Viscosity

Viscosity Defined

Viscosity is the most tangible effect of macromolecules, and it was used to determine that there *were* macromolecules, as opposed to physically attracted aggregates.

Consider the "conceptual viscometer" below, made from two flat plates, a pulley and a weight.
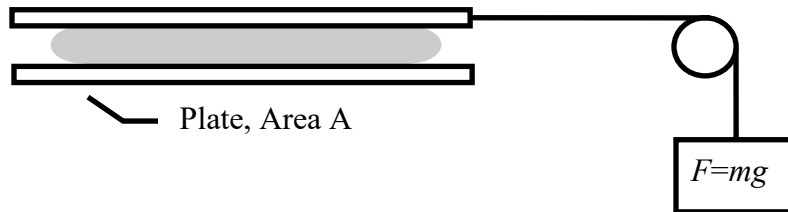

Figure 1

The weight, acting through the pulley, establishes a velocity of the upper plate relative to the stationary lower plate. If the fluid is viscous, the upper plate moves more slowly. Now let's look in more detail, zeroing in on the two plates and fluids only.
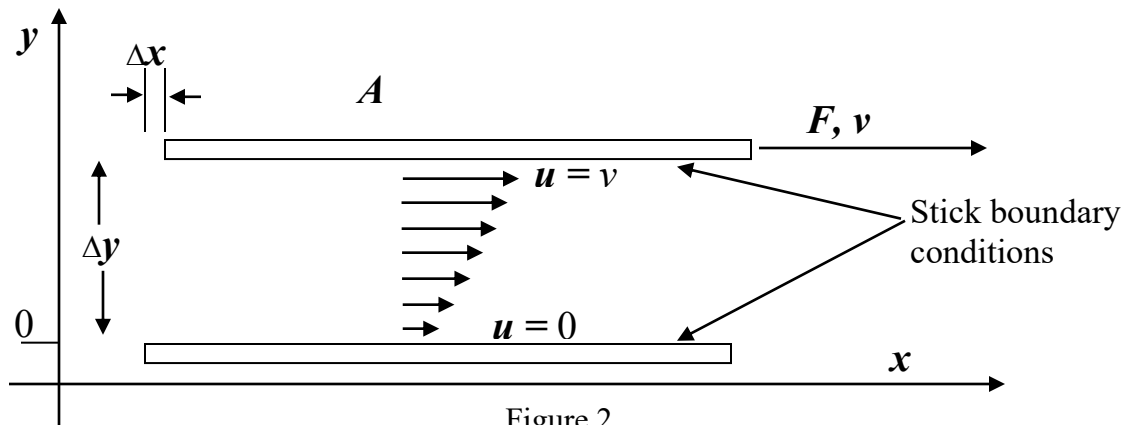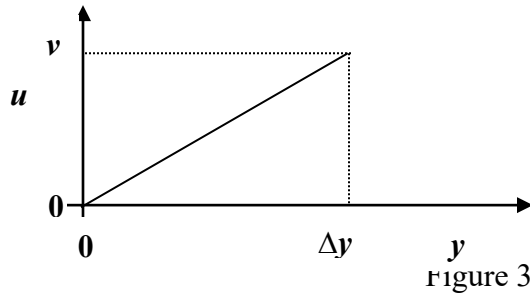

Figure 2

Define:
> F = **force**
> V = **velocity of upper plate**
> u = **local viscosity in fluid**
> A = **area of plate**

Assume *laminar flow* -- i.e., *u* increases linearly with *y*

Figure 3

Note that $\dfrac{\partial u}{dy} = \dfrac{v}{\Delta y}$ (4.1)

Define: $\gamma = \dfrac{\Delta x}{\Delta y}$ = shear strain (4.2)

Define: $\dot{\gamma} = \dfrac{d}{dt}\gamma$ = shear strain rate (4.3)

Since Δy is constant, we get:

$$\dot{\gamma} = \frac{1}{\Delta y}\frac{d}{dt}\Delta x = \frac{v}{\Delta y}$$ (4.4)

