
Physical Properties of Macromolecules/Polymers

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Overview

Natural – polysaccharides, proteins, nucleic acids

**Synthetic – condensation and addition, derivatives
of natural polymers**

**Colloids – aggregates of molecules that can also
behave like macromolecules**

(See previous notes for extended outline.)

Polydispersity of macromolecules

Heterogeneity/Polydispersity

Some macromolecular solutions are not uniform in size, that is there are varying size molecules in the solution. These macromolecules are called heterogeneous or polydisperse. Synthetic polymers are a good example of this.

On the other hand many natural polymers such as proteins are rather uniform in size – there is no variation. Such polymers are said to be homogeneous or monodisperse.

How do we determine the polydispersity? Various techniques that we use to determine the properties of

macromolecular solutions can give us the average molar mass of the macromolecule. It is interesting that the different techniques give different numbers for the average molar mass. This is because there are several ways to define the molar mass. There are 4 common types of molar masses – the number average $\langle M \rangle_n$, the mass average $\langle M \rangle_w$, the z – average $\langle M \rangle_z$, and the viscosity average.

Each gives a different number for the average molar mass if the solution is polydisperse. We will examine each equation in detail. (see notes from board)

The ratio of the mass average to the number average is called the Polydispersity or Heterogeneity Index.

Thus for proteins $\langle M \rangle_w / \langle M \rangle_n = 1$. Synthetic polymers are said to be polydisperse if the ratio is greater than 1.1. A common value is around 5 and it may be as high as 30.

Techniques for property determination

Osmometry

For an ideal solution $\pi = [P] RT$

$$[P] = c/M$$

c is the mass concentration

M is the molar mass

For an non ideal solution

$\pi = [P] RT(1 + B [P] + \dots)$ using a series expansion

This is similar to the virial equation for non-ideal gases

$$\pi = (c/M) RT\{1 + B (c/M) + \dots\}$$

$$\pi/c = RT/M\{1 + B (c/M) + \dots\}$$

If we neglect terms past the 2nd in the series as being small, then graphing π/c vs. c gives a molar mass from

the intercept. The molar mass is a number average molar mass $\langle M \rangle_n$ because osmometry is a colligative property. Colligative properties depend on the # of particles in solution and not the type.

Sedimentation

In a gravitational field, heavy particles settle towards the bottom of a column of solution. The rate depends on the strength of the field and the masses and shapes of the particles. Heavy particles sediment faster than lighter ones and spherical particles sediment much faster than extended molecules. This technique can be used to determine the z-average molar mass, $\langle M \rangle_z$, as well as the mass average, $\langle M \rangle_w$, and the number average, $\langle M \rangle_n$.

An ultracentrifuge accelerates the rate of sedimentation and runs at about 10^5 times the acceleration due to gravity.

Electrophoresis

Electrolyte macromolecules move in an electric field according to mass and shape. This technique generates a mass average $\langle M \rangle_w$ molar mass.

Gel filtration

Beads of a porous polymeric material capture molecules according to size; the elution time can be used to determine the molar mass, a mass average $\langle M \rangle_w$. Size exclusion and gel permeation chromatography make use of this technique. Recent advances also allow the determination of the number average $\langle M \rangle_n$.

Viscosity

The resistance to flow of a solution increases in the presence of macromolecules. At low concentrations

$$\eta = \eta^* (1 + [\eta] c + \dots) \quad \eta [=] \text{ g/cm-s or kg/m-s}$$

η^* is the viscosity of the pure solvent

$[\eta]$ is called the intrinsic viscosity

$[\eta]$ [=] l/concentration

The intrinsic viscosity is defined as

$$[\eta] = \lim_{c \rightarrow 0} [(\eta/\eta^*) - 1]/c$$

so a graph of $[(\eta/\eta^*) - 1]/c$ vs c can be extrapolated back to zero concentration to give the intrinsic viscosity

The Ostwald viscometer can be used to measure time for a solution to flow through a capillary. This is compared to a standard sample and the viscosity coefficient determined as in lab. The ratio of η/η^* can be used to obtain the intrinsic viscosity.

At a temperature called the Flory temperature the solution is ideal and obeys the Mark–Houwink equation

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

M is the viscosity average molar mass ($\langle M \rangle_v$)

“K” and “a” depend on the solvent and macromolecule

Light scattering

When light falls on an object it causes excitation of the electrons in the object. This excitation is usually much more complicated than the simple Bohr model predicts. The excitation can be modeled as the light energy driving the oscillation of a spring.

If the medium is homogeneous (perfect crystal or a dispersion that is down to individual atoms, molecules or ions) there is no scattered light, only light along the direction of the light ray.

If the medium is not homogeneous, light is scattered in all directions (including 90°).

Light scattering by particles smaller than the wavelength of light is called Rayleigh scattering. This occurs in a gas or in liquid solutions of the colloidal phase. The intensity of this scattering depends on the 4th power of the frequency (and thus $1/\lambda^4$) and thus the scattering is more intense for shorter wavelengths (the blue/violet end of the spectrum). Since our eyes are much more sensitive to blue than violet we see the scattering as blue.

Quantitatively for unpolarized light

$$I = A I_0 c M (1 + \cos^2 \theta) \quad (\text{see diagram})$$

c is the concentration of the solute

M is the molar mass ($\langle M \rangle_w$), a mass average

A is a constant that relates distance, refractive index of the solution and the wavelength

Turbidity

Scattering of light reduces the transmitted intensity

$$I_t = I_0 \exp(-\tau l)$$

τ is called the turbidity and has units of inverse length

l is the path length

Mass spectrometry

Although mass spectrometry has long been one of the most accurate techniques for the determination of molar mass it is only recently that it has been applied to macromolecules because of the difficulty producing gaseous ions of large species without fragmentation. The development of matrix-assisted laser desorption/ionization (MALDI) and electrospray ionization has led to the application of mass spec to the determination of number and mass average molecular weights for macromolecules.