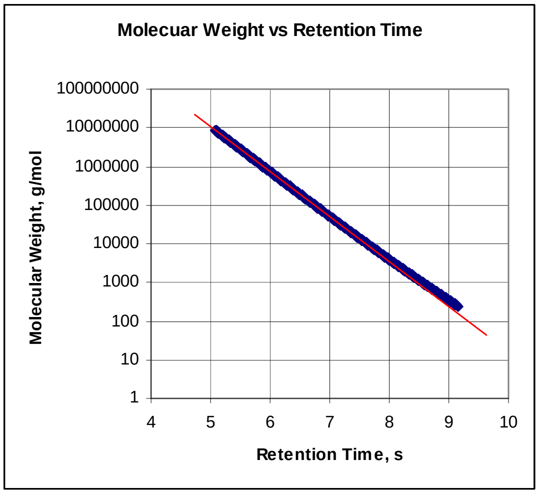
051006 Quiz 2 Introduction to Polymers



(a)



(b)

1) In Plot "(a)", Pick 5 or 6 equally spaced points in molecular weight including the peak position(s) for the ***unimodal*** curve and make a table of P(n) and n. Use this table to calculate a) the mean (number average, n_1), b) second moment, n_2, c) weight average, n_w, d) the polydispersity index, PDI, and e) the standard deviation, σ, about the mean.

2) a) What is *retention time* in Plot "(b)". (Explain by describing the GPC measurement.)
b) Gel Permeation Chromatography is also called Size Exclusion Chromatography (SEC) and High Pressure Liquid Chromatography (HPLC). Explain the origin of the terms GPC, SEC and HPLC by explaining how the GPC works.

3) Figure "(b)", above, indicates a relationship between Molecular Weight and Retention time.
a) Propose a function for the relationship between *n* and retention time, *t*, for the line in plot "(b)".
b) How many unknown parameters must be determined to use the function you have proposed?
c) Explain how *low-PDI* samples are used to obtain a *t* to *n* conversion function.
d) How many *low-PDI* standard samples are needed for a calibration master curve in this case?

4) The 3D-Gaussian function describes the probability of a chain of length N having an end-to-end distance R,

$$P_{Gaussian}(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{3/2} e^{\frac{-3(R-\langle R\rangle)^2}{2\sigma^2}} \qquad (1)$$

where $\sigma = N^{1/2}$ l and l is the chain's step size.
a) Equation (1) is symmetric about the mean <R>. Explain why.
b) What is the effect of increasing σ on the distribution curve? (You may want to sketch P(R) versus R for variable σ to show this.)
c) What effect does the term in brackets (first term after "=") have on the shape of the distribution curve?
d) How would you calculate $\langle R^2\rangle$ in general? (Give an equation.)
e) What is the value of $\langle R^2\rangle$ (in terms of N and l) using this equation (1)?

ANSWERS: 051006 Quiz 2 Introduction to Polymers

1) Unimodal Curve

n	P(n)	nP(n)	$n^2P(n)$
10^3	0.02	20	20,000
10^4	0.4	4000	4×10^7
$5x10^4$	0.92	46,000	2.3×10^9
10^5	0.5	50,000	5×10^9
$5x10^5$	0.08	40,000	2×10^{10}
Sum	1.92	140,020	2.734×10^{10}

a) n_1 = 140,020/1.92 = 72,927 g/mol
b) $n_2 = 2.734 \times 10^{10}/1.92 = 1.42 \times 10^{10}$ (g/mol)^2
c) $n_w = 1.42 \times 10^{10}$/72,927=195,300 g/mol
d) PDI = 195,300/72,927 = 2.677
e) σ = 72,927 g/mol $(2.677\text{-}1)^{1/2}$ = 94,450 g/mol

2) a) GPC involves pumping under high pressure through a gel in a tubular column a dilute polymer solution. The effluent is measured, for index of refraction for instance, as a function of time after injection of the solution. This time is the retention time.
b) This is termed Gel Permeation Chromatography because you pump a solution through a gel and the solution permeates the gel. It is called Size Exclusion Chromatography because the largest molecules exit first, they are excluded from the gel due to size. It is called High Pressure Liquid Chromatography to distinguish it from gel chromatography used to separate DNA and Proteins. The instrument uses a high pressure pump that distinguishes the technique from plate chromatography using gels.

3) a) You should notice that the molecular weight scale is a log-scale (from last week) while the retention time is on a linear scale. Then ln(n) ~ -t. A reasonable function might be,

$$\ln(n) = K_2 - K_1 t \qquad \text{or} \qquad n = \exp(K_2 - K_1 t) = \exp(K_2)\exp(-K_1 t) = K_3 \exp(-K_1 t)$$

n displays an exponential decay in time.
b) Two unknowns, K_3 and K_1.
c) If you run *low-PDI* samples the constants K1 and K2 can be determined so you can construct a conversion function between retention time and molecular weight.
d) For two constants you would require two standards so the number of unknowns and number of equations (one per standard) are equal.

4) a) It is symmetric about <R> because the term (R - <R>) is squared so the sign of this term doesn't matter. This is true for all even powers but is not true for any odd power.
b) Increasing σ broadens the distribution function and lowers the peak value.
c) The first term has no effect on the shape, it re-scales the y axis.
d) $$\langle R^2 \rangle = \frac{\sum (R - \langle R \rangle)^2}{N-1} \qquad \text{or} \qquad \langle R^2 \rangle = \frac{\int P(R)(R - \langle R \rangle)^2\, dR}{\int P(R)\, dR}$$
e) $\langle R^2 \rangle = Nl^2$ so $R \sim N^{1/2}$