

Intrinsic Viscosity

Measure of
Polymer Molecular Weight,
Polymer Hydrodynamic volume,
&
Polymer-Solvent Interaction

Jung Ok Park + Paul Russo

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This presentation is made from LSU 4010 notes + GT 4776/6752 notes.

First part of presentation has these simple goals:

1. What intrinsic viscosity isn't.
2. What intrinsic viscosity is.
3. Why it was historically of interest in polymer science.

Details are in the Virtual Book (Canvas and/or [APTEC](#))

Other info will be on the OPALL site: opall.mse.gatech.edu

Intrinsic viscosity is either simple or extremely complex. We adopt the simple point of view! So, all you really need to know is when to use it. How to use it is not rocket science. Oh, there are little tricks and such, but seriously...its main attribute is simplicity. Try not to be the person who DOES intrinsic viscosity measurements.

This is the most important relation of the day!

$$[\eta] \neq \eta$$

Intrinsic viscosity is NOT viscosity.

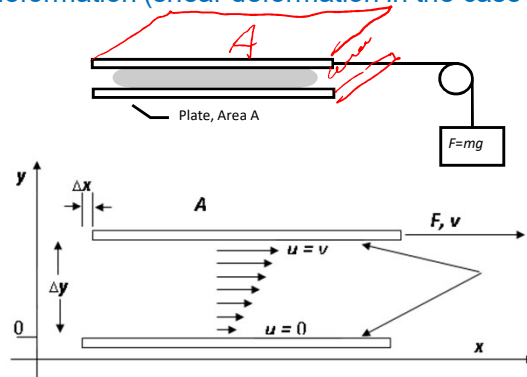
But...both are extremely important to how polymer science developed!

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Let's return to those thrilling days of yester-century, literally about one hundred years ago. THE debate was whether large structures that seemed to be in various solutions and suspensions were covalent. It turns out this is once again an interesting question. People like Alexei Sokholov at Utenn are wondering this kind of thing for ionic liquids and other bulky molecules...e.g., in batteries etc.

Viscosity describes the resistance offered by a fluid to a deformation (shear deformation in the case shown.)



Define:

F = force

V = velocity of upper plate

u = local viscosity in fluid

A = area of plate

<http://macro.lsu.edu/corecourses/msweb4/VirtualMacroBook.htm> >>>> Chapter 4

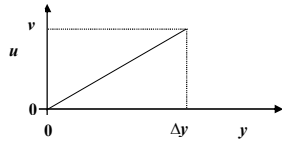
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THIS is viscosity. Well, one of them. Actually, there's a viscosity for other perturbations. Squeeze a liquid and there's a viscosity for that. But usually polymer people mean shear a liquid.

JERGENS HAND CREAM HELPS HERE!

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



Define: $\sigma = \text{shear force/area} = \text{shear stress}$

Note that $\frac{\partial u}{\partial y} = \frac{v}{\Delta y}$ (Eq. A)

Define: $\gamma = \frac{\Delta x}{\Delta y} = \text{shear strain}$

Define: $\dot{\gamma} = \frac{d}{dt}\gamma = \text{shear strain rate}$

Since Δy is constant, we get:

$$\dot{\gamma} = \frac{1}{\Delta y} \frac{d}{dt} \Delta x = \frac{v}{\Delta y} \quad (\text{Eq. B})$$

Comparing Eq. A and Eq. B, we have:

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

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

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

$$\sigma = \eta \dot{\gamma}$$

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!

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The STRAIN is a unitless deviation.

Velocity profile is linear.

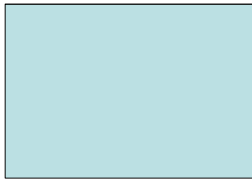
There is no slip.

Viscosity is then force/area divided by shear rate: nt-s/m² or Pa-s.

In This 4776 class, we can just assume you have seen this but in case that's not true.

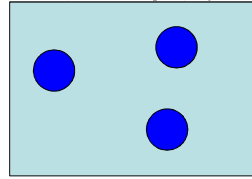
Viscosity is ALSO the power (W) dissipation per unit volume per squared shear rate.*

$$\eta_o = \frac{\dot{W}}{V \dot{\gamma}^2}$$



Solvent

$$\eta \stackrel{?}{=} \frac{\dot{W}}{V(1-\phi)\dot{\gamma}^2}$$



Solution: Solute volume fraction ϕ

Equation on right is a GUESS. Rationale for it: the active ingredient to dissipating energy is the fluid; in the solution, we have effectively reduced its volume by the factor $(1-\phi)$.

