Polymers 1

A (4p)

What is the difference between the worm-like chain and the freely-jointed chain models? When is the worm-like chain model more applicable?

The freely jointed chain models the polymer as fully stiff segments with a certain length and with full freedom to rotate at the connection points. The worm-like chain bend continuously. It is usually a better model for polymers that are stiff, at least in relation to their contour length.

B (3p)

Why does the persistence length of DNA depend on ionic strength?

DNA contains negatively charged groups on the backbone so it is self-repelling, making it relatively stiff. However, at high ionic strength the charges are screened by counterions, which makes the molecule less stiff (shorter persistence length).

C (3p)

Which three types of "natural polymers" are the most important in biology? What is the building block (monomer type) for each type? (No need for details on the chemistry.)

Ribonucleic acids (DNA and RNA): Consist of four different so called base-pairs in a certain sequence. Proteins: Consist of amino acids (about 20 different types). Polysaccharides, like starch and cellulose: Consist of sugars.

Polymers 2

A (3p)

Polydimethylsiloxane (PDMS) has the following structure:
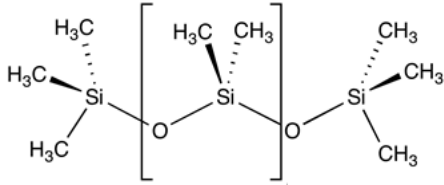
The length of a Si – O bond is 2 Å. In an experiment 20 kD PDMS is dissolved in chloroform and the Flory radius is determined to be 10 nm. What is the Flory radius of 50 kD PDMS under these conditions?

Here M is 2.5 times higher so the scaling relation of RF $\sim M^{3/5}$ gives a $2.5^{0.6}$ times higher end to end distance. This means $R_F = 17.3$ nm.

Comment: The length of the chemical bond (known) and the Kuhn length (unknown) are not relevant!

B (3p)

A ball consisting of PDMS with average $M = 20$ kg/mol and a density of 950 kgm^{-3} is dropped on a hard surface (at room temperature). Assume the friction coefficient of a segment along a chain is 10^{-8} kgs^{-1}. Calculate the terminal time and explain what happens to the ball!

Use the information from (A) to see that the monomer length is 4 Å. Calculate the monomer weight of 74 gmol^{-1} from atomic weights. The number of monomers is M/m $\approx$ 270 and the contour length is then 108 nm. Using the formula for the terminal time from reputation theory then gives 3.9 s. This is obviously longer than the time of contact with the surface for a bouncing ball so the PDMS responds elastically and bounces.

Comment: The density is not needed and there is no need to rescale or know the Kuhn length.

C (4p)

PDMS is exposed to oscillatory strain at 1 kHz. Assume the stress relaxation can be modelled simply as $G(t) = G_e\exp(-At)$ where G_e is the plateau modulus and A is a constant. Determine this constant if the phase delay is 5°.

Using the formula for the dynamic modulus directly and solving the integral should give a dynamic modulus of $i\omega G_e/[A+i\omega]$. Solving for the real part gives $\omega^2 G_e/[A^2+\omega^2]$ and the imaginary part $A\omega G_e/[A^2+\omega^2]$. The formula for phase delay then gives that $\tan(5°) = A/\omega$ which gives $A = 87$ Hz.

Comment: I forgot to say that ω was an angular frequency. It would be OK to multiply it with 2π and get a slightly different answer. Note that the plateau modulus is not needed and it cannot be calculated by the density given in (B) since we have no information about entanglement.

Boltzmann's constant: $k_B = 1.38 \times 10^{-23}$ JK^{-1}

Avogadro's number: $N_A = 6.02 \times 10^{23}$ mol^{-1}

$T(°C) = T(K) - 273.15$

Polydispersity index (M_w/M_n):

$$M_\text{n} = \frac{\sum_i n_i M_i}{\sum_i n_i} \qquad M_\text{w} = \sum_i w_i M_i = \frac{\sum_i n_i M_i M_i}{\sum_i n_i M_i}$$

Random walk:

$$R = aN^{1/2}$$

Worm-like chain model ($b = 2l_\text{p}$):

$$R_\text{wlc} = \left[2l_\text{p} r_\text{max} \left[1 - \frac{l_\text{p}}{r_\text{max}} \left[1 - \exp\left(-\frac{r_\text{max}}{l_\text{p}} \right) \right] \right] \right]^{1/2}$$

Entropy:

$$S = k_\text{B} \log(W)$$

Gibbs' free energy change:

$$\Delta G = \Delta H - T\Delta S$$

Flory radius (in solvent):

$$R_\text{F} = \left[1 - 2\chi \right]^{\frac{1}{5}} aN^{\frac{3}{5}}$$

Alexander - de Gennes brush height:

$$H = \left[\frac{1 - 2\chi}{3} \Gamma \right]^{\frac{1}{3}} a^{\frac{5}{3}} N$$

Reptation theory terminal time:

$$t_\text{T} = \frac{[aN]^2}{2D_\text{CiT}} = \frac{\zeta_\text{segment} a^2 N^3}{2k_\text{B}T}$$

Gelation threshold and gel fraction:

$$f_\text{c} = \frac{1}{z-1} \qquad p_\text{gel} = 1 - p_0{}^z \qquad p_0 = 1 - f + fp_0{}^{z-1}$$

Rubber elasticity modulus:

$$Y = \frac{3\rho k_\text{B}T}{mN_\text{part}} \qquad G_\text{e} = \frac{\rho k_\text{B}T}{M_\text{eff}}$$

Oscillatory deformation $e(t) = e_0\sin(\omega t)$ stress response and dynamic modulus:

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \qquad \tan(\delta) = \frac{\mathrm{Im}(G_{DM})}{\mathrm{Re}(G_{DM})} \qquad G_{DM}(\omega) = i\omega \int_0^\infty \exp(-i\omega t) G(t)\,dt$$

Los Alamos National Laboratory Chemistry Division

Periodic Table of the Elements

Group	1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	11B	12B	3A	4A	5A	6A	7A	8A
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.58	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La* 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 190.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.5	81 Tl 204.4	82 Pb 207.2	83 Bi 208.9	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac~ (227)	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (271)	111 Uuu (272)	112 Uub (277)		114 Uuq (296)		116 Uuh (298)		118 Uuo (?)

Lanthanide Series*

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0

Actinide Series~

90 Th 232.0	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)

element names in **blue** are liquids at room temperature
element names in red are gases at room temperature
element names in black are solids at room temperature

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