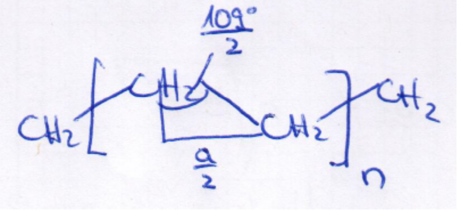
Solutions to Soft Matter exercise, Chapter 5: Polymers

1. Polyethylene

a. The contour length is defined as $L = Na$. To calculate L, we first calculate the degree of polymerization, N. The molecular weight of a repeat unit (C_2H_4) is $2\times 12Da + 4\times 1Da = 28Da$. Hence $N = \frac{128242-2}{28} = 4580$. (We subtract 2 because the two end groups are CH_3 groups instead of CH_2 groups and hence the molecular weight of a CH_3 group is 1 Da higher than that of a CH_2 group.) This means that the polymer has, on average 4580 repeat units.

Next, we calculate the length of a repeat unit. Using trigonometry



$$a = 2\times 0.155nm \times \sin\frac{109°}{2} = 0.25nm$$

Hence, we obtain

$L = Na = 1156nm$

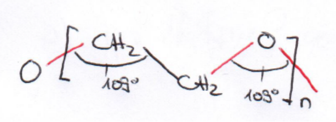
b. The end-to-end distance is defined as

c. $\sqrt{\langle r^2\rangle} = \sqrt{Na^2\left(\frac{1+cos\theta}{1-cos\theta}\right)} = \sqrt{4580\times 0.25^2\left(\frac{1+cos71}{1-cos71}\right)} = 23.7nm$

2. Poly(ethylene glycol)

The radius of gyration is defined as $\sqrt{\langle R_g^2\rangle} = N^{\upsilon}\frac{a}{\sqrt{6}}\sqrt{\frac{1+cos\Theta}{1-cos\Theta}}$ where υ is the Flory exponent.

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



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

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

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

$$N = \frac{M_{w,pol}}{M_{w,r.u.}} = \frac{6000\frac{g}{mol}}{(2\times 12 + 16 + 4\times 1)\frac{g}{mol}} = \frac{6000\frac{g}{mol}}{44\frac{g}{mol}} \approx 136$$

a. For a good solvent, $\nu = 0.588$ and we obtain

$$\sqrt{\langle R_g^2\rangle} = N^{\upsilon}\frac{a}{\sqrt{6}}\times\sqrt{\frac{1+cos\Theta}{1-cos\Theta}} = 136^{0.588}\,\frac{0.359nm}{\sqrt{6}}\times\sqrt{\frac{1+cos71}{1-cos71}} = 3.7\text{ nm}$$

b. For a poor solvent, $\nu = \frac{1}{3}$ and we obtain $\sqrt{\langle R_g^2 \rangle} = N^{\upsilon} \frac{a}{\sqrt{6}} \times \sqrt{\frac{1+cos\Theta}{1-cos\Theta}} = 136^{\frac{1}{3}} \frac{0.359nm}{\sqrt{6}} \times \sqrt{\frac{1+cos71}{1-cos71}}$=1.1 nm

c. The coil overlap concentration is defined as $c_m^* = \frac{N}{R_g^3} = \frac{136}{(3.7nm)^3} = 2.7\frac{r.u.}{nm^3} = 4.5\frac{mol_{monomers}}{l}$. **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 $\alpha = \frac{v}{a_0 l_c}$ 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 $\alpha \approx \frac{R^2_{g,hydrophobic}}{R^2_{g,hydrophilic}}$.

From the text, 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 of hydrophobic chain: $R_{g,hydrophobic} = \sqrt{\frac{A}{\pi}} = \sqrt{\frac{6nm^2}{\pi}} = 1.38nm$

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

$$\left\langle r^2_{PEG} \right\rangle = 6\left\langle R^2_{g,PEG} \right\rangle$$

Therefore, we obtain

$$\sqrt{\left\langle r^2_{PEG} \right\rangle} = \sqrt{6\left\langle R^2_{g,PEG} \right\rangle} = \sqrt{6 \times 1.38^2 nm^2} = 3.39nm$$

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

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

For good solvents, we have $\nu = 0.588$

To determine the length of a repeat unit, we use geometry and obtain

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

Hence, we can determine the degree of polymerization, *N* using

$$N = \left(\frac{\sqrt{\langle r_{PEG}^2 \rangle}}{a} \sqrt{\frac{1 - cos\theta}{1 + cos\theta}} \right)^{\frac{1}{v}} = \left(\frac{3.39nm}{0.359nm} \sqrt{\frac{1 - cos71}{1 + cos71}} \right)^{\frac{1}{0.588}} \approx 26$$

The molecular weight of a PEG repeat unit is 44 g/mol. Thus, 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 or repeat units by 10% would increase the viscosity of the melt as it would increase the time for entangled chains to disentangle. $\eta \propto M_w^{3.4}$ -> An increase in M_w by 10% would increase the viscosity to $1.1^{3.4} = 1.38$ times the initial viscosity. Hence, 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 that have a lower viscosity. This, however, can affect the structure (e.g. crosslinking density) and hence the properties of the resulting polymer.