* <http://macro.lsu.edu/corecourses/mweb4/VirtualMacroBook.htm> >>>> Chapter 4

* See also: Van Holde, K.E. Physical Biochemistry

http://www.amazon.com/Physical-Biochemistry-K-van-Holde/dp/0136662722/ref=si_1_7?s=books&ie=UTF8&qid=1392066767&sr=1-7&keywords=van+holde

A shape factor v is applied to fix the guess, but it is essentially right: viscosity rises as the volume fraction of the solute.



$$\eta = \frac{\dot{W}}{V(1-v\phi)\dot{\gamma}^2} \equiv \frac{\eta_0}{(1-v\phi)} \cong \eta_0(1+v\phi)$$

Define:

$$\eta_r = \text{relative viscosity} = \eta/\eta_0 = (1+v\phi)$$

$$\eta_{sp} = \text{specific viscosity} = \frac{\eta - \eta_0}{\eta_0} = v\phi$$

Note: for spheres, $v = 5/2$

Now we need a lexicon for solutions.

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

$$c = \text{mass/volume concentration} = g/V$$

$$c = \phi\rho$$

ϕ = volume fraction

ρ = density of sphere



$$V_{\text{sphere}} = 4\pi R^3/3$$

$$\rho = (M/N_a)/V_{\text{sphere}} = 3M/(N_a 4\pi R^3)$$

If you put enough spheres in a solution, it will get viscous—even become a glass—but polymers were amazing because rather little was needed to achieve very high viscosities.

What matters: the change in viscosity for the concentration.

Define: $[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = \text{intrinsic viscosity}$

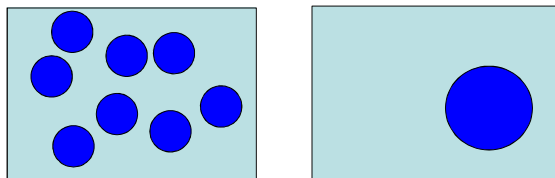
\longrightarrow
Solid spheres $[\eta] = v/\rho$

$[\eta]$ is essentially the inverse of density!

$$[\eta] = \frac{10}{3} \pi R^3 \frac{N_a}{M} \quad N_a = \text{Avogadro Number}$$

Density is an intrinsic property: does not change with size or amount of material...well, most materials.

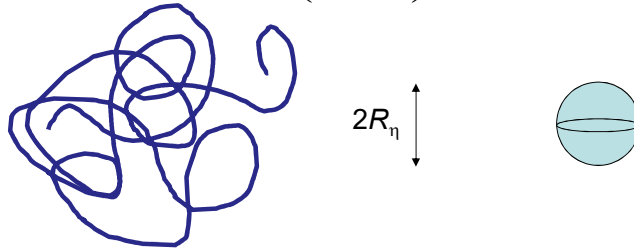
Mathematically, R^3/M is a constant of R .



8 particles have the same volume fraction as 1 particle that is twice as large.
The particle density is the same, so $[\eta]$ is the same.
You couldn't use $[\eta]$ to measure M .

The measured viscosity radius is the radius of a hypothetical sphere that has the intrinsic viscosity and molecular weight of whatever particle or polymer you actually measured.

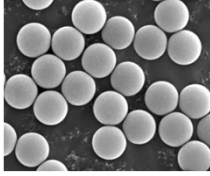
Define $R_\eta = \left(\frac{3[\eta]M}{10\pi N_a} \right)^{1/3} = \text{hydrodynamic radius}$



What you measured.

What viscometer saw.

R_η is a kind of hydrodynamic radius, but there is another one based on diffusion that is easier to compare to theories. One nice thing about R_η : it can be measured at very low concentrations and M values because viscometers are so sensitive. This proves useful in GPC-Vis.



<http://www.microspheres-nanospheres.com/Microspheres/Organic/Melamine/Carboxy/20melamine.htm>

So, if you take typical polystyrene latex particles ($\rho = 1.0 \text{ g/mL}$)
you get $[\eta] \cong 0.025 \text{ dL/g}$.

The same polystyrene, dissolved out of the latex particle
and put into toluene will have a much higher $[\eta]$.

....because the density of the swollen "particle"
(polymer) goes WAY down!

It's the difference between wood and a tree canopy
taken whole.

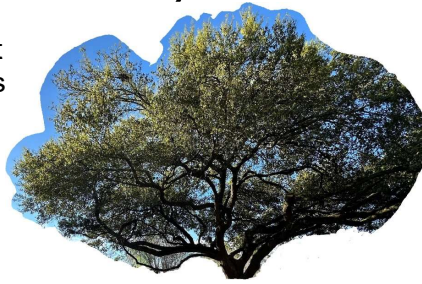
We talked about what $[\eta]$ isn't:


$$[\eta] \neq \eta$$

Now we know what it is:

$$[\eta] = \frac{v}{\rho} \propto \frac{R^3}{M}$$

What do we know about the size of wispy objects like polymers, trees, Mardi Gras beads?

