Polymers 1

A (5p)

The random walk or freely jointed chain segment model is a very simple way to predict the size of a polymer. It contains only one contribution to the free energy. What is the physical meaning of that term? Which two important terms (physical effects) are ignored in this simplified model? (Describe qualitatively with a few sentences per term, no need for equations.) Also, explain two relatively common situations in which the random walk model actually gives an accurate measure of coil size.

Conformational entropy, i.e. that the probability of being stretched out is lower. Ignores excluded volume (self-avoidance) and solvent interactions. Still works in theta solvents or in melts.

Mean: 3.8

B (3p)

Describe (without equations) how polymers crystallize. The description can be brief, but make sure the following questions are answered: What process corresponds to the activation energy? Why does one observe a characteristic thickness of lamellae? How can one influence this thickness in a simple manner?

Polymers never crystallize fully. The amount in crystalline state depends on polymer type, branching, stereochemistry etc. Form lamellae with thickness below contour length. Activation energy is the stretching of the coil before joining the lamellae. Very thin or thick lamellae grow too slow. The average thickness depends on the temperature (the undercooling).

Mean: 1.2

C (2p)

A polymer has a special end group that attaches spontaneously to a surface. How could one prepare a brush using such polymer molecules?
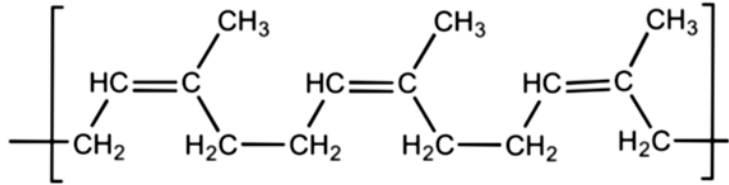
By cloud point grafting, i.e. to let the polymer bind to the surface in a poor solvent, which makes the coils smaller. Upon switching to a good solvent a brush will form (although usually not strongly stretched).

Mean: 1.0

Polymers 2

A (5p)

Poly(cis-isoprene), also known as natural rubber, has the chemical formula:

$$\left[\begin{array}{ccc} & CH_3 & CH_3 & CH_3 \\ HC=C & HC=C & HC=C \\ -CH_2 \quad H_2C-CH_2 & H_2C-CH_2 & H_2C- \end{array}\right]$$

Assume the Kuhn length is twice the monomer length, which is 4.0 Å. Calculate the size (distance between end points) of a coil in a solution with $\chi = 0$ if $M = 10$ kg/mol.

Should use Flory radius since this is normally the "best" model. Should calculate monomer mass from atomic weights ($m = 68$ g/mol) to get the number of monomers ($N = 147$). Should rescale to take into account that Kuhn length is not equal to monomer length. This gives $R_F = 11$ nm.

Comment: A lot of people used the full schematic as one monomer, even though it shows three monomers for clarity. This led to one less point because the definition of chemical monomer is the repeating entity. Still, it was probably unnecessarily confusing to show the structure like this.

Mean: 3.4

B (3p)

The solvent evaporates and the resulting melt has a density of 1.08 g/cm³. The plateau value of the stress relaxation modulus at room temperature is 4.86 MPa. How many monomers are between entanglement points on average?

The plateau value corresponds to rubber elasticity due to entanglement. The formula for G can be used directly, but requires converting units correctly. This gives a mass between entanglement points that corresponds to 8 monomers.

Mean: 1.8

C (2p)

The melt undergoes "vulcanization" during which cross-links to other chains can be formed at the methyl (-CH₃) groups. Estimate the percolation threshold!

The vulcanization can be considered as a type of gelation where each coil has one connection point per monomer (since there is one methyl group per monomer). The threshold is thus 1/[N-1], approximately the inverse of the degree of polymerization: 0.0068

Comment: The term "percolation threshold" was maybe a bit confusing. It could be that a lot of people did not understand this was about gelation.

