Stokes-Einstein equation to determine D and d (More common)

▶For a solution of given viscosity (η), at a constant temperature (T),

the rate of diffusion is given by the Stokes-Einstein equation (Accept),

$$D=(kT)/(6\pi\eta d)$$

- Measure intensity (I) at various time interval (τ),

- I(0) = I(τ) for short τ → "Correlated"

- Define anto-correlation function, **G(τ)= <I(t) I(t+τ)>** = Average

  of the intensity product. Correlation decreases as τ increases.

- High G(τ) means particles have not diffused away during τ.

- Thus G(τ) remaining high for a long time interval indicates large,

  slowly moving particles.

  The time scale of fluctuation is called decay time which is

  related to the particle size. Decay constant (Γ)≡1/Decay time

  Large, slowly moving particles →long decay time and small Γ

For mono-disperse sample

$$G(\tau) = A_o + Ae^{-2\Gamma\tau}$$

$\Gamma = \text{decay constant} = DQ^2$

$D = \text{diffusion coefficient} = \dfrac{kT}{6\pi\eta d}$

$Q = \text{scattering vector} = \left(\dfrac{4\pi}{\lambda}\right)\sin\left(\dfrac{\theta}{2}\right)$

A_o = Background signal, A= Instrument constant,

Procedure to determine D and d.

Measure G(τ) vs. τ

Calculate G(τ) using $G(\tau) = \lim_{T\to\infty}\left(\dfrac{1}{T}\right)\int_0^T I(t)I(t+\tau)d\tau$ (a)

Fit the data to $G(\tau) = A_o + Ae^{-2\Gamma\tau}$ and determine Γ

Determine D using $\Gamma = DQ^2$

Determine d using Stokes-Einstein equation,

3.7 Molecular weight of polymers

MW policy : High enough for good physical properties and low enough for processing, and varies with type and applications.

PVC: 60,000-90,000 g/mol

PMMA-Plexglas $> 1 \times 10^6$

Cellulose: Naturally over 10^8 with Mw/Mn=10-50

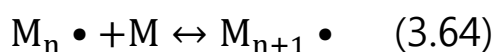For application as rayon, cellulose is degraded to 50,000-80,000

3.7.2 Thermodynamics and kinetics

3.7.2.1 Thermodynamics of chain polymerization

Gibbs energy is related to the equilibrium constant

$$\Delta G^0 = -RT \ln K \quad (3.63)$$
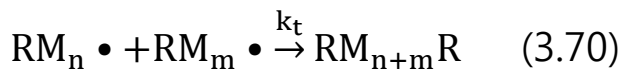
For chain polymerization of monomer M:

$$M_n \bullet + M \leftrightarrow M_{n+1} \bullet \quad (3.64)$$

The equilibrium constant, K is defined as

$$K = \frac{k_p}{k_{ap}} = \frac{[M_{n+1}\bullet]}{[M_n\bullet][M]} = \frac{1}{[M]} \quad (3.65)$$

When the forward and backward reactions have the same rates, concept of ceiling and floor temperature arises (Applied for most polymers). Ceiling temperature is used for recycling whereby scraped

polymer is heated under anaerobic condition to allow distilling off the

reactant molecules.

3.7.2.2 Kinetics of chain polymerization

$$I \xrightarrow{k_i} 2R \bullet \quad (3.66)$$

$$R \bullet + M \xrightarrow{k_2} RM \bullet \quad (3.67)$$

$$RM \bullet + M \xrightarrow{k_P} RM_2 \bullet \quad (3.68)$$

$$RM_n \bullet + M \xrightarrow{k_P} RM_{n+1} \bullet \quad (3.69) \text{ <Assume } k_p \text{ independent of chain length>}$$

$$RM_n \bullet + RM_m \bullet \xrightarrow{k_t} RM_{n+m}R \quad (3.70)$$

Under steady state, $R_i = R_t$, and rate of polymerization is

$$R_p = k_p \left(\frac{k_i}{k_t}\right)^{1/2} [M][I]^{1/2} \quad (3.71)$$

Note the first order wrt [M] and 1/2 order wrt [I]

The kinetic chain length, at steady state is

$$\nu = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p[M]}{2(fk_i k_t[I])^{1/2}} \quad (3.72) \quad \text{<f=Initiator efficiency factor~0.8>}$$

The number average DP (3.72)=2 ν for coupling, which gives 1.5

PDI, while disproportionation (termination by chain transfer)

yields 2.0PDI.

3.7.2.3 Thermodynamics of step polymerization

Consider a polyesterfication,

$$-COOH + -OH \overset{K}{\leftrightarrow} -COO- + H_2O \quad (3.73)$$

The equilibrium constant is given by

$$K = \frac{[COO][H_2O]}{[COOH][OH]} \quad (3.74)$$

The fractional conversion is given by $[COO]=p[M]_o$, where $[M]_o$ is the concentration of ester group. Then

$$DP_n = \frac{1}{1-p} \quad (3.75)$$

And the corresponding weight average degree of polymerization is given by

$$DP_w = \frac{1+p}{1-p} \quad (3.76)$$

Then

$$PDI = 1 + p \quad (3.77)$$

As p→1, PDI→2　　(Most probable distribution).

3.7.2.4 Kinetics of step polymerization

For self-catalyzed reaction,

$$\frac{-d[COOH]}{dt} = k[COOH]^2[OH] \quad (3.78)$$

Assuming equal molar concentrations of carboxyl and hydroxyl groups to start, the extent of reaction is given by

$$\frac{1}{(1-p)^2} = 2[M]_0 kt + 1 \quad (3.79)$$

3.7.3 Molecular weight distributions

Bifunctional monomer (f=2, vinyl monomers)→Linear polymer)

Trifunctional monomers → Branched or cross-linked polymers

Cross-linker=Glycerol (condensation), divinyl benzene (chain rxn)

When will gelation occur?

Gelation=A single molecule extends throughout polymerization vessel

The critical extent of reaction, P_c at the gel point is

$$P_c = \frac{1}{(f-1)^{1/2}} \quad (3.83) \quad \text{(Flory and Stockmayer)}$$

f=Functionality of the branch unit