

Homework 4  
 due Monday April 30, 2007

1. Sun, problem 9.2 (osmotic pressure)
2. (from Painter and Coleman.) The following data are provided for  $K(1 + \cos^2 \theta)c/R_\theta$  (units of mol/g  $\times 10^6$ ) from static light scattering experiments on polystyrene solutions in benzene.

c g/cm <sup>3</sup>	Angle $\theta$ (degrees)										
	30	37.5	45	60	75	90	105	120	135	142	150
0.00200	3.18	3.26	3.25	3.45	3.56	3.72	3.78	4.01	4.16	4.21	4.22
0.00150	2.73	2.76	2.81	2.94	3.08	3.27	3.40	3.57	3.72	3.75	3.78
0.00100	2.29	2.33	2.37	2.53	2.66	2.85	2.96	3.12	3.29	3.38	3.37
0.00075	2.10	2.14	2.17	2.32	2.47	2.64	2.79	2.93	3.10	3.21	3.20
0.00050	1.92	1.95	1.98	2.16	2.33	2.51	2.66	2.79	2.96	3.11	3.12

Construct a Zimm plot and calculate the molecular weight, radius of gyration, and second virial coefficient. What kind of averages are  $M$  and  $s$ ? The incident light had wavelength  $\lambda_0 = 546.1$  nm, the index of refraction is 1.5014 for benzene under these conditions, and the incremental index of refraction  $dn/dc = 0.106$  cm<sup>3</sup>/g.

3. See the in-class handout on dynamic light scattering for some very useful background information and definitions of different correlation functions.

A small amount of an unknown polymer sample is dissolved in a solvent with index of refraction  $\bar{n} = 1.5$  and viscosity  $\eta_0 = 10^{-2}$  P (one poise equals 1 g cm<sup>-1</sup> s<sup>-1</sup>; see p. 80 in Hiemenz). Dynamic light scattering experiments are conducted at 300 K and a scattering angle of  $\theta = 60^\circ$ , using light of wavelength  $\lambda = 500$  nm. The following normalized intensity autocorrelation function values result:

time ( $\mu$ s)	$g_2(t) = \langle I(0)I(t) \rangle / \langle I \rangle^2$	time	$g_2(t)$
0	2.0000	220	1.00879
20	1.5542	240	1.00718
40	1.3133	260	1.00604
60	1.1815	280	1.00520
80	1.1083	300	1.00456
100	1.06684	320	1.00406
120	1.04289	340	1.00366
140	1.02869	360	1.00333
160	1.02005	380	1.00305
180	1.01463	400	1.00281
200	1.01113		

- (a) Plot  $g_1(t)$  vs time. Does the sample appear monodisperse? Why or why not?
- (b) Assuming there are exactly two chain lengths present, calculate the diffusion coefficient for each. HINT: Use the data points at long times to establish the contribution from one species. Then subtract this contribution from the data points at all times. Use the remaining contribution to  $g_1(t)$  to establish the contribution from the other species.

(c) Using the relationships involving the chain friction factor  $f$

$$Df = k_B T \quad (1)$$

$$f = 6\pi\eta_0 R \quad (2)$$

calculate the hydrodynamic radius  $R$  of the chain.

(d) Based on the relationship between radius of gyration and molecular weight, how much longer is one chain length type compared to the other?

4. (Another from Painter and Coleman.) The data below represent results from a gel permeation chromatography experiment on a polydisperse linear polychloroprene in THF, with Mark-Houwink-Sakurada constants at 30°C of  $K = 4.18 \times 10^{-5}$  dL/g and  $a = 0.83$ . Calculate the weight and number average molecular weights, the polydispersity, and the intrinsic viscosity of the mixture.

Elution volume	intensity (i.e. $h_i$ )	Elution volume	intensity (i.e. $h_i$ )
32.5	0.0	26.5	181.5
32.0	0.8	26.0	147.1
31.5	4.5	25.5	120.0
31.0	15.0	25.0	88.0
30.5	30.2	24.5	67.8
30.0	60.0	24.0	50.1
29.5	105.5	23.5	36.2
29.0	165.3	23.0	22.1
28.5	225.1	22.5	12.3
28.0	256.0	22.0	6.9
27.5	250.3	21.5	2.0
27.0	220.6	21.0	0.1
		20.5	0.0

For the same conditions, six monodisperse polystyrene samples have the following elution times in the column:

M	elution volume
2000000	23.3
850000	25.4
470000	26.7
105000	29.3
52000	30.3
11000	32.2

The PS standards have Mark-Houwink-Sakurada constants of  $K = 3.71 \times 10^{-4}$  dL/g and  $a = 0.64$ . Hint: you want to represent this  $M$  vs  $V$  dependency really well, since errors here will propagate elsewhere.