

## Quiz 10 Polymer Properties October 31, 2014

Palangetic et al. from the group of R.E. Cohen at MIT proposed a dependence of the concentration at which fibers can be spun using electro-spinning by associating  $c_{\text{spin}}$  with  $c^*$ ,

$$c_{\text{spin}} \sim c^* \sim M^{(1-3\nu)} = M^{-a} \quad (1)$$

(Palangetic L, Reddy NK, Srinivasan S, Cohen RE, McKinley GH, Clasen C *Polymer* **55** 4920 (2014).) They measured the parameter “a” using intrinsic viscosity and found it to be 0.754. They then experimentally determined the concentration where spinning could first be achieved and made the following plot.

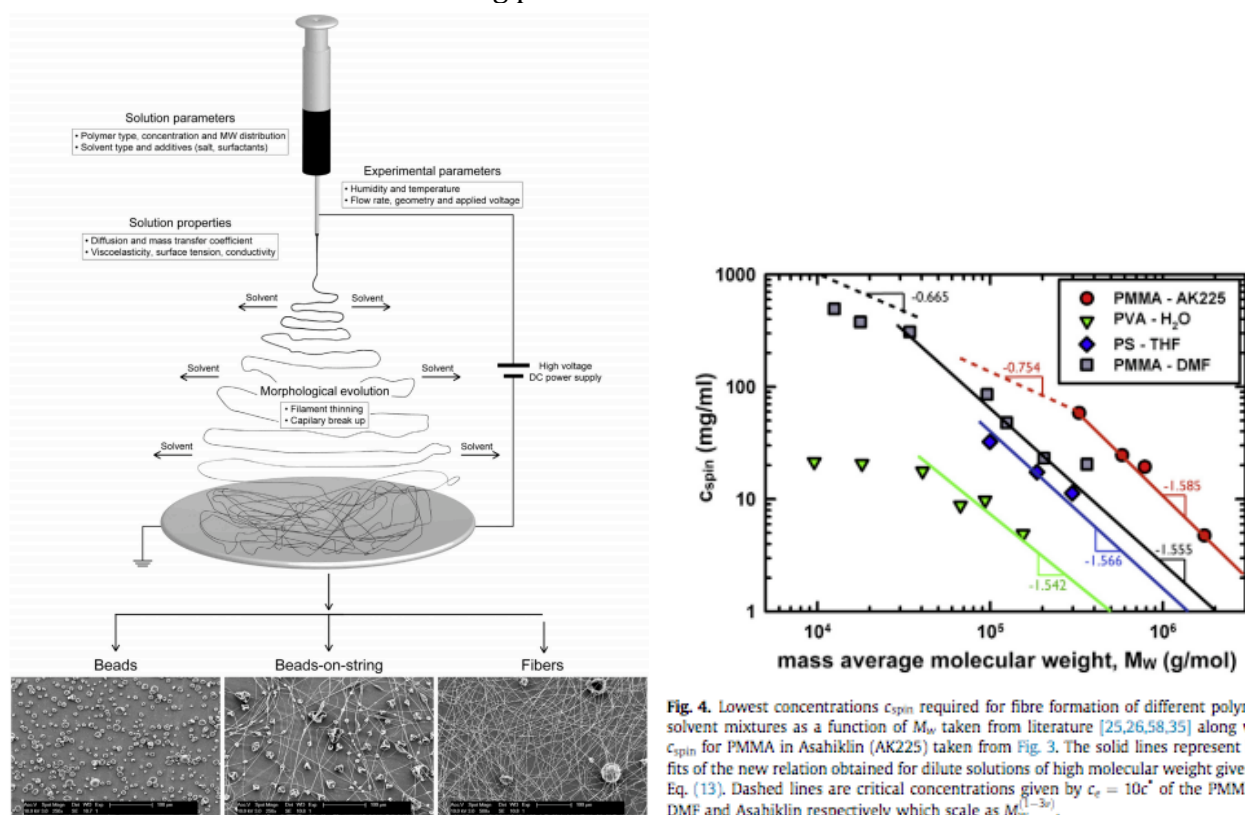


Fig. 4. Lowest concentrations  $c_{\text{spin}}$  required for fibre formation of different polymer/solvent mixtures as a function of  $M_w$  taken from literature [25,26,58,35] along with  $c_{\text{spin}}$  for PMMA in Asahiklin (AK225) taken from Fig. 3. The solid lines represent best fits of the new relation obtained for dilute solutions of high molecular weight given by Eq. (13). Dashed lines are critical concentrations given by  $c_e = 10c^*$  of the PMMA in DMF and Asahiklin respectively which scale as  $M_w^{(1-3\nu)}$ .

- List the expected values for “a” for a Gaussian chain, a self-avoiding walk, a rod, a ceramic aggregate of mass-fractal dimension 1.8, and a 3-d object.
- What kind of structure would display “a” = 0.754? What would display “a” = 1.585?
- If you consider that the polymers in electro-spinning are under extremely high extensional stress, a stress that might be expected to increase on a molecular basis with molecular weight, give an explanation for the behavior seen in Figure 4.
- If the chains were branched how would the molecular weight dependencies in Figure 4 be modified?
- If electro-spinning were done at a higher temperature how would the behavior in Figure 4 be modified?

## ANSWERS: Quiz 10 Polymer Properties October 31, 2014

1) a)

Structure	$d_f$	$\nu$	$a$
Rod	1	1	2
SAW	5/3	3/5	0.8
DLCA	1.8	5/9	2/3
Gaussian Coil	2	0.5	0.5
3d (Sphere)	3	1/3	0

b) For  $a = 0.754$  the chain is a little less expanded than a good solvent coil. This could be due to branching (or interactions between chains that act effectively as branches), inaccuracy of the measurement, some type of phase separation that occurs in this solution. For  $a = 1.585$  the chains are significantly extended and act substantially like extended chains. This could be due to the chains stretching out at high shear rates or it could be due to the inaccuracies of measuring this behavior using optical micrographs as was done in this paper.

c) As molecular weight increases, in Figure 4, higher molecular weight chains have a higher number of entanglements. This means that there is a greater effect on the chains for a given shear rate. The transition between -0.754 and -1.585 slope could be due to the onset of entanglements at molecular weights of about  $10^5$  g/mole (a typical value for synthetic polymers).

d) Branching would reduce the size of the chains but it would increase the connectivity. Branching would decrease the hydrodynamic volume per mass and the intrinsic viscosity ( $[\eta] \sim V_H/M$ ). The mass fractal dimension of the chains would be higher so “a” would be smaller. A smaller “a” means a weaker slope in the plot.

It is more difficult to orient branched chains but their entanglements are greater. The slope at high concentration would be weaker and the transition would be earlier.

So both slopes would be shallower and the transition would move to the left for branched chains.

e) At higher temperature the hydrodynamic radius increases following the plot given below. An increase in  $V_H$  at higher temperature leads to an increase in  $[\eta] \sim V_H/M$ . The slope at low concentration would be closer to 0.8 and the extension at high concentration would be greater so the slope closer to 2 (rod-like). The entanglements would occur earlier in concentration for more expanded coils so the transition would shift to the left.

