

# CHEM355



## Experiment 6

### Viscosity of High Polymer Solutions

A polymer is a large molecule (macromolecule) composed of many simple units that are called **repeating units**. A single polymer molecule may consist of hundreds to a million monomers and may have a linear, branched, or network structure. The repeating units in the polymer molecules are held together by the covalent bonds and groups of polymer chains are held together by secondary bonds such as van der Waals and hydrogen bonding to form the polymeric material.

The term “**repeating unit**” denotes an elementary unit which periodically repeats itself along the polymeric chain. It is defined also as monomer or monomeric unit, but not always in the correct way.

A **monomer** is a low molecular weight compound from which the polymer is obtained through the polymerization reaction. Some of the examples are given in Figure 1.

<i>monomer</i>	<i>repeating unit/ monomeric unit</i>	<i>polymer</i>
$\text{H}_2\text{C}=\text{CH}_2$ ethylene	$\text{---H}_2\text{C---CH}_2\text{---}$	polyethylene
$\text{H}_2\text{C}=\text{CH}$   Cl vinyl chloride	$\text{---H}_2\text{C---CH---}$   Cl	poly(vinyl chloride)
$\text{H}_2\text{C}=\text{CH}$    styrene	$\text{---H}_2\text{C---CH---}$   	polystyrene

**Figure 1.** Structure of some common polymers and their corresponding monomers and repeating units.

The **degree of polymerization** (DP) refers to the average number of repeat units in the chain.

$$DP = \frac{M}{M_0}$$

Where  $M_0$  = molecular weight of one monomeric unit

Several average molecular weights are defined depending on the measuring technique.

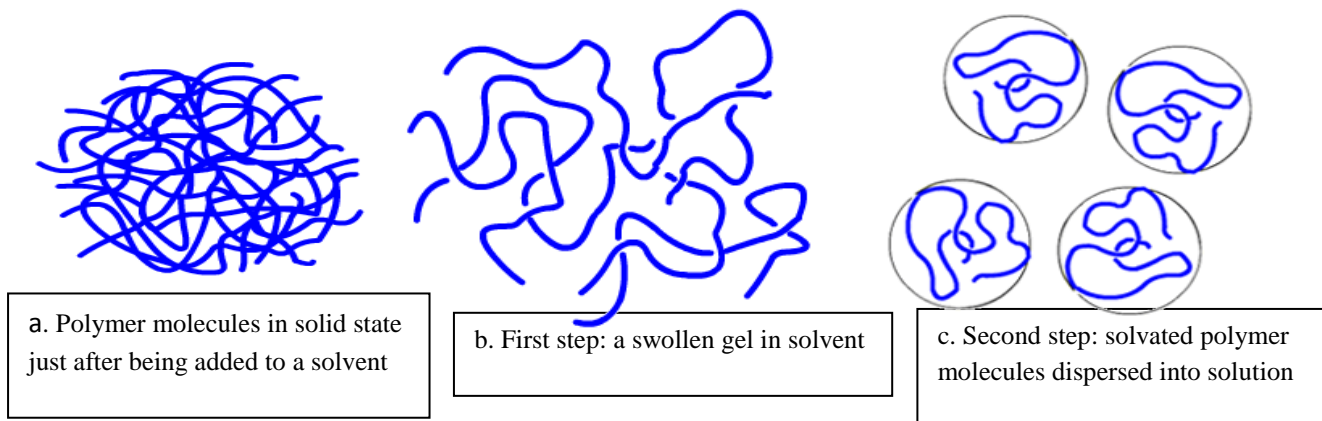
1.  $M_n$ - Number Average Molecular Weight ( $M_n = \frac{\sum N_i M_i}{\sum N_i}$ )
2.  $M_v$ - Viscosity Molecular Weight ( $M_v = \left[ \frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right]^{\frac{1}{a}}$ )
3.  $M_w$ - Weight Average Molecular Weight ( $M_w = \left[ \frac{\sum N_i M_i^2}{\sum N_i M_i} \right]$ )
4.  $M_z$ - Z-average Molecular Weight ( $M_z = \left[ \frac{\sum N_i M_i^3}{\sum N_i M_i^2} \right]$ )
- 5.

### How a polymer gets dissolved?

The dissolution of low molecular weight solute such as sucrose takes place immediately as the sugar molecules can disperse in water easily and form a solution. However, when a polymer is added to a solvent, the dissolution process may take from few minutes to several weeks, depending on the structure and the molecular weight of a given polymer.