Mean: 0.15

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):

$$M_n = \frac{\sum_i n_i M_i}{\sum_i n_i} \qquad M_w = \sum_i w_i M_i = \frac{\sum_i n_i M_i M_i}{\sum_i n_i M_i}$$

Random walk:

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

Entropy:

$$S = k_B \log(W)$$

Gibbs' free energy change:

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

Flory radius (in solvent):

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

Alexander - de Gennes polymer brush height:

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

Reptation theory terminal time:

$$t_T = \frac{[aN]^2}{2D_{CiT}} = \frac{\zeta_{segment} aN^3}{2k_B T}$$

Gelation threshold and gel fraction:

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

Rubber elasticity modulus:

$$Y = \frac{3\rho k_B T}{mN_{part}} \qquad G_e = \frac{\rho k_B T}{M_{eff}}$$

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

Los Alamos NATIONAL LABORATORY

CHEMISTRY

Group	Elements
1A	1 H hydrogen 1.008 ($1s^1$)
	3 Li lithium 6.941 ($[He]2s^1$)
	11 Na sodium 22.99 ($[Ne]3s^1$)
	19 K potassium 39.10 ($[Ar]4s^1$)
	37 Rb rubidium 85.47 ($[Kr]5s^1$)
	55 Cs cesium 132.9 ($[Xe]6s^1$)
	87 Fr francium (223) ($[Rn]7s^1$)
2A	4 Be beryllium 9.012 ($[He]2s^2$)
	12 Mg magnesium 24.31 ($[Ne]3s^2$)
	20 Ca calcium 40.08 ($[Ar]4s^2$)
	38 Sr strontium 87.62 ($[Kr]5s^2$)
	56 Ba barium 137.3 ($[Xe]6s^2$)
	88 Ra radium (226) ($[Rn]7s^2$)

Transition metals

3B	4B	5B	6B	7B	8B	8B	8B	11B	12B
21 Sc scandium 44.96	22 Ti titanium 47.88	23 V vanadium 50.94	24 Cr chromium 52.00	25 Mn manganese 54.94	26 Fe iron 55.85	27 Co cobalt 58.93	28 Ni nickel 58.69	29 Cu copper 63.55	30 Zn zinc 65.39
39 Y yttrium 88.91	40 Zr zirconium 91.22	41 Nb niobium 92.91	42 Mo molybdenum 95.94	43 Tc technetium (98)	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4
57 La* lanthanum 138.9	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.9	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 190.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.5
89 Ac~ actinium (227)	104 Rf rutherfordium (257)	105 Db dubnium (260)	106 Sg seaborgium (263)	107 Bh bohrium (262)	108 Hs hassium (265)	109 Mt meitnerium (266)	110 Ds darmstadtium (271)	111 Uuu (272)	112 Uub (277)

Main group (p-block)

3A	4A	5A	6A	7A	8A
					2 He helium 4.003 ($1s^2$)
5 B boron 10.81	6 C carbon 12.01	7 N nitrogen 14.01	8 O oxygen 16.00	9 F fluorine 19.00	10 Ne neon 20.18
13 Al aluminum 26.98	14 Si silicon 28.09	15 P phosphorus 30.97	16 S sulfur 32.07	17 Cl chlorine 35.45	18 Ar argon 39.95
31 Ga gallium 69.72	32 Ge germanium 72.58	33 As arsenic 74.92	34 Se selenium 78.96	35 Br bromine 79.90	36 Kr krypton 83.80
49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 208.9	84 Po polonium (209)	85 At astatine (210)	86 Rn radon (222)
114 Uuq (296)		116 Uuh (298)			118 Uuo (?)

Lanthanide Series*

| 58 Ce cerium 140.1 | 59 Pr praseodymium 140.9 | 60 Nd neodymium 144.2 | 61 Pm promethium (147) | 62 Sm samarium (150.4) | 63 Eu europium 152.0 | 64 Gd gadolinium 157.3 | 65 Tb terbium 158.9 | 66 Dy dysprosium 162.5 | 67 Ho holmium 164.9 | 68 Er erbium 167.3 | 69 Tm thulium 168.9 | 70 Yb ytterbium 173.0 | 71 Lu lutetium 175.0 |

Actinide Series~

| 90 Th thorium 232.0 | 91 Pa protactinium (231) | 92 U uranium (238) | 93 Np neptunium (237) | 94 Pu plutonium (242) | 95 Am americium (243) | 96 Cm curium (247) | 97 Bk berkelium (247) | 98 Cf californium (249) | 99 Es einsteinium (253) | 100 Fm fermium (253) | 101 Md mendelevium (256) | 102 No nobelium (254) | 103 Lr lawrencium (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