120403 Quiz 1 Polymer Properties

1) In class it was mentioned that polymers are the only class of materials that are defined by their dynamic behavior. For example, polymeric fluids display normal stresses (stress at a right angle to the applied shear stress) in shear flow that cause asymmetry of bubbles.

   a) Sketch the shape of a bubble in a Newtonian fluid (like cooling oil) and a bubble in a polymeric fluid (like shampoo).

   b) In general terms, explain why the polymeric bubble is asymmetric.

   c) The following plot of log viscosity versus log rate of strain shows a transition from Newtonian behavior to a power-law decay. Explain how a time constant for the polymer melt can be obtained from this plot.

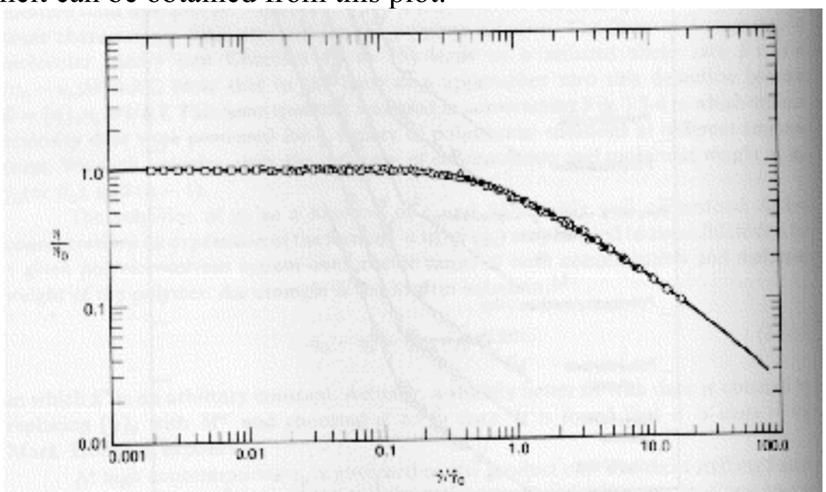


FIGURE 3.6-5. Composite plot of dimensionless viscosity η/η_0 versus dimensionless shear rate for several different concentrated polystyrene *n*-butyl benzene solutions. Molecular weights varied from 1.6×10^5 to 2.4×10^6, concentrations from 0.255 to 0.55 g/cm^3, and temperatures from 303 to 333 K. [W. W. Graessley, *Adv. Polym. Sci.*, 16, 1–179 (1974).]

   d) How could the time constant obtained in part c) pertain to the shape of droplets described in part a). What parts of the plot pertain to each of the two droplets you drew in part a).

   e) Do you think that the polymer chains at the high strain rate end of the plot in question c) are Gaussian? Explain your answer.

2) A Gaussian chain is two dimensional, as is a disk.

   a) Derive a function that shows that a Gaussian chain is 2-dimensional.

   b) How can a scaling dimension be used to distinguish between a disk and a Gaussian chain?

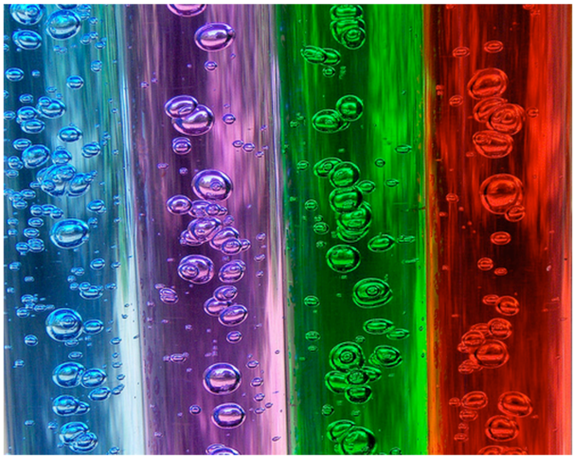
   c) Give an expression for the density of a polymer chain as a function of the mass of the chain, N.

   d) The radius of gyration is one measure of the size of a polymer chain. R_g is given by $R_g^2 = \frac{\langle R^8 \rangle}{\langle R^6 \rangle}$. How can the Gaussian distribution be used to calculate the moments in this equation?

