3.8 Intrinsic viscosity

►Colligative and scattering methods→Absolute MW→ Slow & expensive

►Intrinsic viscosity (M_v) and GPC→Rapid & inexpensive methods

►Intrinsic viscosity is measured in dilute solution to give M_v.

Why viscosity increases in dilute polymer solution?

Consider dilute solution flowing down a capillary (Figure 3.12)

Flow rate and shear rate are different depending on r→Different parts of polymer molecule experience different shear rates, resulting in an increase in the frictional drag and rotational forces on the molecule (Work is converted into heat), yielding the mechanism of viscosity increase.

3.8.1 Definition of terms

η_0=Solvent viscosity [=] poise, Pa s

η = Solution viscosity

Relative viscosity is defined as the ratio of the two:

$$\eta_{rel} = \frac{\eta}{\eta_0} \quad (>1) \qquad (3.84)$$

Specific viscosity is defined as

$\eta_{sp} = \eta_{rel} - 1$ $(0.2<\eta_{sp}<0.6)$ (3.85)

η_{sp} is divided by c and extrapolated to zero [concentration] to define the **intrinsic viscosity** as

$\left[\frac{\eta_{sp}}{c}\right]_{c\to 0} = [\eta]$ (3.86) <Note the bracket>

For dilute solution where relative viscosity is just over unity the following expanded form is useful:

$$\ln\eta_{rel} = \ln(\eta_{sp}+1) \cong \eta_{sp} - \frac{\eta_{sp}^2}{2} + \cdots \qquad (3.87)$$

Intrinsic viscosity is alternatively defined as

$$\left[\frac{\ln(\eta_{rel})}{c}\right]_{c\to 0} = [\eta] \qquad (3.88)$$

,where $\frac{\ln(\eta_{rel})}{c}$ = **Inherent viscosity**

Note the units of $[\eta]$ = cm^3/g. **Note** (36) and (38) are identical as c→0

Note value at c=0 (Solvent) and c→0 (No concentration effect) are different.

3.8.2 The equivalent sphere model

For dilute dispersion of uniform, rigid, noninteracting spheres, **Einstein** derived the increase of viscosity as

$\eta = \eta_0(1 + 2.5\nu_2)$ **Einstein Eq** (3.89)

ν_2= Volume fraction of sphere (Dispersed phase)
So the intrinsic viscosity of a dispersion of Einstein sphere =2.5 for ν_2.
$[\eta] = \eta_{sp} / c = (\eta_{rel} - 1)/\nu_2 = 2.5$

Now assume coiled polymer molecule as being impenetrable to solvent. A hydrodynamic sphere of equivalent radius R_e will approximate the coil dimension. (Figure 3.13)

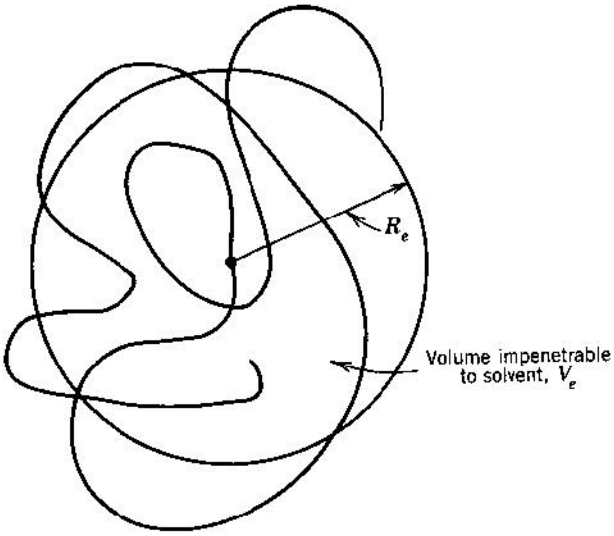

Figure 3.13 The equivalent sphere model.

In shear flow, the frictional coefficient (f_0), according to Stokes law is

$f_0 = 6\pi_1\eta_0 R_e$ (3.90)

The Einstein viscosity relationship (89) may be rewritten

$\frac{\eta-\eta_0}{\eta_0} = \eta_{sp} = 2.5\nu_2 = 2.5\left(\frac{n_2 V_e}{V}\right)$ (3.91)

n_2=# of molecules (spheres)

V= Total volume

$V_e = 4\pi R_e^3/3$ (Volume of one sphere)

$n_2 V_e$= Total volume of spheres

$n_2 V_e/V$= Volume fraction of spheres

Eq. 3.91 shows that viscosity of sphere assembly is independent of the size (R_e), but only on their volume fraction.

Note that

$$\frac{n_2}{V} = \frac{cN_A}{M} \qquad (3.92)$$ <c=Concentration=mass/volume, N_A=Avogadro #)

Plugging this into (91) gives

$$\left[\frac{\eta_{sp}}{c}\right]_{c=0} = [\eta] = 2.5\frac{N_A V_e}{M} \qquad (3.93)$$

Note that

$$\frac{V_e}{M} = \frac{4\pi_1}{3}\frac{R_e^3}{M} = \frac{4\pi_1}{3}\left(\frac{R_e^2}{M}\right)^{3/2} M^{1/2} \quad (3.94) \quad \text{and} \quad R_e = R_{e0}\alpha \qquad (3.95)$$

,where α=Expansion of coil in good solvent over Θ solvent.

Plugging (95) →(94) →(93) yields

$$[\eta] = 2.5\frac{4\pi_1}{3}N_A\left(\frac{R_{e0}^2}{M}\right)^{3/2} M^{1/2}\alpha^3 \qquad (3.96)$$

$\left(\frac{R_e^2}{M}\right)$= Roughly constant

→[η] increases wrt M and α.