Home assignments for the Course of Polymer Physical Chemistry

First section of the course:

1. Calculate polydisperisty index (PDI) for two samples with the following distribution of molecular weights:

M_i	10,000	20,000	30,000	40,000	50,000	60,000	70,000
n_i(sample 1)	1,000	3,000	5,000	10,000	5,000	3,000	1,000
n_i(sample 2)	0	1,000	8,000	10,000	8,000	1,000	0

Sample 1:

$$M_n = \frac{\sum n_i M_i}{\sum n_1} = \frac{1.12*10^9}{28*10^3} = 40{,}000; M_w = \frac{\sum n_i M_i^2}{\sum n_1 M_i} = \frac{50*10^{12}}{1.12*10^9} \approx 44{,}640; PDI = \frac{M_w}{M_n} \approx 1.12$$

Sample 2:

$$M_n = \frac{\sum n_i M_i}{\sum n_1} = \frac{1.12*10^9}{28*10^3} = 40{,}000; M_w = \frac{\sum n_i M_i^2}{\sum n_1 M_i} = \frac{47.2*10^{12}}{1.12*10^9} \approx 42{,}143; PDI = \frac{M_w}{M_n} \approx 1.05$$

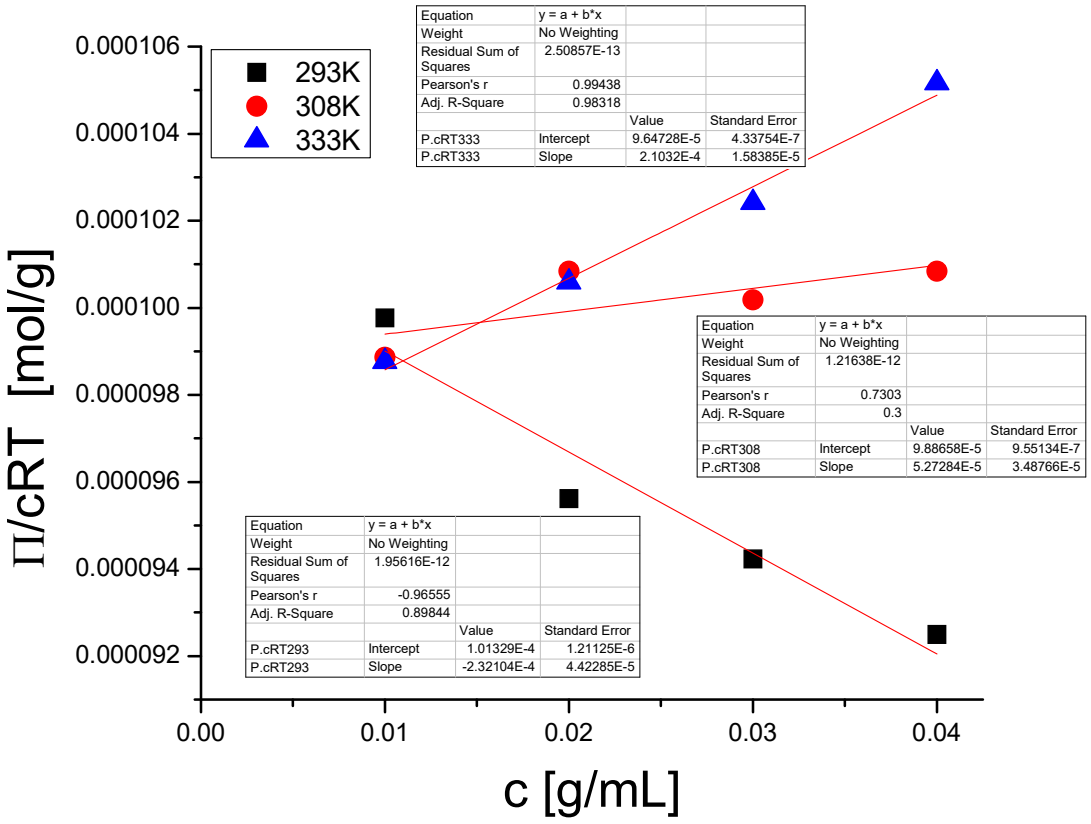
2. Calculate the length of completely extended molecule (end-to-end distance R_n) and the radius of completely packed sphere R formed by the same molecule for the case of atactic poly(propylene), C_3H_6, with molecular weight 2,100,000. Density of a-PP is 0.855 g/cm^3, assume length of each bond l=0.154 nm, and the angle between bonds =68°.

$$R_{n,\max} = nlCos(\theta/2) = 10^5 * 0.154 * 0.83 \approx 12.8\mu m$$

$$R = \sqrt[3]{\frac{3V}{4\pi}} = \sqrt[3]{\frac{3M}{4\pi\rho N_A}} \approx 9.9nm$$

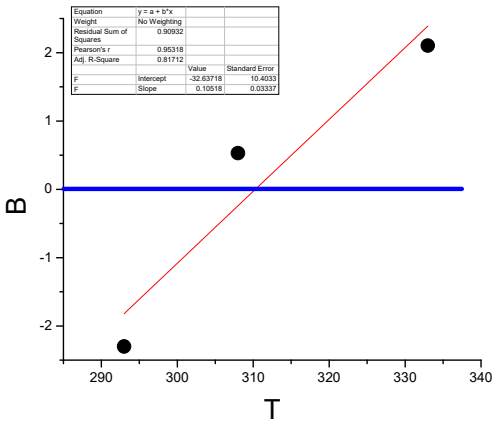
3. The Table presents the osmotic pressure in atm as a function of polymer concentration in g/mL in a solvent at three different temperatures in K. Please, estimate the molecular weight, second virial coefficient and Θ-temperature (use gas constant R=82.1 cm^3*atm/K*mol).

c [g/mL]	Π(293K) [atm]	Π(308K) [atm]	Π(333K) [atm]
0.01	0.024	0.025	0.027
0.02	0.046	0.051	0.055
0.03	0.068	0.076	0.084
0.04	0.089	0.102	0.115



Using the data, we plot Π/cRT vs c. The liner fit of the data provides $1/M_n$ value at c=0, and the slope provides the second virial coefficient B.

Thus from 3 curves we estimate $M_n \approx 1.01*10^4$ [g/mol] and $B(293K)=-2.3*10^{-4}$; $B(308K)=5.3*10^{-5}$; $B(333K)=2.1*10^{-4}$ [mol*cm^3/g^2].



It provides estimate of Θ temperature ~310K.