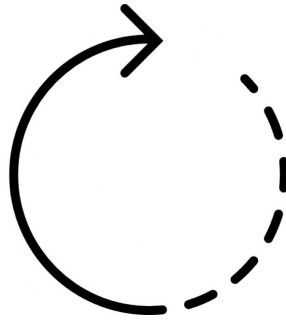


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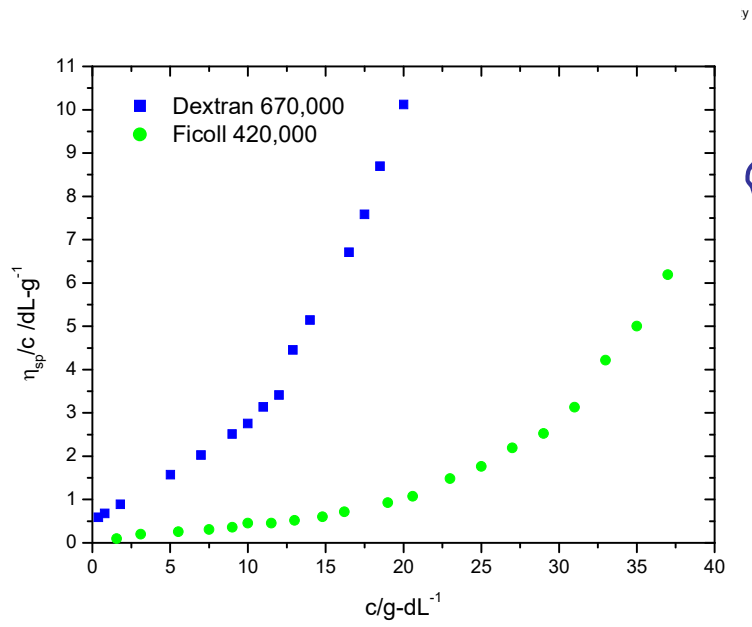
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Answer: wispy objects have non-3 fractal dimensions.

That's one turn...from what $[\eta]$ isn't η to what both actually are.
Let's do it again, this time from some actual measured data.



Here's some actual data from former Russo group member, Randy Cush...
this goes to very high concentrations.



What do you suppose will happen to viscosity when polymer is added?
 Let's write a polynomial expansion for it.

$$\eta = \eta_0 + a'c + b'c^2 + \dots$$

$$\frac{\eta - \eta_0}{\eta_0} = ac + bc^2 + \dots$$

$$\frac{1}{c} \frac{\eta - \eta_0}{\eta_0} = a + bc + \dots$$

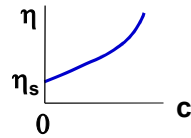
call this $\frac{\eta_{sp}}{c}$ call this $[\eta]$ call this $k'[\eta]^2$

$$\frac{\eta_{sp}}{c} \Rightarrow [\eta] + k'[\eta]^2 c$$

This is an example of a virial expansion. Assume the viscosity of a solution starts at a value near that of the pure solvent when the concentration is small. Then assume it goes up linearly at first. Add curvature terms.

Here it is again. Some people use symbol η_s instead of η_o for solvent viscosity. $\eta_s \equiv \eta_o$

* Viscosity of very dilute polymer solution



- η : solution viscosity
- η_s : solvent viscosity
- c : polymer concentration, in [g/dL = g/100mL]

$$\eta = \eta_s (1 + h_1c + h_2c^2 + \dots)$$

$$\eta_r = \eta/\eta_s = 1 + h_1c + h_2c^2 + \dots$$

$$\eta_{sp} = \eta_r - 1 = h_1c + h_2c^2 + \dots$$

$$\eta_{red} = \eta_{sp}/c = h_1 + h_2c + \dots$$

$$\eta_{inh} = (\ln \eta_r)/c = h_1 + h_2c + \dots$$

η_r : relative viscosity

η_{sp} : specific viscosity

η_{red} : reduced viscosity

η_{inh} : inherent viscosity

* For most polymeric solutions:

$$\lim_{c \rightarrow 0} \eta_{red} = \lim_{c \rightarrow 0} \eta_{inh} = h_1 = [\eta], \quad [\eta] : \text{intrinsic viscosity, in dL/g or mL/g}$$

→ Intrinsic viscosity is a measure of hydrodynamic volume of polymer per gram in solution.

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One of the unavoidable challenges of polymer science & engineering is the inconsistent use of variables. Here, we choose not to shield you from it but deliberately expose you to it: subscript s or subscript o...you have to figure it out by context sometimes. Also note h_1 for [ιντρινσιχ πισχοσιτυψ] and h_2 for....well, it's actually gotta come out as proportional to intrinsic viscosity squared. Why does it HAVE to come out that way?