Comparing Eq. 4.1 and Eq. 4.4, we have:

$$\dot{\gamma} = \frac{du}{dy} = \text{gradient in local velocity} = \text{slope of plot above.}$$ (4.5)

Define: $\sigma = F/A$ = shear stress (force per unit area) (4.6)

Experimentally, it is often found that the shear stress is proportional to the strain rate, *and viscosity (symbol η) is the constant of proportionality*:

$$\sigma = \eta\dot{\gamma}$$ (4.7)

> Engineering textbooks often use the symbol τ instead of σ. Who knows what they then use for turbidity and lag time, but there just no denying the Greeks should have invented a bigger alphabet. Meanwhile, use common sense to recognize that this σ is not the same as degree of polymerization!

Or…..we can say that shear viscosity η is the ratio between shear stress σ and the shear

rate $\dot\gamma$: $\eta = \sigma/\dot\gamma$ (4.8)

Exercise: Show that the cgs units of viscosity are $g \cdot cm^{-1} \cdot s^{-1}$. This is called a poise. For reference, the viscosity of water is about $0.01P = 1$ cP. Another popular unit of viscosity is the Pa$\cdot$s. What is the conversion factor between these two?

Fluids that obey the strict linearity between shear stress and strain rate are called *Newtonian* fluids. Polymers often exhibit non-Newtonian behavior:
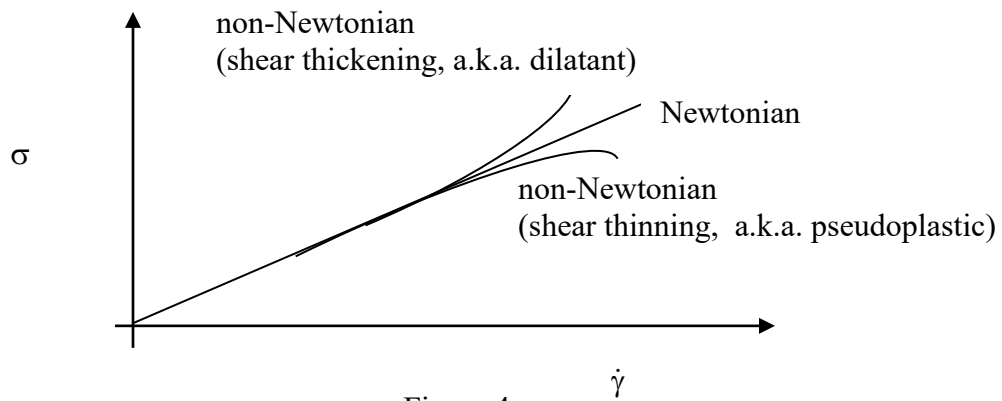

Figure 4

This plot has the equivalent shown below. If you don't see this, then you need to get your money back from Calculus class (or see me, which might be easier).
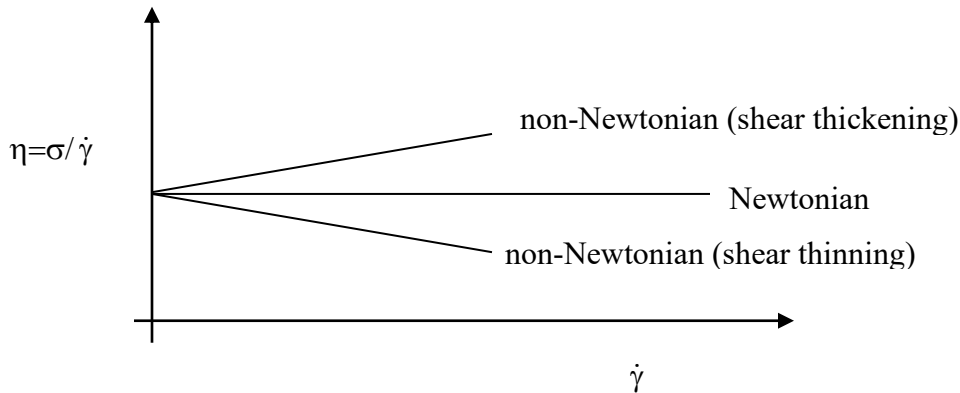

Figure 5

Shear thinning is very common; examples include many polymer solutions (at sufficiently high shear rates), some emulsions, paints and so on. Paint manufacturers design paint to roll on easy, so you don't have to push hard and get worn out, but then to thicken when there is no shear, thus preventing runs and drips.

