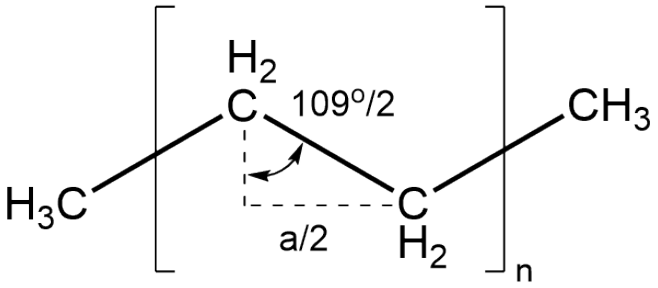
Solutions to Soft Matter Exercise - Chapter 5: Polymers

1. Polyethylene

a. The contour length is defined as $L = Na$. To calculate L, we first must calculate the degree of polymerization, N. The molecular weight of a repeat unit (C_2H_4) is 2×12 Da + 4×1 Da = 28 Da. Therefore, $N = (128242 - 2)/28 = 4580$. (We subtract 2 because the two end groups are CH_3 groups instead of CH_2 groups and the molecular weight of a CH_3 groups is 1 Da greater than that of a CH_2 group.)

Next we calculate the length of a repeat unit using trigonometry:



$$a = 2 \times 0.155\ nm \times \sin\frac{109^\circ}{2} = 0.25 \text{ nm}$$

Now, we can obtain:

$$L = Na = 1156 \text{ nm}$$

b. The end-to-end distance is defined as:

$$\sqrt{\langle r^2 \rangle} = \sqrt{Na^2(\tfrac{1+\cos\theta}{1-\cos\theta})} = \sqrt{4580 \times 0.25^2(\tfrac{1+\cos 71}{1-\cos 71})} = 23.7 \text{ nm}$$

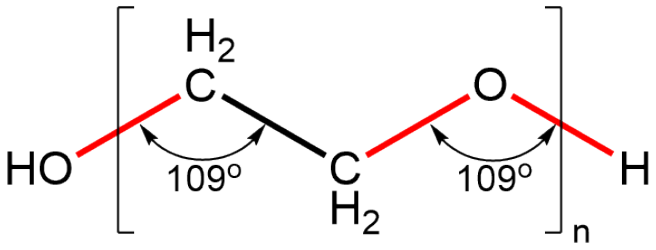
2. Poly(ethylene glycol)

The radius of gyration is defined as:

$$\sqrt{\langle R_g^2 \rangle} = N^v \tfrac{a}{\sqrt{6}} \sqrt{\tfrac{1+\cos\theta}{1-\cos\theta}}$$

where v is the Flory exponent.

We first calculate the length of the repeat unit, a, using trigonometry and obtain:



(C-O bonds indicated in red, C-C bonds in black)

$$a = 2 \times 0.143\ nm \times \sin(109°/2) + 0.155\ nm \times \sin(109°/2) = 0.359\ \text{nm}$$

To calculate N, we relate the molecular weight of the polymer to that of a repeat unit and obtain:

$$N = \frac{M_{w,pol}}{M_{w,r.u.}} = \frac{6000\frac{g}{mol}}{(2\times12+16+4\times1)\frac{g}{mol}} = \frac{6000\frac{g}{mol}}{44\frac{g}{mol}} \approx 136$$

a. For a good solvent, $v = 0.588$, we obtain:

$$\sqrt{\langle R_g^2\rangle} = N^v \frac{a}{\sqrt{6}} \times \sqrt{\frac{1+\cos\theta}{1-\cos\theta}} = 136^{0.588}\frac{0.359\ nm}{\sqrt{6}} \times \sqrt{\frac{1+\cos 71}{1-\cos 71}} = 3.7\ \text{nm}$$

b. For a bad solvent, $v = 0.333$, we obtain:

$$\sqrt{\langle R_g^2\rangle} = N^v \frac{a}{\sqrt{6}} \times \sqrt{\frac{1+\cos\theta}{1-\cos\theta}} = 136^{0.333}\frac{0.359\ nm}{\sqrt{6}} \times \sqrt{\frac{1+\cos 71}{1-\cos 71}} = 1.1\ \text{nm}$$

c. The coil overlap concentration is defined as:

$$c_m^* = \frac{N}{R_g^3} = \frac{136}{(3.7\ nm)^3} = 2.7\frac{r.u.}{nm^3} = 4.5\frac{mol_{monomers}}{l}$$

