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

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

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:

![Chemical structure of poly(cis-isoprene)]

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/cm$^3$. 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 (-CH$_3$) 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: \( k_B = 1.38 \times 10^{-23} \text{ JK}^{-1} \)
Avogadro’s number: \( N_A = 6.02 \times 10^{23} \text{ mol}^{-1} \)
\( T(\degree C) = T(\text{K}) - 273.15 \)
Polydispersity index \((M_w/M_n)\):

\[
M_n = \frac{\sum n_i M_i}{\sum n_i} \quad M_w = \sum w_i M_i = \frac{\sum n_i M_i M_i}{\sum n_i M_i}
\]

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):

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

Alexander - de Gennes polymer brush height:

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

Reptation theory terminal time:

\[
t_T = \left[\frac{aN^2}{2D_{\text{CT}}}\right] = \frac{\zeta_{\text{segment}} aN^3}{2k_B T}
\]

Gelation threshold and gel fraction:

\[
f_c = \frac{1}{z - 1} \quad p_{\text{gel}} = 1 - p_0^z \quad p_0 = 1 - f + fp_0^{z-1}
\]

Rubber elasticity modulus:

\[
Y = \frac{3\rho k_B T}{mN_{\text{part}}} \quad G_e = \frac{\rho k_B T}{M_{\text{eff}}}
\]

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

\[
\sigma(t) = \sigma_0 \sin(\omega t + \delta) \quad \tan(\delta) = \frac{\text{Im}(G_{DM})}{\text{Re}(G_{DM})} \quad G_{DM}(\omega) = i\omega \int_0^\infty \exp(-i\omega t) G(t) dt
\]