Shear thickening is less common; examples include corn starch in water and sand/water mixtures. A really fascinating application is found in sophisticated, lightweight bulletproof vests. This application is based on dispersion of silica particles. Another use is in torque converters for some all-wheel-drive systems; if slippage occurs, the shear rate rises and the material stiffens to "get a grip".

Plastic behavior

Some materials appear to be real solids…as long as you do not try too hard. Then they flow like liquids. These are called plastics.
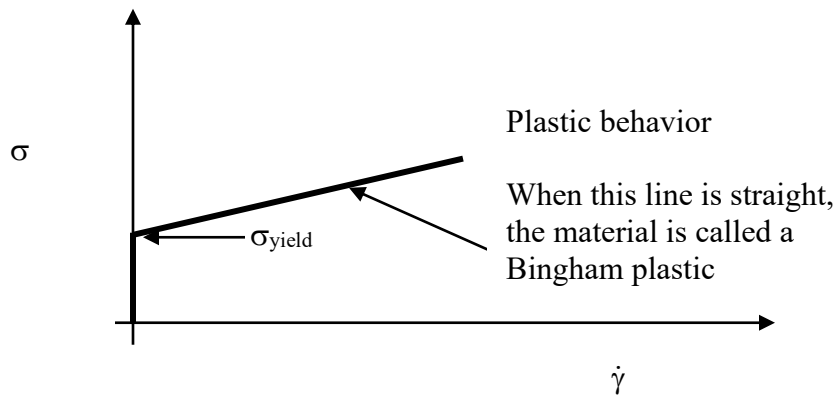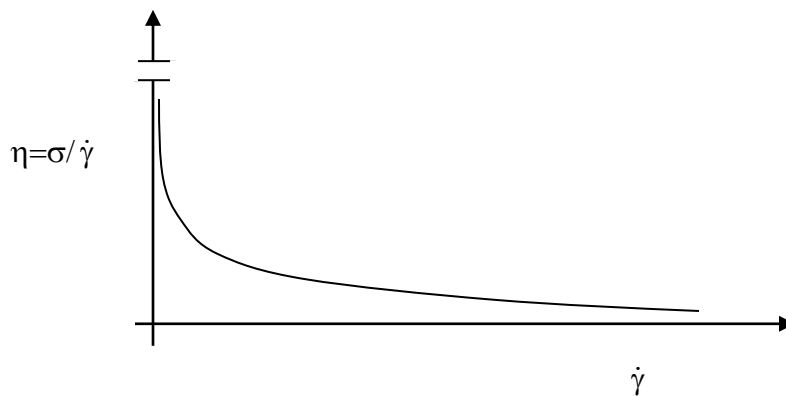

Figure 6

Figure 7

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Ketchup is a good example; only after you supply a sudden force or shock does it flow. Fortunately, the solution to this polymer problem (of critical importance to Minnesotans and those who eat Minnesota style as a result of marriage) is now known, and it is a polymer-based fix, too: put the ketchup in a plastic container and squeeze it to make it come out.

Time-dependent behavior: thixotropy & rheopexy

Rheopexy: the apparent viscosity increases with time at a steady rate of shear; this is rare.

Thixotropy: the apparent viscosity decreases with time at a steady rate of shear. This is fairly common, and occurs in some inks, paints and greases. When a thixotropic material is subjected to increasing rates of shear, then slowly returned to a lower rate of shear, a hysteresis loop may open up, as shown below.
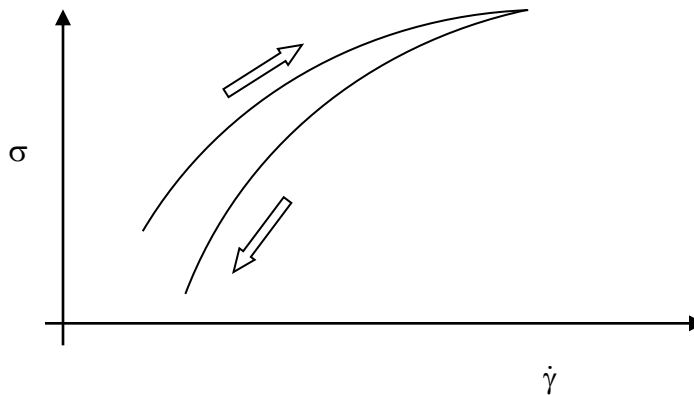