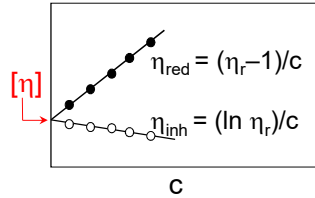
Relationships for Intrinsic Viscosity

* Huggins equation:

$$\eta_{red} = \frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2c + \dots$$

* Kraemer equation:

$$\eta_{inh} = \frac{\ln \eta_r}{c} = [\eta] + k''[\eta]^2c + \dots$$



For linear flexible polymers:

$k' : 0.35 \sim 0.4$ (a.k.a. k_H), $\square \rightarrow k' - k'' = 0.5$
 $k'' \sim -0.15$ (a.k.a. k_K)

← This is mathematically required at low concentrations.

* One-point measurement: Solomon and Gottesman

$$\left\{ \frac{2(\eta_{sp} - \ln \eta_r)}{c} \right\}^{1/2} = [\eta] + (1/3 - k')[\eta]^2c + \dots$$

For linear flexible (coil) chain:

- when $A_2 \gg 0 \rightarrow$ good solvent $\rightarrow k' \sim 1/3$
- when $A_2 \sim 0 \rightarrow$ q solvent $\rightarrow k' \sim 1/2$

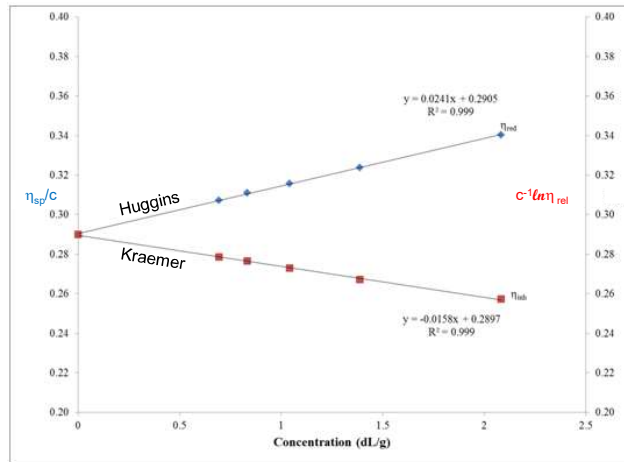
¹ Solomon and Gottesman, Die Makromolekulare Chemie 127, 153-164 (1969)
 Sperling, L. H., "Introduction to Physical Polymer Science", Wiley, 2001.

I predict some of you will seem to have violated mathematics once you have analyzed your data (assuming we are measuring intrinsic viscosity during this class)! When you get your k' and k'' , let me know!


Intrinsic viscosity comes as the intercept of a double plot.
 If you're a good experimentalist, the intercepts are the same!
 Convince yourself that $\ln(\eta_r) \cong \eta_{sp}$ at $c = 0$.



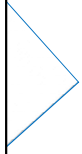
Brook Taylor



Ronald P. D'Amelia et al. The Determination of the Solubility Parameter (δ) and the Mark-Houwink Constants (K & α) of Food Grade Polyvinyl Acetate (PVAc). Journal of Polymer and Biopolymer Physics Chemistry, 2014, Vol. 2, No. 4, 67-72. doi:10.12691/jpbpc-2-4-2

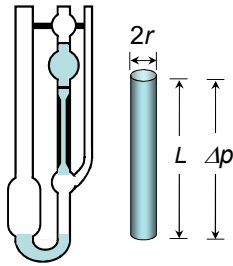
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Prove that $k'' = k' - 1/2$ at sufficiently low concentrations.



Much of polymer science is based on a simple, glass tube!
 These Ubbelöhde viscometers are still used. Amazon: \$100-\$200.

Flow through a capillary tube:



(Hagen-)Poiseuille Equation

$$\text{Flow Rate} = \frac{\pi r^4 \Delta p}{8 \eta L} \sim \frac{1}{t}$$

* t : flow time for a liquid to flow through a length, L .

* Δp : the pressure drop between the two end points $\sim \rho g L$

$$\Rightarrow \eta_r = \frac{\eta}{\eta_s} = \frac{\rho_s t}{\rho_t^s} \sim \frac{t}{t_s}$$

The flow time ratio = viscosity ratio

* Kinetic energy correction:

- The Poiseuille equation does not consider the pressure drop due to the motion of the fluid itself.
- The necessary adjustment increases as the flow time decreases, hence the kinetic energy increases.
- The correction is negligible when $t > 100 \sim 150$ s.

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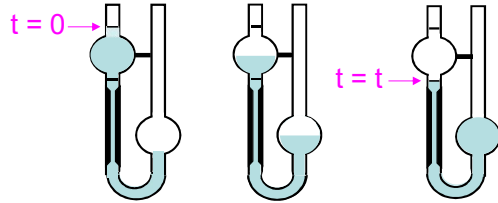
Ubbelohde Demo: <https://www.youtube.com/watch?v=ploYM5F14xl>

We still have not said much about actually measuring viscosity! The simplest way is based on gravity pulling a fluid down a tube. Pretty reliable stuff.

How is Intrinsic Viscosity Measured?

