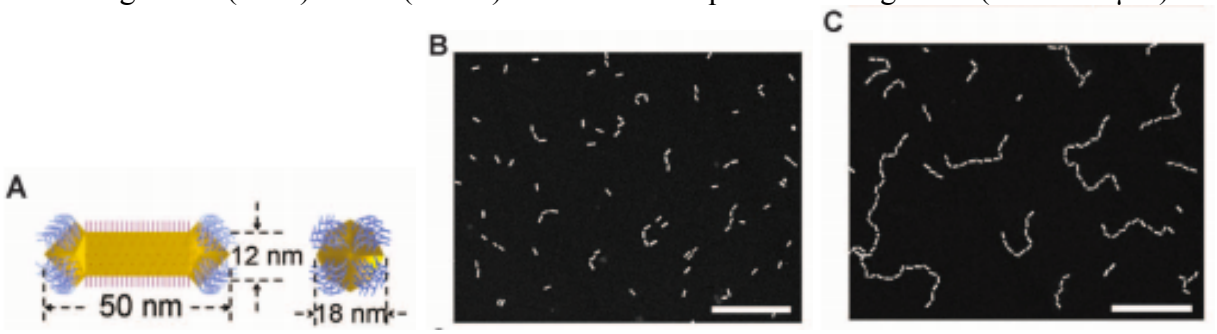
Quiz 7 Properties of Materials CME 300
November 14, 2011

1) Liu et al. (*Science* **329** 197-199 (2010)) created thiol terminated gold nanorods that can bind through S-S bonds (the dark hairs at the ends of the rods in A below are the thiol sites). Figures B (8 hrs) and C (24 hrs) show a time sequence of the growth (bar is 0.5 μm).



a) Make a plot of average number of gold nanorods in a linear cluster as a function of time (explain your choice of functionality).

b) Do you think that this process will lead to clusters with a large number of nanorods? Explain why or why not. (What do you think the extent of reaction is in figure C?)

c) What is the path you would suggest to increase the number of nanorods in a cluster?

d) How do nanoparticles and aggregates differ in physical behavior when compared to atomic-scale monomers and polymers? (You may want to consider the effect of temperature on the motion of atomic-scale and nano to micron scale structures. Also the time it would take for a 1 μm aggregate to find another aggregate and couple end-to-end and the relative magnitude of the enthalpy of bonding compared to the energy associated with motion of the aggregate, etc.)

2) Percolation can occur in reactions where the monomers have a higher functionality than 2.

a) Explain what percolation is for a condensation reaction between trifunctional and bifunctional monomers.

b) For the structures of question 1, branches (see below) occur in about 0.5% of the nanorod units. Calculate the average functionality and the extent of reaction at percolation, p_c. Is Figure C in question 1 close to percolation?

c) In class we observed a Monte Carlo computer simulation that could determine if percolation had occurred. Explain how this program worked by first describing the construction of a random set of reacted sites, then a process to determine if percolation occurred in the horizontal direction.

d) In a polymer/solvent system what physical property could indicate that percolation had occurred.

e) How could you test for percolation in the gold nanoparticle system?

ANSWERS: Quiz 7 Properties of Materials CME 300
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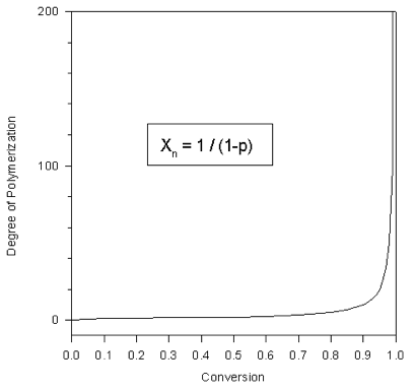
1) a) Make a plot of average number of gold nanoparticles in a linear cluster as a function of time (explain your choice of functionality).

