

Solution Rheology: Dilute Solutions



$$\frac{\eta - \eta_s}{\eta_s} = 2.5 \phi \quad \text{Einstein}$$

$$R \sim N^{1/2} \quad (\Theta \text{ solvent})$$

$$\phi = v R^3 \quad v \text{ macromolecules per unit volume}$$

$$v = \frac{c N_A}{M}$$

$$\therefore \frac{1}{c} \frac{\eta - \eta_s}{\eta_s} = 2.5 \frac{R^3}{M} \quad \left. \begin{array}{l} j \rightarrow 0 \\ c \rightarrow 0 \end{array} \right\} \Rightarrow [\eta] = 2.5 \frac{R^3}{M}$$

- Viscosity depends strongly on M
 - Viscosity depends on solvent quality
- (sensitivity to hydrodynamic size)

Rearrange: $\eta - \eta_s = v R^3 \eta_s = v kT \left(\frac{R^3 \eta_s}{kT} \right)$

$$G = v kT$$

$$\tau = \frac{\eta_s R^3}{kT}$$

$$\boxed{\eta_p = G \tau}$$

Analysis: $\tau = \frac{\eta_s R}{kT} R^2 = \frac{J}{kT} R^2$

$$D = \frac{kT}{J} \quad \left. \right\} \tau = \frac{R^2}{D}$$

BASICS — good solvent

$$G \propto c$$

$$G \propto M^{-1}$$

$$\tau \propto c^0$$

$$\tau \propto M^{1.8}$$

$$\eta_p \propto c$$

$$\eta_p \propto M^{0.8}$$

Solution Rheology: Non-dilute Solutions

$$c^* \approx \frac{M}{R^3} \approx \frac{1}{[\eta]} \quad \text{overlap}$$

- System becomes network of interpenetrating chains
- Chain "loses" identity $\rightarrow G$ to become independent of M
- Scaling analysis in semi-dilute solutions (deGennes)

Dimensional analysis

$$G = G_0 f\left(\frac{c}{c^*}\right) \quad G_0 = \nu kT \propto M^{-1}$$

$$c < c^* \Rightarrow f = 1$$

$$c > c^* \Rightarrow G \sim M^0$$

$$\therefore G = G_0 \left(\frac{c}{c^*}\right)^\alpha$$

$$c^* \sim \frac{1}{[\eta]} \propto M^{-0.8}$$

$$\left. \begin{array}{l} \\ \\ \end{array} \right\} \Rightarrow G \propto M^{-1} c^\alpha M^{0.8\alpha} \Rightarrow \alpha = 1.25$$

$$G = G_0 \left(\frac{c}{c^*}\right)^{1.25} \propto c^{2.25}$$

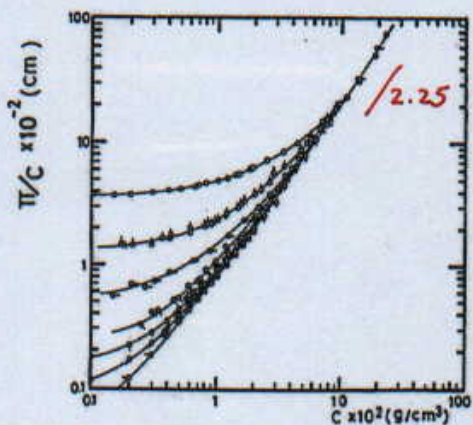
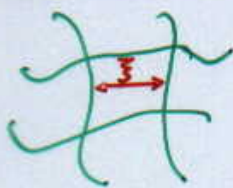


Figure 4. Osmotic pressures of poly(α -methylstyrenes) in toluene at 25 °C. The symbols \circ , \square , \triangle , \square , \circ , \square , and \circ denote data for α -104, α -12, α -103, α -110, α -112, α -113, and α -111, respectively. The data for α -112 were obtained by both osmotic pressure and light scattering measurements, and the data for α -113 and α -111 were obtained by light scattering measurements.

Calculate network grid size ξ (or blob size)



Dimensional analysis: $\xi = R_0 f\left(\frac{c}{c^*}\right)$ chain dimension in dilute solution

• $c < c^* \Rightarrow f = 1$

• $c > c^* \Rightarrow \xi \propto M^0$

But $R_0 \propto M^{0.6}$, $c^* \propto M^{-0.8}$

$$\xi = R_0 \left(\frac{c}{c^*}\right)^{-0.75}$$

• Express modulus as

$$G = \frac{kT}{\xi^3}$$

general result:

$$G = \nu \frac{kT}{\text{network}}$$

$$G = \frac{kT}{R_0^3} \left(\frac{c}{c^*}\right)^{2.25} = \frac{kTc}{R_0^3 c^*} \left(\frac{c}{c^*}\right)^{1.25} = \frac{kTc}{M} \left(\frac{c}{c^*}\right)^{1.25} = G_0 \left(\frac{c}{c^*}\right)^{1.25}$$

Calculate configurational quantities

g monomers per blob

$$R_0 = b N^{0.6}$$

Similarly:

$$\xi = b g^{0.6}$$

But $\xi = R_0 \left(\frac{c}{c^*}\right)^{-0.75}$

$$\therefore g = N \left(\frac{c}{c^*}\right)^{-1.25}$$

Number of blobs per chain: $N_{\text{blob}} = \frac{N}{g} = \left(\frac{c}{c^*}\right)^{1.25}$

- Excluded volume interaction is screened for distances larger than ξ .
- Chain becomes a random walk of step length ξ .

