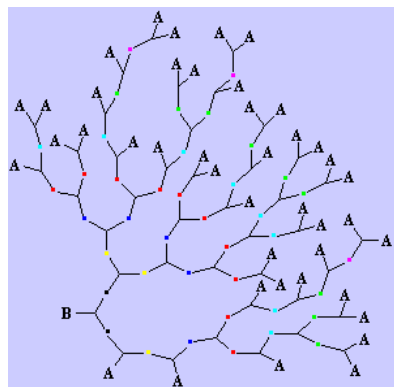


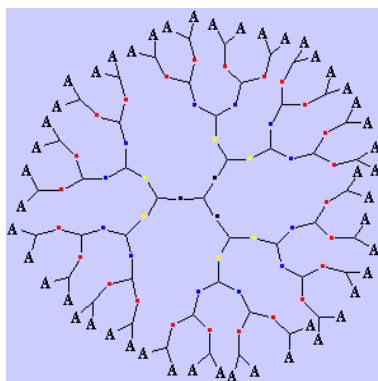
## 060414 Quiz 3 Polymer Properties

This week we considered measures of the overall coil size, mostly the hydrodynamic radius but also briefly the radius of gyration.

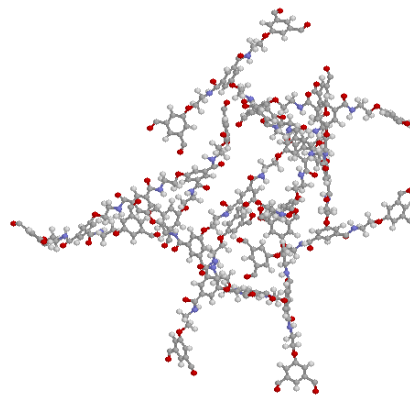
- 1) There seem to be a number of methods to measure size of a coil. Consider a hyperbranched polymer (or a dendrimer) such as shown in the figures below.



Hyperbranched



Dendrimer



Dendrimer

[www.ipfdd.de](http://www.ipfdd.de) and [www.ipf-analysis.de](http://www.ipf-analysis.de)

- a) If you could see these structures in a microscope how would you describe the size. Especially consider the structure in an equilibrated state such as the last image and subject to thermal motion (like a living, 'drunken', branched worm say).
- b) In class we discussed the root-mean-square end-to-end distance. What is the RMS end-to-end distance for these structures? Is it related to what you perceive as the size?
- c) Would you expect the RMS end-to-end distance to be larger or smaller for these objects compared to an unbranched polymer chain of similar molar mass?
- d) What problems might you expect in measuring the hydrodynamic radius for these structures?
- e) What problems would there be in measuring/interpreting the radius of gyration?
- 2) The hydrodynamic radius is measured in a dynamic experiment such as observation of flow or diffusion.
- a) Write an equation for the viscosity of a polymer solution that describes the increase in viscosity with concentration. (Give the units of all constants in this equation).
- b) Write an expression for the intrinsic viscosity,  $[\eta]$ , based on the units of this constant using the hydrodynamic radius and the molecular weight.
- c) Give a function of  $[\eta]$  in terms of molecular weight for a Gaussian chain, a self-avoiding walk and for a rod.
- d) How is the diffusion coefficient related to the hydrodynamic radius?
- e) Explain qualitatively how the dynamic light scattering experiment (DLS) can measure the diffusion coefficient.

- 3) The moment of inertia of an object is defined by  $I = \sum m_r (r - r_{COM})^2$  where the summation is over all points "r" in an object and  $r_{COM}$  is the center of mass defined by  $r_{COM} = \frac{\sum m r}{M}$ , and  $m_r$  is the mass at point r. The torque,  $\tau$ , on an object resulting from an angular acceleration  $\alpha$  is given by  $\tau = I\alpha$ . The kinetic energy, K, of a rotating body is given by  $K = \frac{1}{2} I \omega^2$  where  $\omega$  is the angular velocity. For rotating bodies I serves the place of m for linear motion. (From Wikipedia).
- a) Compare the definition of the radius of gyration to the definition of the moment of inertia.
  - b) How can scattering be used to measure the radius of gyration? (Give a universal equation.)
  - c) How would you relate the end-to-end distance of a linear polymer chain to its moment of inertia? (just give an equation do not derive).
  - d) What is the advantage of radius of gyration or moment of inertia over other measures of chain size such as the hydrodynamic radius or the end-to-end distance?
  - e) It is natural to consider twice the radius to obtain size. In the case of radius of gyration, does it make sense to consider  $2 R_g$ ? (What meaning does  $2 I$  have?)

### ANSWERS: 060414 Quiz 3 Polymer Properties

1) a) The branched worm would be hard to describe in terms of size since it doesn't have a beginning or an end and because it displays many different sizes, in fact this is the definition of a fractal. We could compare two different objects of the same type (same  $d_f$ ,  $c$  and  $d_{min}$ ) and determine which is larger. This would be more difficult for objects of different dimensions. In the end, most people gravitate to the concept of the radius of an enclosing sphere which is basically the end to end distance of the minimum path,  $p$ , so  $l_p z^{1/df}$  would be a measure of this type.

b) The RMS end-to-end distance is the end to end distance of the minimum path,  $p$  as described in part a. This is  $l_p p^{1/d_{min}} = l_p z^{1/d_{min} c} = l_p z^{1/df}$ .

c) The RMS end-to-end distance would be larger for a linear chain.

d) Distortion of the structure under shear flow would be a problem. Also, if the structures are asymmetric the hydrodynamic radius could be inaccurate.

e) There would be no problem in measuring the radius of gyration but interpretation could be difficult if the extent of branching in the structure is not known.

2) a)  $\eta = \eta_s (1 + \phi[\eta])$  where  $[\eta]$  is the intrinsic viscosity with units of volume per mass.

b)  $[\eta] = R_H^3/N$ , where  $N$  is the molar mass.

c) For a Gaussian Chain we have  $R \sim N^{1/2} l_p$

For a SAW  $R \sim N^{3/5} l_p$

For a Rod  $R \sim N l_p$ , so,

$$[\eta] \sim N^{1/2}$$

$$[\eta] \sim N^{0.8}$$

$$[\eta] \sim N^2$$

d)  $D = 3kT/(6\pi\eta_0 R_H)$

e) In DLS we observe the intensity at a fixed scattering angle. The intensity is recorded as a function of time and the flickering that results from motion of particles in and out of the beam leads to a randomly oscillating pattern in time. The time correlation function decays in time difference between measurements and this is fit with  $I(q,t) = \exp(-tq^2D)$  to yield  $D$ .

3) a) The radius of gyration squared is the moment of inertia divided by the total mass.

b) Measure  $I$  versus  $q = 4\pi/\lambda (\sin(\theta/2))$ , and fit with  $I(q) = G \exp(-q^2 R_g^2/3)$ .

c)  $\langle R^2 \rangle = R_g^2/6 = I/(6M)$  where  $M$  is the total mass of the sample.

d) The radius of gyration is not subject to distortion due to the application of force to the object. The radius of gyration has a strict mathematical definition for any object.

e) It does not make sense to consider  $2 R_g$  since the radius of gyration is not really a radius. For example, for a linear Gaussian chain we should consider  $\sqrt{6} R_g$  for the size of the object.  $2 R_g$  has no meaning.