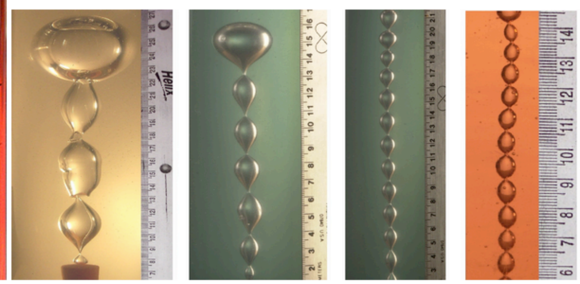
   e) Sketch a plot of $P_G(R)$, $RP_G(R)$, $R^2P_G(R)$, $R^4P_G(R)$. What happens to the peak in the plot as n increases in the term $R^nP_G(R)$. ($P_G(R)$ is the Gaussian Distribution Function.)

ANSWERS: 120403 Quiz 1 Polymer Properties

1) a)



Newtonian Fluid Bubbles



Bubbles in Polymer Solution

b) The coils are deformed as the bubble passes and push back do to their entropic spring constant. The shape should become more distorted with higher temperature since the entropy of the chain increases. The shape should also become more distorted with lower molecular weight. The shape should become more distorted with higher bubble velocity since the shear rate depends on the bubble velocity.

c) In the Newtonian plateau (flat part of the curve at low shear rate) the fluid is Newtonian and the experimental time (1/shear rate) is longer than the materials response time or time constant. At higher shear rates the experimental time is smaller than the response time and the fluid shows power-law behavior with a decaying viscosity as the polymers are deformed by the shear force and remain deformed on the time scale of the experiment (1/shear rate). The time constant is 1/shear rate at the transition between the plateau and the power-law fluid regimes.

d) The bubbles distort when the shear rate is higher than 1/time constant for relaxation of the polymer chain. The bubble shape could be a way to measure the time constant for the fluid.

e) The chains are probably non-Gaussian since we are observing an effect of distortion of the chain structure by the applied shear. Distorted chains are becoming extended and decidedly non-Gaussian.

2) a)

The chain is composed of a series of steps with no orientational relationship to each other.

So <R> = 0

$<R^2>$ has a value:

$$\langle R^2 \rangle = \sum_i \sum_j r_i \bullet r_j = \sum_i r_i \bullet r_i + \sum_i \sum_{j \neq i} r_i \bullet r_j$$

We assume no long range interactions so that the second term can be 0.

$$\langle R^2 \rangle = Nr^2$$

The first term has a value Nr2 and the second term is 0 because there is no relationship between i and j vectors since the process is random. This means that there is an equally likely probability that the vector will go positive and negative so the average is 0 for the second term.

The final function is 2-dimensional since mass goes with size squared.

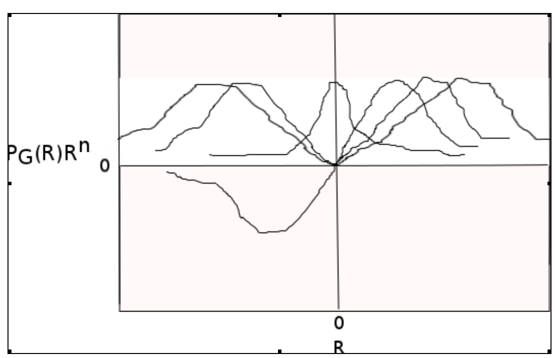
b) If we run a current through the object we obtain a path of length p, the minimum path or short circuit path. The mass of the path p scales with the mass of the object to the power 1/c. c is called the connectivity dimension. c is 1 for a linear object and 2 for a disk. If we crumple a sheet of paper the dimension c remains 2 just as c for a rod remains 1 even when the rod is crumpled. The extent of crumpling is measured by the overall size, R to minimum path length p, R ~ pd_{min}, where d_{min} increases as the object is crumpled. $d_f = c\ d_{min}$.

c) Density is Mass/Volume and Volume is R^3. For a polymer coil R ~ $N^{1/2}$, so density ~ $N/N^{3/2}$ or $N^{-1/2}$. So the density decreases with size, a larger polymer has a lower density than a smaller polymer.

d) Moments are obtained from the distribution function,

$$\langle R^n \rangle = \int_{-\infty}^{\infty} R^n P_G(R) dR$$

e)



Center is Gaussian, progressing powers of R have the peak moving outwards. (best I can draw this on the computer)