Capillary Viscometers for Intrinsic Viscosity Measurements

Ostwald Viscometer

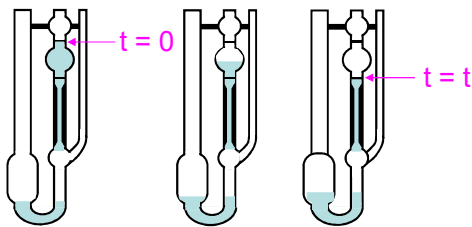


Flow rate:

- * Depends on initial fluid volume (→ one must use **constant volume** for all sol'ns).
- * Not constant during the measurement.



Ubbelöhde Viscometer



- * Flow rate does **not** depend on initial fluid volume.
- * **Successive dilution** is possible.
- **advantage!**



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https://www.amazon.com/Photo-Dr-Ubbelohde-inventor-viscometer/dp/B06WWNHP4V/ref=sr_1_19?ie=UTF8&qid=1504098064&sr=8-19&keywords=ubbelohde

Ubbelohde photo: If you had to use Ubbelohde's viscometer, you would look crabby and stern too!

Guideline for Use of the Ubbelohde viscometer:

- A suitable solvent must be used for the polymer of interest; if you are trying to get molecular weight, use a thermodynamically good solvent.
- One must select the viscometer with the right capillary size and then the initial concentration.
- The flow time of the pure solvent, t_s , should exceed 100 s (preferably $t_s \geq 150$ s).
- The stock polymer solution: the flow time $< 2 t_s$.
- Take 5 flow times within ± 0.2 s range (I've been known to settle for 3 times).
- Keep diluting the solution with known amount of solvent until your two plots become straight (= linear) and give (nearly) identical intercepts.
- If viscometer gets full and it becomes impossible to add more solvent before reaching the linear region in the plot, take out measured amount of this last solution, and keep diluting.
- The flow time of the diluted solutions: best if $t/t_s = 1.1 \sim 1.5$.
- Temperature bath has to be used to maintain ± 0.05 °C.



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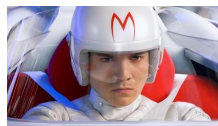
Speed Racer Tricks in a Large Group

A group of 6 can get 6 points using 6 different viscometers!

Each team member measures solvent flow time (5 times for good reproducibility) and each measures (5 times) a different concentration.

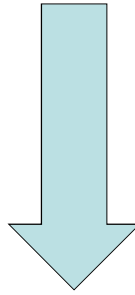
Start from a single stock solution.

The viscometers do not have to be at exactly the same temperature (though this is desirable) unless you are near an aggregation or molecular collapse temperature.

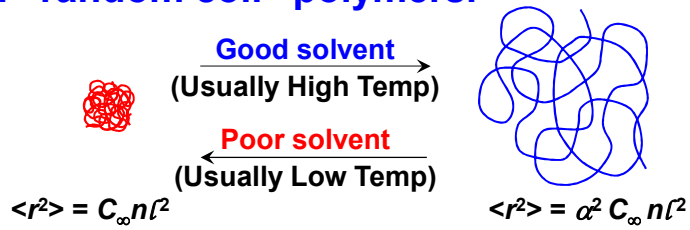


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Below here: factoids and examples concerning intrinsic viscosity.



Polymer-Solvent interaction affects size of “random coil” polymers.



Good solvent

polymer-solvent attraction > polymer-polymer or solvent-solvent
 → polymer expands to its fullest size
 → less effective as the concentration increases

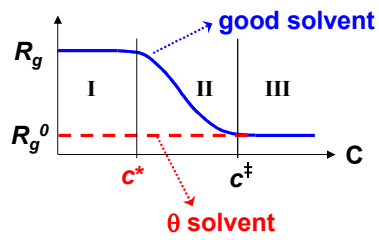
Poor solvent

polymer-solvent attraction < polymer-polymer or solvent-solvent
 → polymer collapses → phase separation
 → no concentration effect

Flory θ solvent

polymer-solvent interaction ~ polymer-polymer or solvent-solvent
 → constant polymer chain dimension
 → no concentration effect

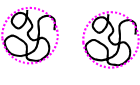
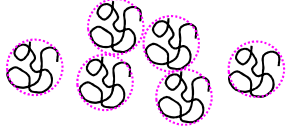
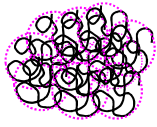
Solvent Effect: Polymer Dimension vs Concentration



- R_g : radius of gyration $\sim N^{0.6}$
- R_g^0 : radius of gyration of unperturbed chain $\sim N^{0.5}$
- c^* : overlap concentration

$$c^* = [\eta]^{-1}$$

R. Simha, J. Chem. Phys., 13, 188 (1945)

Region I	Region II	Region III
Dilute solution	Semidilute, Semiconcentrated, Moderately concentrated	Concentrated, Undiluted
		

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Intrinsic Viscosity vs Molecular Weight