Figure 8

Theoretical expression

Lots of effort has gone into trying to predict and explain viscosity behavior, such as shear thinning. It isn't easy. The most important equation involves a power law, and many fluids, described as "power law fluids", follow this equation:

$$\sigma = k\dot{\gamma}^{n} \tag{4.9}$$

The lead term is called the consistency index, and the exponent n is the flow index. Clearly, if $n = 1$, k is just viscosity. Values of $n < 1$ correspond to shear thinning.

For materials with a yield stress, it is customary to subtract off that yield stress before making the analysis for n.

There is even a special expression that works well for chocolate! It is called the NCA/CMA Casson expression.

Energy Picture of Viscosity

Everyone is familiar with the famous wave-particle dual nature of fundamental quanta such as electrons and photons. Often it is convenient to have two ways to look at a problem, and viscosity is such a case. We have seen the traditional definition in terms of shear stress. Now let's look at it from the viewpoint of energy dissipation because when you stir a solution it does dissipate the mechanical energy you apply.

Since a force (i.e., σA) is applied over a distance (i.e., Δx) work is done on the fluid.

$$W = F\Delta x = \sigma A \Delta x \tag{4.10}$$

The *rate* at which work is done is the power dissipation into the fluid.

$$\dot{W} = \frac{dW}{dt} = A\sigma \frac{d}{dt}\Delta x = \text{Power dissipation} \tag{4.11}$$

But $\Delta x = \gamma \Delta y$ where Δy is constant, so

$$\dot{W} = A\sigma\dot{\gamma}\Delta y \tag{4.12}$$

Now let $V = A\Delta y$ represent the volume. Recall that $\sigma = \eta\dot{\gamma}$ and we obtain:

$$\dot{W} = V\eta\dot{\gamma}^2 \tag{4.15}$$

Viscosity is the power dissipation per unit volume per squared shear rate.

Exercise: Check that the units on both sides of the last equation are the same.

Viscosity of Solutions

We must first define a few things about solutions. Suppose the fluid contains particles that occupy a fraction, ϕ, of the total volume, V. (In a typical suspension, say a latex paint, ϕ might be ~0.10 or about 10% of volume). Let g represent the total mass of particles, and assume they have density ρ. The mass is given by:

$$g = V\phi\rho = \text{(volume)(fraction that is solid particles)(mass/volume of solids)}$$
(4.16)

Define: c = mass/volume concentration = g/V. (4.17)

Thus, $c = \phi\rho$. (4.18)

Now it is easy to "guess" a theory of the viscosity of suspensions. We showed that the viscosity was inversely proportional to the power dissipation rate per unit volume:

$$\eta = \frac{\dot{W}}{V\dot{\gamma}^2}$$
(4.19)

The "active ingredient" that dissipates the power is the solvent. If we fill it partly with inert ingredients, the effective volume is reduced: $V_{\text{effective}} = V(1-\phi)$. Thus, we can guess:

$$\eta = \frac{\dot{W}}{V\dot{\gamma}^2(1-\phi)} \cong \frac{\dot{W}}{V\dot{\gamma}^2}(1+\phi)$$
(4.20)

The last approximation follows as long as ϕ is small. (If your boss pays you 90% of your normal wage one day, and 110% the next, you almost break even, the difference being only about 1%).

Define: η_o = solvent viscosity (same as equation above, except $\phi = 0$). (4.21)

Define η_r = relative viscosity = η/η_o = $(1+\phi)$. (4.22)

Define η_{sp} = specific viscosity = $\dfrac{\eta - \eta_0}{\eta_0} = \phi$ (4.23)

This final equation is not quite correct, due to that lame effective volume guess. Einstein showed that we need an extra parameter, called the shape parameter, ν.