Attention: That is the concentration of *monomers* in solution!

d. To convert the average concentration of monomers in solution to the concentration of a polymer (PEG) in solution, we must divide the monomer concentration by the average number of repeat units contained in a polymer:

$$c_{PEG} = \frac{c_m^*}{N} = \frac{4.5\frac{mol_{monomer}}{L}}{136} = 33\frac{mmol_{polymer}}{L}$$

3. Polymers in Solution

For block-copolymers to self-assemble into vesicles, the packing parameter $\alpha = v/a_0 I_c$ should be close to 1. The packing parameter is the ratio of the cross-section of the hydrophobic block to that of the hydrophilic block. For block-copolymers, we can approximate it to be:

$$\alpha \approx \frac{R_{g,hydrophobic}^2}{R_{g,hydrophilic}^2}$$

We know the cross-section of the hydrophobic block, and from that we can deduce $R_{g,hydrophobic}$, assuming the cross-section to be a circle:

$$R_{g,hydrophobic} = \sqrt{\frac{A}{\pi}} = \sqrt{\frac{6\ nm^2}{\pi}} = 1.38 \text{ nm}$$

Assuming $\alpha = 1$, we can approximate $R_{g,PEG} \approx R_{g,PLA} = 1.38$ nm The end-to-end distance of the polymer, which allows us to calculate N is defined as:

$$\langle r_{PEG}^2 \rangle = 6\langle R_{g,PEG}^2 \rangle$$

Therefore, we obtain:

$$\sqrt{\langle r_{PEG}^2 \rangle} = \sqrt{6\langle R_{g,PEG}^2 \rangle} = \sqrt{6 \times 1.38^2\ nm^2} = 3.39 \text{ nm}$$

Because the angle θ between two bonds is fixed, we must correct for this restriction in the chain mobility and can calculate the mean end-to-end distance using:

$$\sqrt{\langle r_{PEG}^2 \rangle} = N^v a \times \sqrt{\frac{1+\cos\theta}{1-\cos\theta}}$$

For good solvents, we have $v = 0.588$. To determine the length of a repeat unit, we use geometry and obtain:

$$a = 2 \times 0.143\ nm \times \sin\frac{109^\circ}{2} + 0.155\ nm \times \sin\frac{109^\circ}{2} = 0.359 \text{ nm}$$

Then, we can determine the degree of polymerization, N using:

$$N = \Big(\frac{\sqrt{\langle r_{PEG}^2 \rangle}}{a}\sqrt{\frac{1-\cos\theta}{1+\cos\theta}}\Big)^{\frac{1}{v}} = \Big(\frac{3.39\ nm}{0.359\ nm}\sqrt{\frac{1-\cos 71}{1+\cos 71}}\Big)^{\frac{1}{0.588}} \approx 26$$

The molecular weight of a PEG repeat unit is 44 g/mol. Therefore, the PEG molecular weight should be around:

$$M_w = N \times M_{w,PEG} = 26 \times 44\frac{g}{mol} = 1144\frac{g}{mol}$$

4. Polymer Melts

a. An increase of the number of repeat units by 100, or 10%, would increase the viscosity of the melt as it would increase the time for entangled chains to disentangle. $\eta \propto M_w^{3.4} \rightarrow$ An increase in M_w by 10% would increase the viscosity to $1.1^{3.4} = 1.38$ times the initial viscosity. Therefore, the viscosity would increase by 38%.

b. Possibilities include increasing the processing temperature (but it must be below the decomposition temperature of the polymer) or the addition of some solvents or other polymers with a lower viscosity. This, however, can affect the structure (e.g. crosslinking density) and thus the properties of the resulting polymer.

5. Poly(styrene)

We, again, use the equation relating the shear modulus (G) to the molar mass between two entanglements (M_X):

$$G = \frac{\rho RT}{M_x}$$

$$M_x = \frac{\rho RT}{G} = \frac{1050\frac{kg}{m^3} \times 8.31\frac{J}{K \times mol}(273+160)\ K}{2 \times 10^5\ Pa} = 18.9\frac{kg}{mol}$$