5. Viscosity of entangled melts

a. The molar mass between two entanglements can be deduced from the shear modulus using the equation $G = \frac{\rho RT}{M_x}$

Hence, we find

$$M_x = \frac{\rho RT}{G} = \frac{900 \frac{kg}{m^3} \times 8.31 \frac{J}{K \times mol} \times 298K}{1.15 \times 10^6 Pa} = 1.9 \frac{kg}{mol}$$

b. For entangled polymers, the diffusion coefficient can be estimated as

$$D \approx \frac{\langle r^2 \rangle}{6\tau_d}$$

Because the polymer is contained in a melt, the Flory exponent is υ = 0.5 (theta solvent): The intermolecular interactions between the solute molecules and the solvent are the same as those between the solute molecules themselves because the solvent is the solute.

$$D \approx \frac{\langle r^2 \rangle}{6\tau_d} = \frac{\langle R_g^2 \rangle}{\tau_d} = \frac{Na^2}{6\tau_d}$$

We calculate the degree of polymerization using

$$N = \frac{M_{w,poly}}{M_{w,r.u.}} = \frac{100000 \frac{g}{mol}}{54 \frac{g}{mol}} = 1852$$

Hence, we find

$$D \times 6\tau_d = Na^2 = 1852 \times 0.65^2 nm^2 = 782 nm^2$$

To determine τ_d, we use η_0 by approximating

$$\eta_0 \approx G\tau_d$$

$$\tau_d \approx \frac{\eta_0}{G} = \frac{3.86\times10^{-3}\times\exp\left(\frac{1404}{298-128}\right)\times1852^{3.4}Pas}{1150000Pa} = \frac{1.9\times10^{12}Pas}{1150000Pa} = 1.7\times10^{6}s$$

$$D \approx \frac{Na^2}{6\tau_d} = \frac{782nm^2}{6\times1.7\times10^6 s} = 7.8\times10^{-23}\frac{m^2}{s}$$

c. This diffusion coefficient is very low. Reasons for the low diffusion coefficient include the high molecular weight and the entanglements of the polymers.

6. Poly(styrene)

We use again the equation that relates the shear modulus to the molar mass between two entanglements

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

$$M_x = \frac{\rho RT}{G} = \frac{1050\frac{kg}{m^3}8.31\frac{J}{K\times mol}(273+160)K}{2\times10^5 Pa} = 18.9\frac{kg}{mol}$$

7. Crosslink density of an elastomer

a. To calculate the molecular weight between crosslinks, which gives information on the crosslink density, we use the relation between the shear modulus and the molecular weight between crosslinks.

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

To determine G, we assume for small strains the relation between the stress and strain to be linear and the slope to be equal to G. Taking the difference between point 4 and 1 (other points at low strains can be taken) we obtain

$$\sigma = \varepsilon G$$

$$G = \frac{\Delta\sigma}{\Delta\varepsilon} = \frac{0.327MPa}{0.433} = 0.755MPa$$

Hence, we obtain

$$\frac{\rho}{M_x} = \frac{G}{RT} = \frac{7.55\times10^5 Pa}{8.31\frac{J}{K\times mol}293K} = 305\frac{mol}{m^3} = 0.183\frac{bonds}{nm^3}$$

Using the prediction of rubber elasticity, we obtain

b. $$\tau = \frac{\rho}{M_x}k_B T\left[(1+\varepsilon) - \frac{1}{(1+\varepsilon)^2}\right]$$

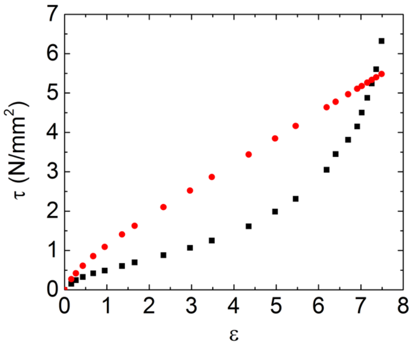


Figure 1: The measured data (black squares) and the calculated ones (red spheres) for the shear stress as a function of the strain.

We see that there is only a reasonable agreement at very low strains. As soon as the material starts to yield (flattening of the black curve), we observe a significant discrepancy. The discrepancy could come from inhomogeneous crosslink-distributions, or hardening effects at higher strains.

8. Thermosets

a. Resins (starting materials) are heated to initiate a crosslinking reaction where covalent bonds are formed. This crosslinking reaction is irreversible. Thus, it is important that the material is shaped before the crosslinking reaction starts or during early stages of the crosslinking reaction.
b. Examples of thermosets are poly(urethanes) used e.g. as insulating foams or poly(imides), used e.g. as medical tubings, insulating films, or as cladding of cables.