Dissolution process of polymer molecules may be different due to long chains with a large number of segments, forming tightly folded coils which are even entangled to each other. Several intra and intermolecular forces that generally in play to hold these coils together are *dispersion, dipole-dipole interaction, induction, and hydrogen bonding*.

Due to their size, coiled shape, and the forces between them, polymer molecules may dissolve quite slowly than low molecular weight molecules. According to the Billmeyer Jr. (1975) description there are *two* stages involved in the process: the first step is the polymer swelling and next the dissolution step itself.



**Figure2.** Dissolution process of a polymer

## Viscosity

Viscosity is described in simple terms as a measure of resistance to flow thus determines the rate of flow. The slower a solution moves, the more viscous it is said to be.

To measure viscosity of a material, one must determine flow in the presence of a velocity gradient. Poiseuille derived a formula for the volume,  $\Delta V$ , of an incompressible fluid of viscosity,  $\eta$ , moving through a tube of length  $l$  and radius,  $r$ , in a time,  $t$ , under a pressure drop,  $\Delta P$ .

$$\frac{\Delta V}{t} = \frac{\pi r^4}{8\eta l} \Delta P$$

Let  $\eta_0$  be the viscosity of the pure solvent,  $\eta$  be the viscosity of a solution using that solvent, and  $c$  be the concentration. The most common solution viscosity terms are:

### 1. Relative viscosity

$$\eta_r = \frac{\eta}{\eta_0}$$

### 2. Specific viscosity

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1$$

### 3. Inherent Viscosity

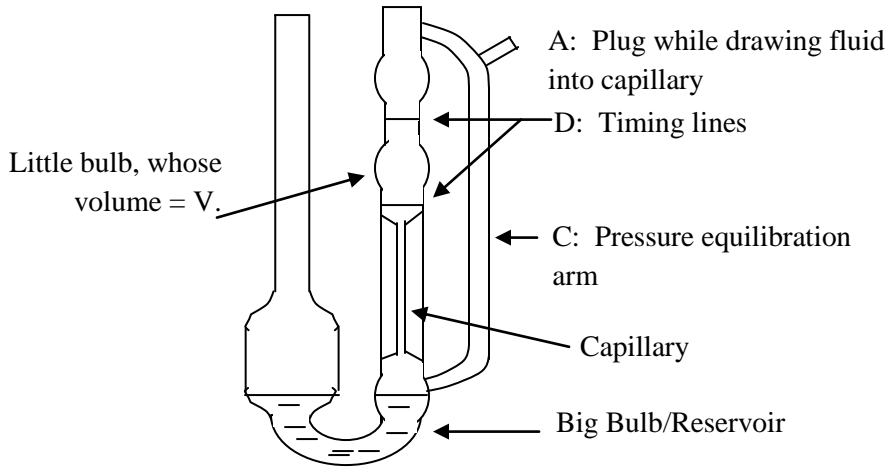
$$\eta_i = \frac{\ln \eta_r}{c}$$

### 4. Intrinsic Viscosity

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c}$$

### The Ubbelohde capillary viscometer

Ubbelohde viscometer is the most useful kind of viscometer for determining intrinsic viscosity, sketched below:



**Figure3.** Schematic representation of an Ubbelohde viscometer.

Capillary viscometry is conceptually simple: the flow time of a given volume of polymer solution through a thin capillary is compared to that of a solvent. It turns out that the flow time for either is proportional to the viscosity, and inversely proportional to the density.

$$t_{\text{solvent}} = \frac{\eta_{\text{solvent}}}{\rho_{\text{solvent}}}$$

$$t_{\text{solution}} = \frac{\eta_{\text{solution}}}{\rho_{\text{solution}}}$$

We define the relative viscosity to be the ratio  $\eta_{\text{sol'n}} / \eta_{\text{solvent}}$ . For most polymer solutions at the concentrations of interest,  $\rho_{\text{sol'n}} / \rho_{\text{solvent}} \approx 1$ . Thus, to a very good approximation, the relative viscosity is a simple time ratio:

$$\eta_{\text{rel}} = \frac{t_{\text{solution}}}{t_{\text{solvent}}}$$

Both  $\eta_{\text{rel}}$  and  $\eta_{\text{sp}}$  depend on the polymer concentration, so to extract the "intrinsic" properties of the polymer chain itself, one must extrapolate to zero concentration.