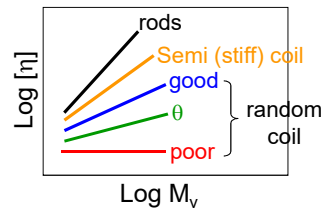
$$[\eta] = K M_v^a$$

Mark-Houwink(-Sakurada) Equation

$$\text{Log } [\eta] = \text{Log } K + a \text{ Log } M_v$$

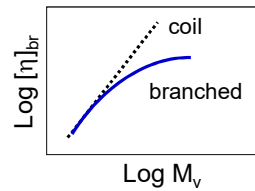
a : 1) related to the “stiffness” of the polymer chains:

- * Rigid rods: $a = (1.8) \sim 2$
- * Stiff coil (semicoils, wormlike): $a = 1$
- * Random coil : $a = 0.5 \sim 0.8$
- * Hard spheres: $a = 0$
- * Globular proteins: $a \sim 0$
- * Polysaccharide: $a = 0.5 \sim 1.3$



2) related to the “solvent power” for coil:

- * Good solvent: $a \sim 0.8$
- * Flory theta solvent: $a = 0.5$
- * Poor solvent: $a = 0$



3) related to the polymer “branching”:

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How do you know you are in the good solvent limit?

Intrinsic Viscosity vs MW: Mark-Houwink-Sakurada Parameters

<i>Polymer</i>	<i>Solvent</i>	<i>K</i> ($\times 10^5$)	<i>a</i>	<i>Molecular Weight Range</i> ($\times 10^{-3}$)
Polypropylene	Benzene	27	0.71	60–300
Polystyrene	Benzene	722.7	0.72	2–8
Polyvinyl alcohol	Water	20	0.76	6–20
Polyvinyl acetate	Acetone	21.4	0.68	40–300
Polyvinyl acetate	Chloroform	20.3	0.72	40–300
Polyvinyl acetate	Methanol	101	0.5	40–300
Polyvinyl pyrrolidone	Water	67.6	0.55	10–40
Polymethyl methacrylate	Acetone	7.5	0.70	15
Polyethylene glycol	Water	156	0.5	0.2–8

Source: J. Brandrup and E. H. Immergut, *The Polymer Handbook*. Wiley-Interscience, New York, 1966.

Temperature information is missing !

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In green: here's a polymer with different values of *a* according to conditions. Acetone and chloroform are close to good solvents while methanol is ideal.

Intrinsic Viscosity vs MW: Mark-Houwink-Sakurada Parameters

Table 7.6 Parameters for the Mark-Houwink-Sakurada equation [18]

Polymer	Solvent	Temperature, °C	$K' \times 10^6$	a
Cellulose triacetate	Acetone	25	8.97	0.90
SBR rubber	Benzene	25	54	0.66
Natural rubber	Benzene	30	18.5	0.74
	<i>n</i> -Propyl ketone	14.5	119	0.50
Polyacrylamide	Water	30	68	0.66
Polyacrylonitrile	Dimethyl formamide	25	23.3	0.75
Poly(dimethylsiloxane)	Toluene	20	20.0	0.66
Polyethylene	Decalin	135	62	0.70
Polyisobutylene	Benzene	24	107	0.50
	Benzene	40	43	0.60
	Cyclohexane	30	27.6	0.69
Poly(methyl methacrylate)	Toluene	25	7.1	0.73
Polystyrene				
Atactic	Toluene	30	11.0	0.725
Isotactic	Toluene	30	10.6	0.725
Poly(vinyl acetate)	Benzene	30	22	0.65
	Ethyl <i>n</i> -butyl ketone	29	92.9	0.50
Poly(vinyl chloride)	Tetrahydrofuran	20	3.63	0.92

http://biomed.tamu.edu/biomaterials/bmen482/Handouts_2-4.pdf

Here's a system with a > 0.8. What does THAT mean?

Intrinsic Viscosity vs MW: Mark-Houwink-Sakurada Parameters

Table 3.10 Selected intrinsic viscosity–molecular weight relationships, $[\eta] = KM_v^a$ (77)

Polymer	Solvent	$T(^{\circ}\text{C})$	$K \times 10^{3^1}$	a^*
<i>cis</i> -Polybutadiene	Benzene	30	33.7	0.715
<i>is</i> -Polypropylene	1-Chloronaphthalene	139	21.5	0.67
Poly(ethyl acrylate)	Acetone	25	51	0.59
Poly(methyl methacrylate)	Acetone	20	5.5	0.73
Poly(vinyl acetate)	Benzene	30	22	0.65
Polystyrene	Butanone	25	39	0.58
Polystyrene	Cyclohexane (θ -solvent)	34.5	84.6	0.50
Polytetrahydrofuran	Toluene	28	25.1	0.78
Polytetrahydrofuran	Ethyl acetate hexane (θ -solvent)	31.8	206	0.49
Cellulose trinitrate	Acetone	25	6.93	0.91

Source: J. Brandrup and E. H. Immergut, eds., *Polymer Handbook*, 2nd ed., Wiley, New York, 1975, sec. IV.

