**Solutions to Soft Matter Exercise - Chapter 7: Gels**

**1. Sol-gel Process**

*Sol*: A sol is a solution or dispersion that behaves like a liquid ($G'' > G'$).
*Gel*: A gel is a percolating network of polymers or colloids that displays an elastic behavior. Thus, a gel behaves as a solid ($G'' < G'$).

**2. Gel**

a. The best choice would likely be a covalently-linked, biocompatible hydrogel. Covalent linkages ensure that the shape of the hydrogel is maintained even if it is repeatedly sheared. The entrapped water ensures moistening of the wound. The hydrogel must be biocompatible and, ideally, act as a barrier against bacteria and other infectious pathogens because the skin, which typically acts as this protective layer, is partially destroyed.

b. A highly-hydrated material with good biocompatibility is poly(ethylene glycol) (PEG), which has at least two functional groups that can form bonds with neighbors, such as acrylates or methacrylates.

c. The hydrogel swells due to differences in osmotic pressures. Inside the hydrogel, the monomer concentration, and very often the ion concentration as well, is much higher than outside the gel. As a result, water diffuses into the hydrogel.

d. With the choice of the monomers hydrogels are made from: the mechanical properties of hydrogels strongly depend on the crosslinking density (the molecular weight of the chains between two adjacent crosslinks, number of functional groups). The higher the crosslinking density, the stiffer the gel and the lower the degree of hydration (less water is incorporated into the gel per unit volume).

**3. Percolating Network**

a. The most efficient way to form a percolating network within a few generation is to use monomers with as many chemically reactive groups as possible. For example, monomers with 4 reactive groups easily form percolating networks.

b. To determine if we form a percolating network at any point, we determine the percolation threshold as:

$$f_c = \frac{1}{z-1} = \frac{1}{4-1} = \frac{1}{3}$$

In this case, $f_c$ is smaller than 0.4 such that we form a percolating network. The number of bonds formed, $N$, in the $n^{\text{th}}$ generation can be described as:

$$N \approx [f(z-1)]^n \rightarrow n = \frac{\log N}{\log(f(z-1))} = \frac{\log 1000}{\log(0.4(4-1))} \approx 38$$

c. In this case, $f < f_c = 1$, so the system will not form a percolating network.

d. The rigidity is inversely proportional to the molecular weight between two crosslinking points ($G = \rho RT/M_x$). To increase the shear modulus, the crosslink density must be increased. This can, for example, be achieved by taking trifunctional low molecular weight monomers (or monomers with four or more reactive groups).

## 4. Crosslink Rate

a. A sol transitions into a gel if the degree of reaction, $f$, is equal to the percolation threshold, $f_c$. Therefore, to determine the time needed for $f = f_c$, we determine $f_c$ using:

$$f_c = \frac{1}{z-1} = \frac{1}{2}$$

To determine the time, the equation given in the exercise must be integrated:

$$\frac{df}{(1-f)^2} = k\ dt$$

By integrating the two sides we obtain:

$$\frac{1}{1-f} = kt + A$$

For $t = 0$, we must have $f = 0$ such that $A = 1$. From this, we find:

$$t = \frac{\frac{1}{1-f}-1}{k} = \frac{\frac{1}{1-\frac{1}{2}}-1}{k} = \frac{1}{4\times10^{-4}\ s^{-1}} = 2500\ s \approx 42\ \text{min}$$

b. From the text, we know $f = 0.75$. Using the equation derived for (a), we find:

$$t = \frac{\frac{1}{1-f}-1}{k} = \frac{\frac{1}{1-\frac{3}{4}}-1}{k} = \frac{3}{4\times10^{-4} s^{-1}} = 7500\ s \approx 2.5\ \text{h}.$$

c. The probability that a site is connected to the percolation network is $P = 1-Q$, where $Q$ is the probability that a site is not connected to the percolating network. From the text, we know that $P = 0.75$. Q is the probability that a site is not connected to its neighbors $(1-f)$ plus the probability that the site is connected to one of its neighbors but that the neighbor is not connected to the percolating network ($fQ^{(3-1)}$). Thus, we obtain: $Q = 1 - f + fQ^2$. We can rewrite this equation as: $f(Q^2-1) = Q-1 \rightarrow f = (Q-1)/(Q^2-1)$. With $Q = 1 - P = 1 - 0.75 = 0.25$, we find:

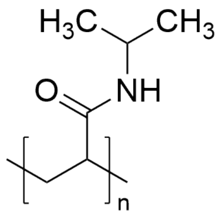
$$f = \frac{Q-1}{Q^2-1} = \frac{0.25-1}{0.25^2-1} = 0.8$$

Using the equation derived for (a), we find:

$$t = \frac{\frac{1}{1-f}-1}{k} = \frac{\frac{1}{1-0.8}-1}{k} = \frac{4}{4\times10^{-4} s^{-1}} = 10000\ s \approx 2.8\ \text{h}.$$

**5. Thermo-Responsive Polymers**

The chemical structure of a repeat unit of PNIPAM is:




PNIPAM has a lower critical solution temperature (LCST). Therefore, it is swollen at $T <$ LCST and collapsed at $T >$ LCST.

**At T < LCST:** H-bonds between the NG group of PNIPAM and water can form and PNIPAM is hydrated (surrounded by water molecules). In this state, the system maximizes entropy.

**At T > LCST:** The H-bonds become weaker relative to the thermal energy. At $T >$ LCST, H-bonds are broken and the system maximizes enthalpy my minimizing the contacts of water molecules with PNIPAM. Thus, PNIPAM collapses.