It is expected to follow step growth kinetics so the plot of average number of gold nanoparticle in a linear cluster would be low throughout the reaction except when p => 1.00.



b) Do you think that this process will lead to clusters with a large number of nanorods? Explain why or why not. (What do you think the extent of reaction is in figure C?)

The process will be limited in number of particles in a cluster since it is not possible to drive this reaction to p = 1.00 with the reaction scheme described here. Figure C shows about 200 nanorods with 41 free ends so p = (400-41)/400 = 0.90. (Incidentally, there is one trifunctional branch site in the bottom right, 1/400 = 0.25% branches)

c) What is the path you would suggest to increase the number of nanorods in a cluster?

The extent of reaction needs to be driven to 1.00 or as close as possible. This might be achieved through manipulation of the solvent so as to force sulfur groups together due to hydrophobicity for instance. The addition of water or polar solvents to the nanorod system could drive the reaction towards completion.

d) How do nanoparticles and aggregates differ in physical behavior when compared to atomic-scale monomers and polymers? (You may want to consider the effect of temperature on the motion of atomic-scale and nano to micron scale structures. Also the time it would take for a 1 μm aggregate to find another aggregate and couple end-to-end and the relative magnitude of the enthalpy of bonding compared to the energy associated with motion of the aggregate, etc.)

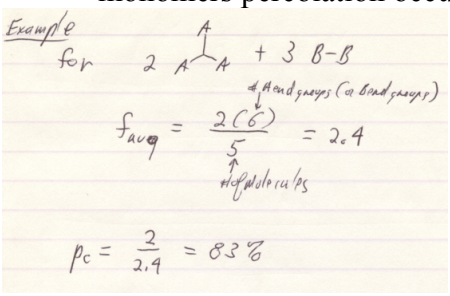
Nanoparticles close to 1μm in size are not subject to thermal motion, thought they can be impacted by gas or liquid molecules that can impart motion. These particles do not strictly follow Fick's law and we expect that many of the concepts of random systems do not apply most importantly, Carother's model for polymerization in step growth systems. The enthalpy associated with bonding of two nanorods in this case is negligible compared with the energy needed to move these relatively large particles. There is no real thermodynamic balance between

entropy and enthalpy for the nanorod system, i.e. the concept of free energy applies to a very large number of small particles not to the relatively small number of relatively large particles involved in this system. So there are many differences between this nanoparticle system and a molecular-based step-growth polymerization.

2) Percolation can occur in reactions where the monomers have a higher functionality than 2.

a) Explain what percolation is for a condensation reaction between trifunctional and bifunctional monomers.

Percolation occurs when the reactants have reacted to an extent that there is a pathway across the sample through chemical bonds. For a reaction between trifunctional and bifunctional monomers percolation occurs at 83% conversion following the Carother's equation,



b) For the structures of question 1, branches (see below) occur in about 0.5% of the nanorod units. Calculate the average functionality and the extent of reaction at percolation, p_c. Is Figure C in question 1 close to percolation?

1 group of functionality 3 for 200 groups of functionality 2 so f_{avg} = 403/200 = 2.015 and p_c = 2/2.015 = 0.993. Figure C is not close to percolation since p = about 0.90.

c) In class we observed a Monte Carlo computer simulation that could determine if percolation had occurred. Explain how this program worked by first describing the construction of a random set of reacted sites, then a process to determine if percolation occurred in the horizontal direction.

The program flips a coin weighted by p for each reaction site to decide if it has reacted. In the computer program you would first check in the vertical direction if you have an occupied site, then go to the next layer to check for an occupied site, if yes then you would continue on until no occupied sites were found testing each possible path. This would be used to identify clusters. If one of these clusters reached the opposite side then percolation would have occurred in the vertical direction. You would need to repeat this for the horizontal direction.

d) In a polymer/solvent system what physical property could indicate that percolation had occurred.

Experimentally, the percolation threshold is found at the gel point where the viscosity goes to infinity.

e) How could you test for percolation in the gold nanoparticle system?

You could test for conductivity across the sample. When percolation occurs you could see a step increase in conductivity across the system.