¹ European units, concentrations in g/ml. Units do not vary with a . Units of K are $\text{cm}^3 \cdot \text{mol}^{1/2} / \text{g}^{3/2}$.

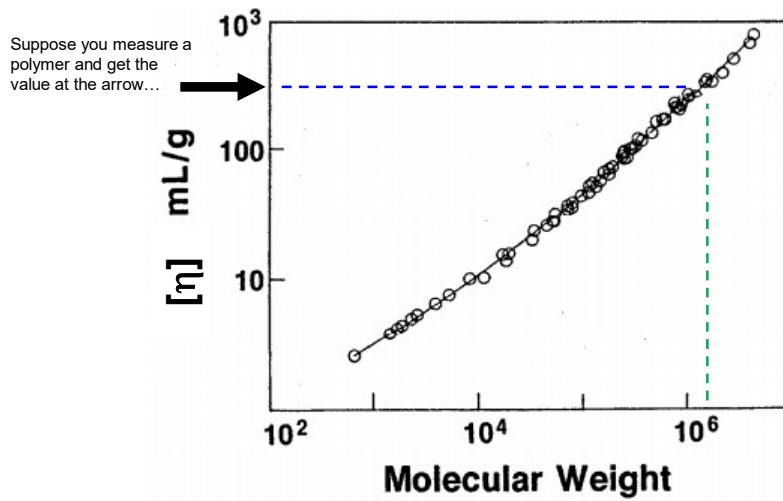
* The quantity a , last column, is the exponent in equation (3.97).

http://biomed.tamu.edu/biomaterials/bmen482/Handouts_2-4.pdf

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Can anyone think of a reason why we would even WANT to find a theta temperature?

An important use of the Mark-Houwink-Sakurada plot is getting the molecular weight of an unknown polymer. Only works if the unknown is the same kind of polymer.



2. Composite plot of the polystyrene-toluene viscosity data referred to in Table 2.

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H.L. Wagner, J. Phys. Chem. Ref. Data 14(4), 1985.

Application: Intrinsic Viscosity in Highly Branched Polymers

- Quite different viscosity-vs-molecular weight properties are seen for highly branched polymers.
- Shown here for both dendrimers and hyperbranched.
(Hobson & Feast, Chem Comm 1997, p2067)
- Intrinsic viscosity begins to fall with increasing Mw at high Mw.

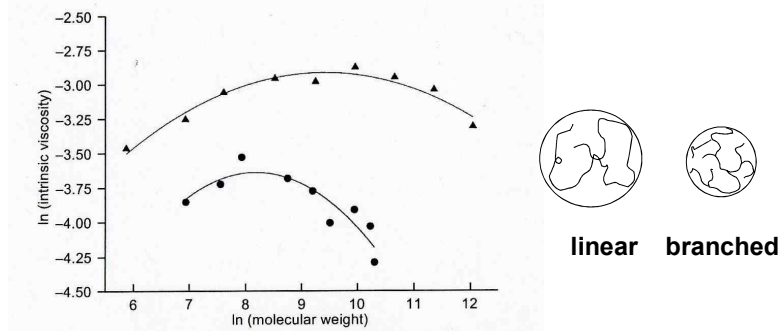


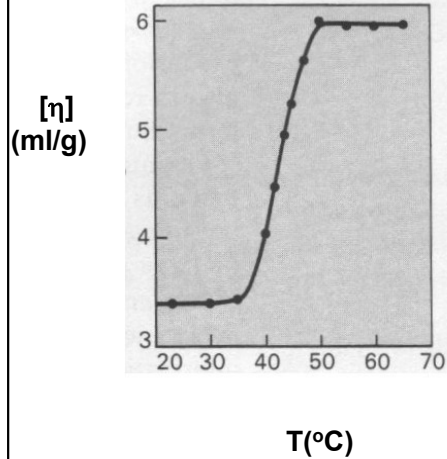
Fig. 2 The molecular weight vs. intrinsic viscosity relationship for AB₂/B₆ copolymers: (●) AB₂/B₆ copolymers and (▲) Tomalia's PAMAM dendrimers (ref. 13)

www.dur.ac.uk/r.l.thompson/resources/SolutionDynamics_RLT07.ppt

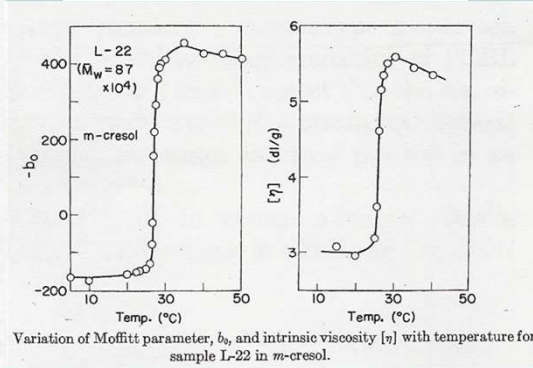
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Application: Intrinsic Viscosity for monitoring conformation change