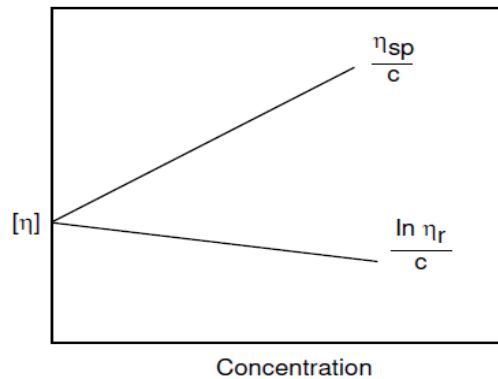
### Huggins Equation:

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2c$$

### Kraemer Equation:

$$\frac{\ln \eta_{rel}}{c} = [\eta] + k_K[\eta]^2c$$

Plots of  $\eta_{sp}/c$  or  $\ln(\eta_{rel})/c$  versus concentration yield the intrinsic viscosity when extrapolated to zero concentration.



**Figure4.** Typical plots of  $\eta_{sp}/c$  and  $\ln(\eta_{rel})/c$  as a function of concentration. The curves extrapolate to the same  $[\eta]$  at zero concentration, but approach zero concentration with different slopes

### Mark–Houwink equation

The equation describing the dependence of the intrinsic viscosity of a polymer on its relative molecular mass (molecular weight) is:

$$[\eta] = KM^a$$

where  $[\eta]$  is the intrinsic viscosity,  $K$  and  $a$  are constants the values of which depend on the nature of the polymer and solvent as well as on temperature, and  $M$  is usually one of the relative molecular mass averages.

- $a = 1/2 \Rightarrow$  flexible polymer chain in "ideal" solvent
- $0.5 < a < 0.8 \Rightarrow$  flexible polymer chain in "good" solvent
- $a > 0.8 \Rightarrow$  "stiff" chain

### Apparatus and chemicals

Apparatus: Ubbelohde viscometer, pipette, volumetric flask.

Chemicals: polystyrene, toluene.

## Procedure

1. Prepare 0.5 g polystyrene in 100 mL of toluene solution (0.5 g/dL).
2. Put 20 mL toluene into the viscometer.
3. Wait 5 minutes (for thermal equilibrium).
4. Take 3 measurements and record on your data sheet.
5. Pour the solvent into the waste bottle and put 20 ml polymer solution.
6. Wait 5 minutes.
7. Take 3 measurements and record on your data sheet.
8. Add 5 mL toluene into viscometer(do not forget to mix the solution by the help of the pump)
9. Wait 5 minutes.
10. Take 3 measurements and record on your data sheet.
11. Add 5 mL toluene into viscometer
12. Wait 5 minutes.
13. Take 3 measurements and record on your data sheet.
14. Add 3 mL toluene into viscometer(do not forget to mix the solution by the help of the pump)
15. Wait 5 minutes.
16. Take 3 measurements and record on your data sheet.
17. Pour the polymer solution into the waste bottle and wash the viscometer with a little amount of toluene.

**(Waste container of experiment: toluene waste container)**

### Treatment of data

1. Calculate new concentrations of the polymer solutions.
2. Calculate  $\eta_{rel}$ .
3. Calculate  $\eta_{sp}$ .
4. Calculate  $[\eta]$  (by the help of Huggins and Kraemer equations) and  $M_v$ (viscosity average molecular weight) of the polymer solution.

### Questions

1. Why does the molecular weight that you found is called as 'average' molecular weight?
2. What are 'a' and 'K' in Mark-Houwink equation?
3. Why did you use toluene? Can you use another polar solvent?
4. According to Poiseuille's equation; viscosity can be found by

$$\frac{\Delta V}{t} = \frac{\pi r^4}{8\eta l} \Delta P$$

How can you make the assumption below:

$$\eta_{rel} = \frac{t_{solution}}{t_{solvent}}$$

**DATA SHEET****Experiment 6.Viscosity of High Polymer**

Group Number:..... Group Members:.....

Date:..... Assistant name and Signature:.....

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<b>Solution</b>	<b>Time(sec)</b>
20 mL toluene	
Polymer solution	
Polymer solution + 5 mL toluene	
Polymer solution + 10 mL toluene	
Polymer solution + 13 mL toluene	