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \nu\phi$$
(4.24)

Note: for spheres, $\nu = 5/2$. (4.25)

The equation says we don't have to worry much about the change in viscosity due to solids. For example, a small amount of dust in the solution doesn't upset viscosity (it *does* upset some other macromolecular methods).

Return to Staudinger's Hypothesis

Recall that Staudinger was interested in trying to beat the "polymer effect" out of the system by diluting it. Now the specific viscosity is just the difference added by the particles, divided by the initial viscosity, a sort of fractional difference. His plan was to see how this fractional difference changed with concentration. He realized that η_{sp} would tend to zero, but would it do so faster than the concentration itself? If not, then there was some *intrinsic* viscosity due to the polymer. Staudinger thought the polymers would be extended, but he had no real way of estimating their volume fraction. He chose mass/volume concentration as more convenient.

Define: $[\eta] = \dfrac{\lim}{c \to 0} \dfrac{\eta_{sp}}{c} = $ intrinsic viscosity (4.26)

This parameter is usally applied to polymers, but it's instructive to see what it does for spheres. Following the equations above:

$$[\eta] = \nu/\rho$$ (4.27)

Now ρ for a solid particle is its mass (Molecular weight/Avogadro's Number) divided by its volume, V_p.

$$[\eta] = \frac{\nu W_p N_a}{M}$$ (4.28)

For a sphere ($V_p = 4\pi R^3/3$ and $\nu = 5/2$) we obtain

$$[\eta] = \frac{10}{3} \pi R^3 \frac{N_a}{M}$$ (4.29)

The intrinsic viscosity does not change with mass for solid objects! Volume and mass increase in lock-step and so cancel each other out for solid objects. The intrinsic viscosity is quite low for solids--for spherical polystyrene latex particles (density ~ 1 g/mL) the intrinsic viscosity is 2.5 mL/g. The conventional units are (don't ask why-- maybe Staudinger liked 100 mL volumetric flasks) dL/g. On this scale, the polystyrene latex has an intrinsic viscosity of 0.025 dL/g.

Now the key point. Many polymers have intrinsic viscosities quite a bit higher than this. Not only that, their intrinsic viscosities in many good solvents were similar. If

