Question 1

A (2p)

To account for the interactions between a polymer and its surrounding water, one can use a regular solution model and let one water molecule be equal in size to a monomer. Does this predict an upper or a lower critical solution temperature? Explain why!

This model will predict an upper critical solution temperature because it only accounts for the configurational entropy of mixing, which is always positive. In reality the hydrophobic effect may give a lower critical solution temperature below which all mixtures are stable.

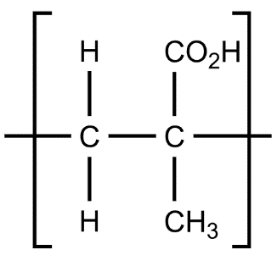
B (3p)

A suspension of colloids is stabilized at room temperature by poly(n-isopropylacrylamide) coils grafted to their surface. Explain what happens (and why) when the temperature is raised above the polymer transition temperature.

The polymers will collapse onto the colloid surface above the critical temperature to phase separate from water. Colloids will aggregate to minimize contact area between polymer and water. Then the aggregated colloids will sediment due to their weight.

Question 2 (4p)

Poly(methacrylic acid) of molecular weight 30 kg/mol is soluble in water:



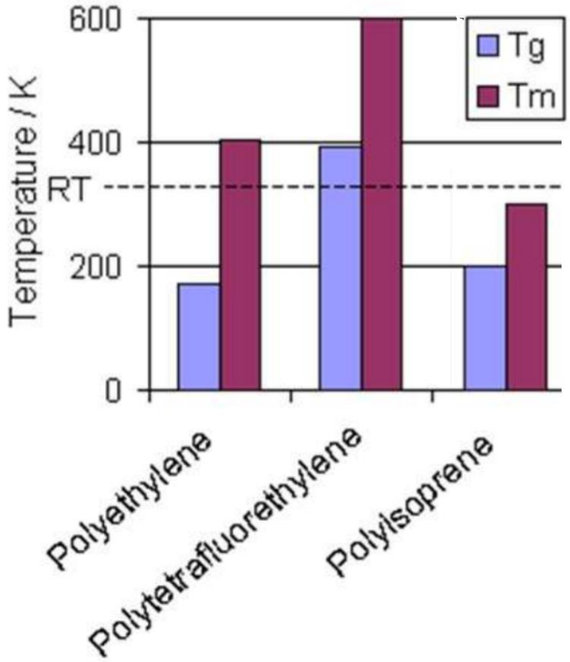
The monomer size is 4 Å, the Kuhn length is 2 nm and the excluded volume parameter is 0.08 nm^3. Estimate the volume fraction of polymer inside its own coil, i.e. how densely packed the coil is. You may use the Flory radius: $R_F = [abv]^{1/5}N^{3/5}$

The monomer weight is 86 g/mol so $N = 30000/86$. Using $a = 0.4$ nm, $b = 2$ nm and $v = 0.08$ nm^3 gives $R_F = 19$ nm. The volume fraction is best estimated as Na^3/R_F^3 which becomes 0.003.

Note: Using v as the volume of a monomer is not very accurate (although I should have chosen a values which differed more from a^3). Actually the main point of this question is to test if you understand the meaning of the parameters. You got maximum 2 points if you did not use Na^3 for polymer volume.

Question 3 (6p)

The diagram shows typical glass transition and melting temperatures for three different polymers.



Make an educated (well-motivated) guess about which polymer will give which material properties at room temperature: (1) hard and brittle, (2) elastic (at least a little bit) and (3) viscoelastic.

If T_m and T_g are above RT, the polymer is either crystalline or glassy on the microscale, but regardless it will be hard and brittle (polytetrafluorethylene). If T_m and T_g are below RT, the polymer should be viscoelastic since the chains are free to move but still entangled (polyisoprene). When $T_g < RT < T_m$ the material properties will depend highly on the degree of crystallinity. The crystalline domains are hard but the regions in between are soft. Some elasticity can be expected since the crystalline domains can act as cross-links (polyethylene).

Note: Many people wrote that polyethylene is in the "liquid" state, but also that it is viscoelastic. This is rather inconsistent. Viscoelasticity is not the same thing as liquid behavior. Melts do not behave as typical liquids at room temperature unless the molecular weight is very low. Overall I got the correct answers from many people but with very poor motivations.