Denaturation of ribonuclease



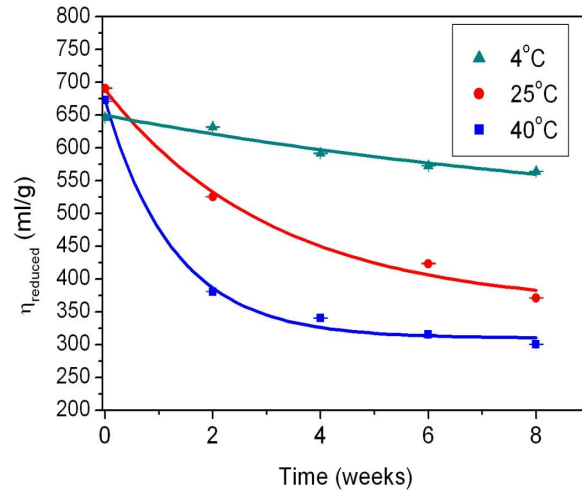
Helix-Coil Transition in Synthetic Polypeptide



Matsuoka, M., Norisuye, T., Teramoto, A., Fujita, H. *Biopolymers*, 1973, 12, 1515-1532

Application: Intrinsic viscosity for monitoring stability

Storage of chitosan (used in nasal drug delivery)

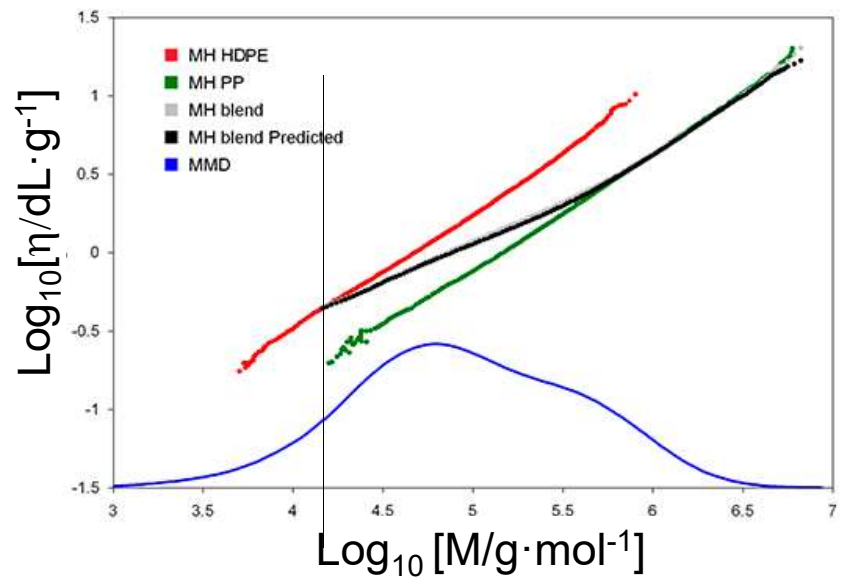


Fee et al, 2006

www.nottingham.ac.uk/ncmh/lecture.../D24BT1_Viscositylecture.ppt

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So many points in these Mark-Houwink plots that they look like smooth curves! How did they do that?



Preview: Some Other Methods for Determining Size

We assume a *linear flexible chain* and slight deviations thereof.

The molecular weight strongly influences the R_g .

- **Absolute** measurements of molecular weights are made with *primary* methods.
- *Secondary* methods estimate molecular weights, through comparison to narrow distribution standards.

Primary	Secondary
* Osmometry * Light Scattering * Sedimentation	* GPC (SEC) * Intrinsic viscosity
Absolute values (time-consuming)	Relative values (compared with standards)

History of Intrinsic Viscosity

* Einstein (1906, 1911) : Impermeable sphere, $\eta_{sp} = 2.5 N_A V_H / M$

* Jeffery (1923), Simha (1940): Ellipsoids, $\eta_{sp} = f(a) N_A V_H / M$

* Staudinger (1930)

* Kirkwood, Riseman (1948), Auer, Gardner (1955), Zimm (1956)

* Flory (1951): Polymers are impermeable,

$$[\eta] = KM^a, \quad \begin{array}{l} 0.5 < a < 0.8 : \text{ for good solvent} \\ a = 0.5 \quad : \text{ for } \theta \text{ solvent} \end{array}$$

* Krigbaum, Carpenter (1955)

* Rouse (1953), Zimm (1956): $[\eta] = (kT/N_A \eta_s M) \tau_r S(h^*)$

* Brochard (1970): Polymer chains in nematic solvents,

$$[\eta] = (kT/N_A \eta_s M) \tau_R f(R_{||}/R_{\perp})$$