the units of the polymer were only physically attracted, certain solvents might have been expected to reduce the intrinsic viscosity while others would increase it. Not only that, the data were precise and believable. And finally, the intrinsic viscosity depended on the mass, suggesting extended (if not so much as Staudinger originally thought) chainlike particles. We are not ready for it yet, but it turns out that the way in which [η] depends on M gives us a handle on the actual shape of the polymers. Meanwhile, it is important to understand *why* the polymer intrinsic viscosities are so much higher than spheres. The reason is that polymers give a large radius for a little mass. Defining the radius of polymers is the part of this that we are not ready for yet, but perhaps it will help to consider a tree:
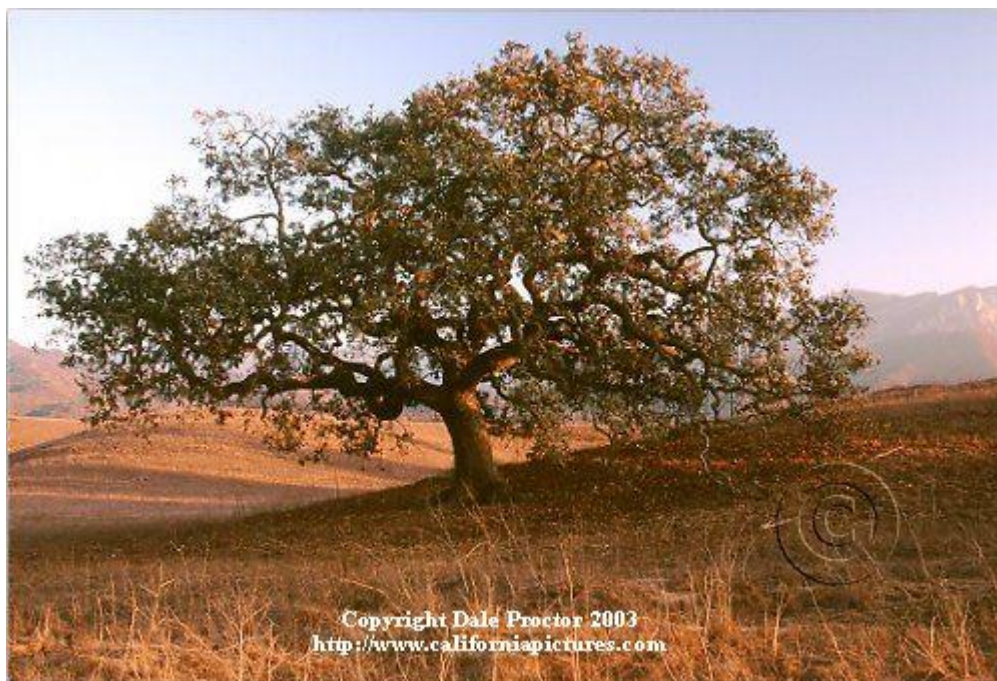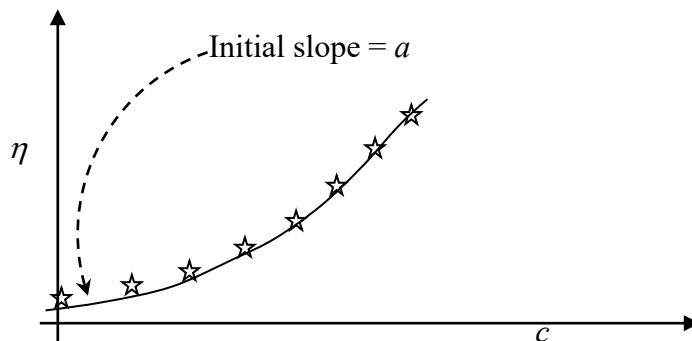

Figure 9

The canopy of a tree is mostly air—i.e., empty. Similarly, about 80-90% of a polymer's interior is filled with solvent. Were you to climb into this tree (doesn't that seem tempting and fun?) you would observe that there is almost no wind inside. The air stream goes OVER and AROUND the tree. It is the same with polymers—the solvent stream goes over and around them during shear flow. This great hydrodynamic volume (we will eventually call it R_h^3) is achieved with very small mass of added polymer. Thus, [η] of polymers is much higher than that of solids. Also, it will turn out that it depends on molecular weight—a most useful fact.

Another View of Staudinger's Hypothesis

We could approach the problem of how visocisty depends on concentration from a graphical point of view. This will show us [η] in a somewhat different light. Referring to the plot below, we can write viscosity as:

$$\eta = \eta_o + a \cdot c + b \cdot c^2 + ... \qquad (4.30)$$

Figure 10

where a and b are parameters with appropriate units. All this says is η will start at the value for solvent, η_o, and rise with concentration…linearly at first, then with curvature. Considering the definition of η_{sp} (Eq. 4.23) we can write

$$\frac{\eta - \eta_o}{c\eta_o} = \frac{\eta_{sp}}{c} = \frac{a}{\eta_o} + \frac{b}{\eta_o}c + ... \qquad (4.31)$$

By comparison with the definition of $[\eta]$ (Eq. 4.26) we can see right away that $[\eta]=a/\eta_o$ or initial slope $a = [\eta]\eta_o$. The initial slope of viscosity *vs* concentration is proportional to the solvent viscosity, and the constant of proportionality is $[\eta]$. That initial slope is what you cannot eliminate by dilution. By convention, the second term (the curvature in Figure 10) is rewritten as $b/\eta_o = k'[\eta]^2$ and we can write

$$\frac{\eta_{sp}}{c} = [\eta] + k'c[\eta]^2 + ... \qquad (4.32)$$

This ungainly expression, called the Huggins-Kramer equation, has a cleaner form which is unitless on both sides:

$$\eta_{sp} = [\eta]c + k'c^2[\eta]^2 + ... \qquad (4.33)$$

By comparison to Eq. 4.24 you can see that the product $[\eta]c$ is something like the volume fraction. It is the volume fraction that the polymer chain has managed to "tie up" hydrodynamically speaking! At the *overlap concentration* $c^* = 1/[\eta]$ the polymers effectively (hydrodynamically) touch to control (hydrodynamically) all the space. This is typically at a few percent concentration by mass…polymers *very* effectively tie up the solvent in a hydrodynamic sense.