- The size R of the chain now becomes:

$$R = \xi N_{\text{blob}}^{1/2} = R_0 \left(\frac{c}{c^*}\right)^{-0.75} \left(\frac{c}{c^*}\right)^{0.625} = R_0 \left(\frac{c}{c^*}\right)^{-0.125}$$

∴ The chain shrinks with increasing concentration

- For distances larger than ξ , also hydrodynamic interactions are screened, and hence the friction coefficient of the chain becomes additive over blobs.

$$\begin{aligned} J &= N_{\text{blob}} J_{\text{blob}} \\ \text{But } J_{\text{blob}} &= \eta_s \xi = \eta_s R_0 \left(\frac{c}{c^*}\right)^{-0.75} \end{aligned} \left. \vphantom{\begin{aligned} J &= N_{\text{blob}} J_{\text{blob}} \\ \text{But } J_{\text{blob}} &= \eta_s \xi = \eta_s R_0 \left(\frac{c}{c^*}\right)^{-0.75} \end{aligned}} \right\} \therefore \boxed{J = \eta_s R_0 \left(\frac{c}{c^*}\right)^{0.5}}$$

Friction coef. increases with c .

Semidilute unentangled solutions:

- Relaxation time:

$$\tau = \frac{R^2}{D} = \frac{R^2 J}{kT} = \frac{R_0^3 \eta_s}{kT} \left(\frac{c}{c^*}\right)^{0.25} = \tau_0 \left(\frac{c}{c^*}\right)^{0.25}$$

$$\tau \propto R_0^3 [\eta]^{0.25} \propto M^{1.8} M^{0.8 \times 0.25} = M^2 \quad (\text{Rouse result})$$

- Viscosity:

$$\eta = G \cdot \tau = G_0 \tau_0 \left(\frac{c}{c^*}\right)^{1.5} \propto c^{2.5}$$

$$G_0 \sim M^0 \quad \therefore \eta \sim M^2$$

Basics - semidilute unentangled

$$\left\{ \begin{array}{l} \zeta = b g^{0.6} \quad (\text{good solvent}) \\ G \propto M^0 \\ \zeta \propto M^0 \end{array} \right.$$

$$G \propto c^{2.25}$$

$$\tau \propto c^{0.25}$$

$$\eta \propto c^{2.5}$$

$$G \propto M^0$$

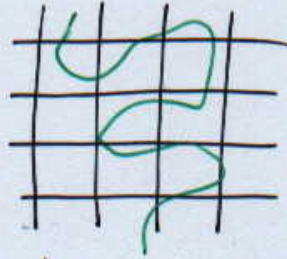
$$\tau \propto M^2$$

$$\eta \propto M^2$$

$$D \propto M^{-1}$$

Entangled solutions:

- chain uncrossability
- architecture



Chains longer than several ξ

Reptation:

Longitudinal motion along a "tube"

- Curvilinear tube length $L = N_{\text{blob}} \xi$

- Reptation $\rightarrow L$

$$\text{Relaxation time} \\ \therefore \tau = \frac{L^2}{D} = \frac{L^2 \eta}{kT} = \eta_s \frac{N_{\text{blob}}^3 \xi^3}{kT} = \frac{\eta_s R_0^3}{kT} \left(\frac{c}{c^*}\right)^{1.5} = \tau_0 \left(\frac{c}{c^*}\right)^{1.5}$$

Much stronger c -dependence compared to semidilute unentangled

$$\tau \propto M^{1.8} M^{0.8 \times 1.5} = M^3$$

Viscosity

$$\eta = G \tau = G_0 \tau_0 \left(\frac{c}{c^*}\right)^{2.75} \propto c^{3.75}$$

$$\eta \propto M^3$$

Experimental evidence: somewhat stronger dependence

- Diffusion coefficient of the chain center-of-mass:

$$D_M \approx \frac{R^2}{\tau} = D \frac{R^2}{L^2} = \frac{D}{N_{\text{blob}}} \propto M^{-2}$$

Confirmed experimentally.

Basics - entangled systems

(good solvent)

$$G \propto c^{2.25}$$

$$G \propto M^0$$

$$\tau \propto c^{1.5}$$

$$\tau \propto M^3$$

$$\eta \propto c^{3.75}$$

$$\eta \propto M^3$$

$$D_H \propto M^{-2}$$