Intrinsic viscosity yields molecular weight…not for solids.

Equation 4.29 says the intrinsic viscosity of a solid does not vary with mass or size because $M \propto R^3$. But for polymers, we shall see in Ch. 6 (Dimensions) that M ∝ Rn where n typically ranges from 0.5 to 0.6 for flexible, random flight polymers. Thus we may expect $[\eta] \propto R^3/M \propto M^a$ where $a = 0.5$ to 0.8. A constant of proportionality is usually specified, leading to the Mark-Houwink-Sakurada equation, one of the most famous expressions in polymer science:

$$[\eta] = KM^a \qquad\qquad (4.34)$$

If the intrinsic viscosity and molecular weights are determined for a series of polymers, a Mark-Houwink-Sakurada plot can be built connecting molecular weights to intrinsic viscosity for unknown polymers of the same type, as shown in Figure 11. The K and a parameters have been determined for many polymers. The a parameter is particularly illuminating, as it gives an indication of the shape of stiffness of polymers. For example, $a = 0.5$ signifies a polymer for which intramolecular attractions between the chain segments exactly cancel the natural tendency of the polymer to expand in order to avoid two segments separated by a long distance along the backbone having to occupy the exact same space. The a value associated with Figure 11 is considerably higher than 0.8, indicating chain stiffness.
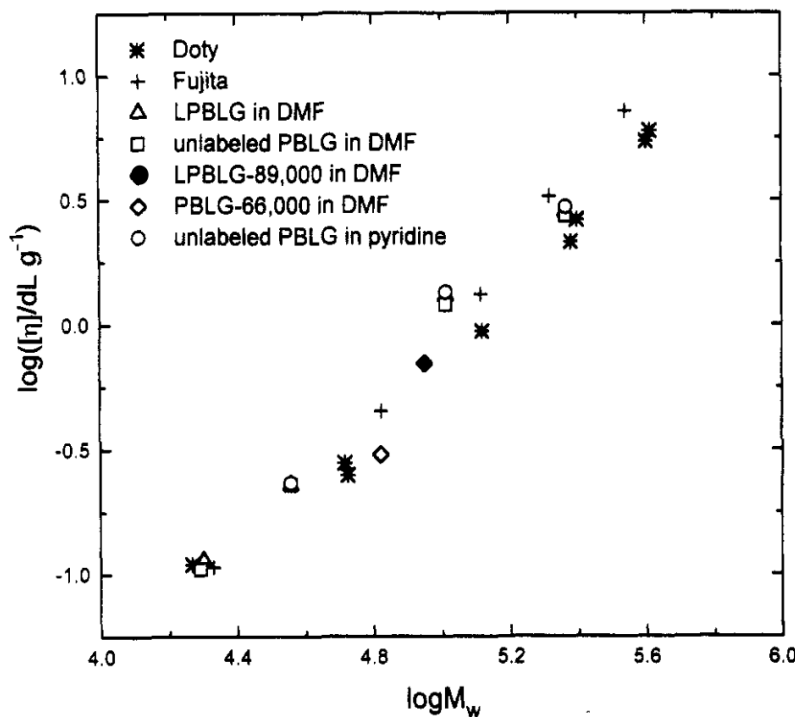

Figure 11

Related Links & References

1) The books by Van Holde and the older Flory text are useful.
2) Some of this has taken from the Brookfield Engineering publication, *More Solutions to Sticky Problems*.
3) Experimental links to viscosity info:
   http://russo.chem.lsu.edu/howto/WELBROOK.DOC
   http://russo.chem.lsu.edu/howto/IntrinsicVisc.doc
4) Figure 11 is by Bu et al. 10.1021/ma00101a027